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STUDY OF HYDROGEN TRANSPORT, ELECTROLYTIC CHARGING AND THERMO-
HYDROGEN PROCESSING OF HIGH PRESSURE COLD SPRAYED Ti6Al4V

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Pressure Cold Sprayed Ti6Al4V

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_____ (Signed)

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Dedication

*To my mom, dad, brother, grandma, uncle, and aunt,
thank you for your unwavering love and support in
pursuing my dreams.*

Abstract

Cold spray is a kinetic energy-based deposition method that has aroused interest in additive repair of high-value metallic aerospace assets, such as titanium components. Cold spray can fabricate ultra-thick deposits without melting and phase change, where the dense nanograins distribute across the entire deposit due to severely deformed particles. Hydrogen embrittlement in metallic parts is a critical safety risk in systems and processes involving hydrogen. Despite heat treatment being a common method to retrieve the ductility of cold-sprayed deposits, the effect of microstructural evolution in cold-sprayed deposits against hydrogen damage is unclear.

This study used cathodic charging with high current density to investigate the hydrogen damage on samples of helium cold-sprayed Ti6Al4V coatings on CP-Ti substrates along with post-spray heat treatments. Hydrogen damage mechanisms varied with heat treatment temperature. The 750 °C heat treatment triggered diffusion bonding to increase the interparticle strength, but hydrogen damage occurred with blistering. Severe hydrogen pitting and splats debonding were observed in the 540 °C stress relieved samples due to the absence of metallurgical bonding. The as-sprayed coating was found to be the most resistant against hydrogen damage, since its highly dense nanocrystalline structure restricted the hydrogen mobility.

There is a lack of hydrogen diffusion prediction methods for cold-sprayed deposits since their irregular microstructures are formed by the supersonic impact of particles. This study presents the image-based realistic modelling and hydrogen diffusion simulation with a grain-boundary network approach on cold-sprayed Ti6Al4V microstructure with heat treatments at 540°C and 750°C. Grain boundaries (GB) with a misorientation angle of less than 15° in EBSD mapping were categorized as special boundaries, or else the boundaries were random. The simulation was conducted by utilizing the accessible MATLAB Im2mesh tool and ABAQUS to obtain repeatable results. The

high fraction of special boundaries in cold-sprayed deposits due to particle deformation shows its potential as a GB engineering method to improve hydrogen resistance. Dense special boundaries trap hydrogen and overcome the “short-circuit diffusion effect” by random boundaries. Heat treatment induces recrystallization and reduces the fraction of special boundaries, consequently deteriorating the performance of hydrogen mitigation. The simulation results reveal that the accuracy highly depends on the quality of EBSD characterization and the experimentally measured hydrogen properties. The image-based framework demonstrates its capability to simulate 2D diffusion across the complicated GB network of cold-sprayed deposits, as well as using GB maps from literature, despite the raw EBSD data not being provided.

The fluid transport properties of cold-sprayed deposits have hitherto barely been addressed compared to the mechanical properties. This study used a small cold-sprayed Ti6Al4V “tsunami” deposit with a unique porous structure, which was consolidated by helium carrier gas on a mild steel substrate holder due to instantaneous fluctuations of nozzle traverse speed. The porosity was measured to be 15% by densitometer, 35.5-54% by optical microscope and 1-34% by XCT experiments with selected ROIs. The XCT tensor simulated porosity, mean absolute permeability and mean effective diffusivity were able to be correlated statistically with power functions. The transport properties posted a positive-linear relationship at porosities ranging from ~2.5-30%, where the ranges of permeability and diffusivity were from $\sim 1.0\text{E}+2$ to $5.0\text{E}+4$ mD and from $\sim 1.0\text{E}-9$ to $1.0\text{E}-7$ m²/s, respectively. It was also noted that the changing formation factor and the cementation factor in the computing algorithms led to unaligned diffusivity prediction at critical porosity, which was below 13% in this study. The range of fluid transport properties can thereby be potentially predicted on-site with a statistical correlation approach based on porosity.

Developing cold spray additive repair for aerospace applications remains a significant challenge due to the lack of ductility and adhesion of hard metal deposits, such as titanium alloys. This study compares the effect of multi-step heat treatment (MSHT) in vacuum and hydrogen atmospheres on cold-sprayed Ti6Al4V coatings on CP-Ti using nitrogen and helium carrier gas. All the as-sprayed coatings were delaminated at strains of 1-3% during three-point bending tests, with detached fragments struck on surroundings. The nitrogen-sprayed Ti6Al4V sample after MSHT in vacuum was the only specimen exhibiting ductile deformation without fracture or delamination, which had an ultimate flexural strength (UFS) of 887 MPa at a strain of 11.1%. The superior ductility was contributed by the fully equiaxed microstructure in the coating with α grains $<10\ \mu\text{m}$ and submicron-thin β laths, where the adhesion was improved by the $40\ \mu\text{m}$ thick interfacial diffusion bonding. However, the effectiveness of MSHT was limited by the as-sprayed quality. The porous helium-sprayed coating due to nozzle clogging underwent the same heat treatment but broke into powder and debris upon bending load. Hydrogen charging could enhance interfacial diffusion bonding, leading to the formation of pentagonal α_2 grains. This study was also the first to capture the morphology of twinned-pentagonal α_2 grains in Ti6Al4V particles, as observed through the SEM fractography of helium-sprayed Ti6Al4V coatings that underwent a MSHT in hydrogen. The thermo-hydrogen refinement of microstructure (THRM) was applicable to Ti6Al4V but not to CP-Ti, as it triggered excess grain growth and severe embrittlement in CP-Ti substrates.

Overall, this thesis utilizes simulations and experiments to address the hydrogen degradation and integrity concerns about using cold spray as a novel additive repair method for aviation, energy and manufacturing industries. Simulation with realistic model provides insights into understanding hydrogen diffusion behavior in grain-boundary networks and developing techniques to predict the

hydrogen-affected zone over the service life of components. Statistical correlation between porosity, permeability and diffusivity provides insights into developing comprehensible process and inspection guidelines for cold-spraying components for fluid transport and fluid-tight applications. Cathodic hydrogen charging reveals that the as-sprayed Ti6Al4V is resistant to hydrogen embrittlement during plating compared to the heat-treated deposits. Vacuum MSHT proves its capability to enhance ductility and adhesion of cold-sprayed Ti6Al4V coatings, where inevitable hydrogen uptake at high temperature can be utilized to further improve diffusion bonding followed by proper desorption.

Publications arising from the thesis

Journal papers

[1] **B. C. Wong**, C. Zhang, Y. X. Wang, R. C. Voyle, T.-M. Chan and M. W. Fu, “Enhancing Ductile and Adhesive Performance of Cold-sprayed Ti6Al4V Coatings by Multi-Step Vacuum Heat Treatment,” *International Journal of Advanced Manufacturing Technology*, Dec. 2025. doi: 10.1007/s00170-025-17065-7

[2] **B. C. Wong** and M. W. Fu, “Unraveling of the Statistical Correlation between Porosity, Permeability and Diffusivity of Cold-sprayed Ti6Al4V,” *Journal of Manufacturing Processes*, vol. 152, p. 375-389, Oct. 2025. doi:10.1016/j.jmapro.2025.08.028

[3] **B. C. Wong** and M. W. Fu, “Macroscopic simulation of hydrogen diffusion across the grain-boundary networks in cold-sprayed Ti6Al4V,” *Materials Today Communications*, vol. 45, p. 112423, Apr. 2025. doi:10.1016/j.mtcomm.2025.112423

Conference poster presentation

[4] **B. C. Wong** and M. W. Fu, “Metals degradation assessment of hydrogen powered aircraft,” *Nature Conference on Air Pollution and Climate Change 2024*, Beijing, China, May 22-24, 2024.

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Table of Contents

CERTIFICATE OF ORIGINALITY	I
Dedication	II
Abstract	III
Publications arising from the thesis	VII
Acknowledgements	VIII
Table of Contents	X
List of figures	XIV
List of tables	XXVI
List of abbreviations and acronyms	XXVII
List of nomenclatures	XXIX
Chapter 1: Introduction	1
1.1 Research background	1
1.2 Research objectives	4
1.3 Outline	4
Chapter 2: Literature Review	6
2.1 Principle of cold spray	6
2.1.1 Bonding mechanisms	7
2.1.2 Deposition velocity window	11
2.1.3 Mechanical Properties	16
2.1.4 Microstructure evolution during heat treatment	19
2.1.5 Applications	26
2.2 Hydrogen damage	28
2.2.1 The classification of hydrogen embrittlement	30
2.2.2 Hydrogen absorption scenarios	34
2.2.3 Hydrogen in metal microstructure	37
2.2.4 Evolution of hydrogen embrittlement	40
2.2.5 Hydrogen damage scenarios	42
2.2.6 Hydrogen in future aviation	44
2.3 Electrolytic hydrogen interaction in cold-worked microstructure	46

2.3.1. Hydrogen concentration and ductility.....	46
2.3.2. Effect of cold-worked microstructure.....	48
2.4 Simulation of Hydrogen Diffusion across the Grain-boundary Networks	52
2.4.1 Modeling of grain-boundary networks	52
2.4.2 Simulation parameters	55
2.5 Permeability and diffusivity of porous structure	55
2.5.1 Porous structure of cold-sprayed deposits	55
2.5.2 Traverse speed induced porosity.....	57
2.5.3 Dynamic control of spraying	60
2.6 Ductility enhancement by heat treatments.....	69
2.6.1 Hot-isostatic pressing.....	69
2.6.2 High temperature heat treatment.....	73
2.6.3 Thermo-hydrogen processing	78
2.6.4 Multi-step heat treatment (MSHT)	83
2.7 Summaries.....	86
Chapter 3: Hydrogen Damage on Cathodic Charged Cold-sprayed Ti6Al4V Coatings	87
3.1. Introduction.....	87
3.2. Methodology	88
3.2.1 Materials	88
3.2.2 Sample Preparation	88
3.2.3 Cathodic Charging	90
3.2.4 Microstructural and Mechanical Characterization.....	90
3.3 Results & Discussion	92
3.3.1 Effect of feedstock powder on deposition	92
3.3.2 Effect of substrate surface preparation and heat treatments on microstructure and hydrogen damage	93
3.3.3 Effect of hydrogen interactions on compositions, grain size and phases	100
3.3.4 Effect of hydrogen damage on nano-indentation properties.....	108
3.3.5 Challenges in SEM Analysis of etched CS Coatings.....	109
3.4 Summaries.....	112

Chapter 4: Macroscopic Simulation of Hydrogen Diffusion across the Grain-boundary Networks in Cold-sprayed Ti6Al4V	114
4.1. Introduction.....	114
4.2. Methodology	115
4.2.1 Sample Preparation	115
4.2.2 Characterization	115
4.2.3 Modelling.....	116
4.3 Results & Discussion	122
4.3.1 Diffusion across GB Networks after Heat Treatments	122
4.3.2 Comparison with Diffusion in Whole-Random Boundaries.....	126
4.3.3 Comparison with Diffusion in Whole-Special Boundaries	129
4.3.4 Effect of Hydrogen Properties of β Grains	130
4.3.5 Limitations	132
4.3.6 Challenges in 3D Extension.....	136
4.4 Summaries.....	138
Chapter 5: Unravelling the Statistical Correlation between Porosity, Permeability, and Diffusivity of Cold-sprayed Ti6Al4V.....	140
5.1. Introduction.....	140
5.2. Methodology	141
5.2.1 Materials & Sample Preparation.....	141
5.2.2 Characterization	142
5.2.3 Simulation	143
5.3 Results & Discussion	144
5.3.1 Archimedes' Density	144
5.3.2 Optical Microscopy.....	145
5.3.3 XCT Scanning and Analysis.....	147
5.4. Summaries.....	165
Chapter 6: Enhancing Ductile and Adhesive Performance of Cold-sprayed Ti6Al4V Coatings by Multi-Step Vacuum Heat Treatment.....	167
6.1. Introduction.....	167
6.2. Methodology	168

6.2.1 Materials & Sample Preparation.....	168
6.2.2 Multi-Step Heat Treatment.....	169
6.2.3 Three-Point Bending Test.....	170
6.2.4 Characterization.....	171
6.3. Results & discussion.....	172
6.3.1 Flexural Properties.....	172
6.3.2 Fracture Mechanisms.....	175
6.3.3 Pore structure evolution.....	184
6.3.4 Relationship between ductility and microhardness.....	188
6.3.5 Phase precipitation in the recrystallized microstructures.....	190
6.3.6 Composition profiles at the coating-substrate boundary.....	192
6.3.7 Microstructure evolution.....	194
6.4. Summaries.....	198
Chapter 7: Conclusions and future work.....	200
7.1. Conclusions.....	200
7.2. Suggestions for Future Research.....	202
7.2.1 Hydrogen damage by electrochemical charging.....	202
7.2.2 Simulation of hydrogen diffusion across the grain-boundary networks.....	202
7.2.3 Statistical correlation between porosity, permeability and diffusivity.....	204
7.2.4 Ductility and adhesion improvement by multi-step heat treatment.....	205
Appendices.....	207
References.....	210

List of figures

Fig. 2.1. Schematic diagram of typical cold spray system [57]	7
Fig. 2.2. Schematics of (a) interfacial plastic deformation resulting in cold welding, (b) deformation localization due to shear instability in particle impact in cold spraying, (c) explosive and/or magnetic pulse welding, and (d) shear banding under compression, resulting in breakup and failure [1]	8
Fig. 2.3. Schematic representation of jetting in cold spray: Stage I. Impact induces a shock wave. Stage II. Shock detaches from the leading edge. Stage III. Jet forms on the basis of pressure releases [59]	9
Fig. 2.4. (a) Schematic of the intermixing interface formation mechanism. (b) Microstructure of the Cu coating-Al substrate interfaces deposited at various gas temperatures [60].....	10
Fig. 2.5. Windows of sprayability (WS) in terms of particle velocity over (a) particle temperature [61] and (b) metals at room temperature [62]	12
Fig. 2.6. (a) Velocity and (b) temperature profiles of particles and gases across cold spray nozzle in simulation [57]	13
Fig. 2.7. SEM micrographs of the substrate surfaces (top view) and the attached Al-12Si particles onto the mild steel substrate (45° angle tilting view). Impact with a mean particle velocity of (a) 500 m/s, (b) 700 m/s and (c) 1000 m/s [63]	14
Fig. 2.8. Calculated adhesion energy and rebound energy for various sized Al-Si feedstock impacting onto a mild steel substrate [63].....	15
Fig. 2.9. Side and top views of cold-sprayed Ti6Al4V samples at crack locations after bending test: (a) bare substrate and (b to e) coated samples with coating thicknesses of (b) 0.1 mm, (c) 0.5 mm, (d) 1 mm and (e) 3 mm thick [65].....	17

Fig. 2.10. Stress-strain curves as a function of coating thickness: (a) bare substrate and coated samples with 0.1 mm and 0.5 mm thin coatings and (b) coated samples with 1 mm and 3 mm thick coatings [65].....	17
Fig. 2.11. Images of (a) compressive loaded, (b) tensile loaded, (c) cold-rolled specimens after four-point bending tests and their corresponding load-displacement curves in (d) as-sprayed and (e and f) heat-treated conditions [66]	19
Fig. 2.12. Coating and interface: (a) sprayed at 800 °C; (b) sprayed at 1100 °C; (c) sprayed at 1100 °C with subsequent heat treatment [68]	21
Fig. 2.13. Schematic illustration of the evolving cold-sprayed coating during heat treatment from (a) as-sprayed condition to phases of (b) diffusion, (c) recrystallization, and (d) grain growth [13]	23
Fig. 2.14. Pores shrinkage and expansion mechanism along with heat treatment in (a) schematic illustration, and (b) porosity profile [70]	24
Fig. 2.15. Evolution of microstructure of deformed Ti6Al4V particles at IPB of CS deposits after HT [16].....	25
Fig. 2.16. Applications of cold spray: (a) cold-sprayed steel coating on rice cooker inner pot for induction [71], (b) cold spray of NASA HR-1 onto a LPBF GRCop-84 subscale chamber [73], (c) cold spray repair the accessory gearbox of GE90 engine in Boeing 777 [74], (d) cold spray inside of main-landing-gear cylinder of Northrop F-5 [75], and (e) cold spray dimensional restoration of aircraft fuel flow proportioner [76].....	28
Fig. 2.17. Classification of HEE, IHE and HRE types based on hydrogen, stress, and material factors [12].....	31

Fig. 2.18. Schematic of (a) hydrogen attack, (b) blistering and (c) metal hydride formation phenomena [86]. (d) Voids formed by methane in a carbon steel exposed to a hydrogen atmosphere at high temperature [87]. (e) Backscattered electron imaging of an intergranular crack of the H-charged Al 7XXX alloy subjected to tensile fracture [88]. (f) TEM image of 96 h H-charging heat-treated LPBF Ti6Al4V [29]	33
Fig. 2.19. Hydrogen absorption scenarios in manufacturing process and operation [89].....	37
Fig. 2.20. Schematic diagram of hydrogen trapping and transport sites in metals [122]	38
Fig. 2.21. Interstitial octahedral (O) sites and tetrahedral (T) sites in FCC, HCP and BCC lattices [136]	40
Fig. 2.22. Schematic diagrams of HE mechanisms: (a) hydride formation and fracture, (b) HEDE, (c) HELP, and (d) AIDE [144]	42
Fig. 2.23. Hydrogen damage (a) blistering phenomena in steel pipe [145], (b) fractured nut in clutch of R22 Beta helicopter with beach marks extending away from the nut bearing face [146], (c) Boeing 737 slat tracks failed a quality test indicating the presence of hydrogen embrittlement [147], and (d) fractured axle of right main landing gear in Korean Airlines HL7573 Boeing 777 associated with stress corrosion cracking [150]	44
Fig. 2.24. Schematic diagram of large turbofan hydrogen combustion engine [152].....	46
Fig. 2.25. Relationship between cold work versus (a) hydrogen diffusivity, (b) hydrogen concentration, (c) fracture toughness, and (d) fracture strain [157]	48
Fig. 2.26. Hydrogen diffusivity models based on (a) the “GB cross effect” [163], and (b) dislocations density near surface [123].....	50
Fig. 2.27. EBSD images of the cross-sectional microstructure of CS and HT Ti6Al4V deposits: grain orientation of (a) CS sample, and (b) HT sample [16]	52

Fig. 2.28. Virtual GB network modeling methods of (a) heterogenous grains and homogeneous boundaries [37], (b) heterogenous boundaries only [168], and (c) homogeneous grains and heterogenous boundaries [33]	54
Fig. 2.29. Porous structure characterized by (a) SEM-BSE, and XMT at regions of (b) low porosity and (c) high porosity. Percolating porosity and non-percolating porosity clusters are in white and gray, respectively. (d) FFT-predicted vs. experimentally measured permeability [41]	57
Fig. 2.30. Optical micrographs of polished and etched cross sections of cold-sprayed Ti6Al4V with traverse speed at (a and b) 100 m/s, (c and d) 300 m/s, and (e and f) 500 m/s [178].....	58
Fig. 2.31. Cross sections of all the deposited beads [179]	59
Fig. 2.32. The optimization of pitch distance for the trajectories can be derived from the dynamic pattern [180]	60
Fig. 2.33. (a) Cold-sprayed microstructures of 316L, Al Cu, Ti, and Ti6Al4V in traditional and metal knitting strategy. (b) Metal knitting strategy scheme elements of (1) cold spray gun, (2) virtual frustum of cone path, (3) substrate, (4) radius, and (5) angle. (c) Cold-sprayed curved parts made by the Metal Knitting strategy. (d) Cold-sprayed 316L complex geometries made by the metal knitting strategy [181]	61
Fig. 2.34. Influence of traverse speed vs. corner radius on the presence of defects at the corner of the square frame: (a) photographs of the corner region, (b) profile along the XY direction measured by laser scanning, and (c) profile along the XX direction measured by laser scanning. (d) Porosity distribution of Ti deposit at traverse speed of 25 mm/s and a corner radius of 0.3 mm [182]	63
Fig. 2.35. (a) The spraying session of the optimized jet engine bracket using the PCS-1000 L (Plasma Giken, Japan). (b) Finished optimized jet engine bracket on the substrate. The dotted red	

circles represent the bolt holes to be drilled through. (c) Cracking occurred around the bolt holes interface 30 min after spraying and cooling to room temperature 20 °C [183]	64
Fig. 2.36. Real-time 4D reconstruction for cold spray robot control: (a) hardware setup, (b) computation routine, and (c) microstructure of the cold-sprayed CP-Ti [184]	65
Fig. 2.37. Local defects due to fluctuation of nozzle traverse speed during cold spray: (a) real part, (b) 3D scanned part, and (c) comparison with TCP speed variation of toolpath [185]	66
Fig. 2.38. Tool center points of the respective tools, (a) sensor for scanning, (b) milling tool, (c) cold spray gun in the automated repair system. (d) Damaged area, (e) pre-machined area, (f) cold-sprayed Al6061 deposit on the Al6061 component [186]	67
Fig. 2.39. Cold-sprayed Ti6Al4V with helium at 530°C in (a) as-sprayed condition, and (b) after HIP. (c) Stress-strain plot comparing the as sprayed, heat-treated and HIPed properties for Ti6Al4V specimens. (d) Cold sprayed Ti6Al4V with 450 psi helium, gas and powder coil temperatures at 500°C, and (e) the diffusion of the GB between the coating and substrate after heat treating at 1750°F for eight hours [195]	70
Fig. 2.40. Microstructure of the Ti6Al4V samples (a) as-deposited using the spherical feedstock powders and (b) changes after the performed post-treatment. (c) Mechanical properties of the as-deposited and post-treated CSAM Ti6Al4V samples. (d) Interstitial content analysis in crystalline and spherical powders and their deposits in as-deposited and post-treated state [199]	72
Fig. 2.41. (a) Etched microstructure of the final Ti6Al4V samples deposited from the two feedstock powders and changes after the performed heat treatment. (b) Stress-strain curves of the as-deposited and heat-treated CSAM Ti6Al4V specimens [200]	72
Fig. 2.42. SEM micrographs showing microstructures obtained after heat treatment [201]	74

Fig. 2.43. (a) Porosity level in cold sprayed samples evaluated using optical micrographs. (b) Room temperature stress-strain curves of cold sprayed samples showing the evolution of the tensile behavior following post-process heat treatments [201]	74
Fig. 2.44. Typical etched microstructures ($\times 1000$) of N_2 -sprayed Ti6Al4V coatings in (a) as-sprayed condition and (b) annealed at 600 °C for 2 h, (c) 800 °C for 2 h, and (d) 1000 °C for 1 h. Typical fracture surfaces ($\times 5000$) at the pores of N_2 -sprayed Ti6Al4V tensile specimens annealed at (e) 800 °C for 2 h, and (f) 1000 °C for 1 h [14]	76
Fig. 2.45. Typical stress-strain curves for Ti6Al4V substrate, He-sprayed Ti6Al4V coatings (as-sprayed and annealed at 600 °C for 2 h), and N_2 -sprayed Ti6Al4V coatings (as-sprayed and annealed at 1000 °C for 4 h) [14]	77
Fig. 2.46. Cross-sectional etched micrographs of as-sprayed and heat-treated Ti6Al4V coatings fabricated at three nitrogen flow rates of 0.5, 1 and 1.5 m ³ /min [204]	78
Fig. 2.47. Engineering stress-strain curves for as-sprayed and heat-treated Ti6Al4V coatings fabricated at three nitrogen flow rates of (a) 0.5, (b) 1.0 and (c) 1.5 m ³ /min [204]	78
Fig. 2.48. Schematic of the thermal profile, microstructural evolution, and the β -transus (as a function of hydrogen content) during HSPT and subsequent heat treatments to produce Ti6Al4V with bi-modal and globularized microstructures [207]	79
Fig. 2.49. SE/SEM (a-c, g) and STEM (d-f) of Ti6Al4V microstructures by HSPT [207]	80
Fig. 2.50. Stress-strain curves for Ti6Al4V produced via (a) HSPT [207] and (b) LPBF as-built + SR and THRM [208].....	81
Fig. 2.51. SEM micrographs of the (a) as-sprayed, (b) spray only with HIP, (c) spray only with THRM, (d) bimetal with HIP, and (e) bimetal with THRM conditions. The α (hexagonally close packed) phase appears as dark while the β (body centered cubic) phase appears as light [27] ...	82

Fig. 2.52. Schematic map of (a) MSHT and (b) conventional heat-treatments. (c) Engineering tensile stress-strain curves of the SLM as-fabricated Ti6Al4V samples and those after post-heat treatments [210]	84
Fig. 2.53. Microstructures of the Ti6Al4V samples after post-heat treatments: (a) STA, (b) annealing, (c) stress-relieving, and (d) MSHT [210].....	85
Fig. 2.54. Microstructural evolution of the Ti6Al4V sample during MSHT (a) 950 °C/2 h to 850 °C, (b) 850 °C/2 h to 750 °C, (c) 750 °C/2 h to 650 °C, and (d) 650 °C/2 h to room temperature. The white lines pertain to the LAGBs. The boxes and arrows indicate the cylinderization and boundary splitting, respectively [210].....	85
Fig. 3.1. Cold spray process flow chart	89
Fig. 3.2. Cathodic charging setup in schematic illustrations	90
Fig. 3.3. Optical micrographs of Ti6Al4V particles with different morphologies and sizes. (a) Spherical particles were about 10 µm in diameter, captured at 50x magnification with a scale mark of 20 µm. (b) Agglomerated particles had a CE diameter of about 85.50 µm, captured at 20x magnification with a scale mark of 50 µm. (c) Agglomerated Ti6Al4V particles about 78.85 µm CE diameter at 20x magnification with a scale mark of 50 µm	93
Fig. 3.4. Stitched optical micrographs (200x) showing the cross-sectional profile of coatings (a) LAHT1, (b) LAHT2, (c) FMHT1, and (d) FMHT2; (i) before and (ii) after cathodic charging. The coating thickness of samples LAHT1, LAHT2, FMHT1 and FMHT2 after top face-milling were measured to be about 1382, 2322, 2247, and 2274 µm, respectively	94
Fig. 3.5. Optical micrographs (1000x) showing microstructure at the coating/substrate interface on the left and right sections of samples (a) LAHT1, (b) LAHT2, (c) FMHT1, and (d) FMHT2....	95
Fig. 3.6. SEM micrographs of internal microstructure of uncharged samples	97

Fig. 3.7. Optical micrographs (500x, scale mark of 50 μm) showing microstructure after hydrogen charging at the interfaces between coating-coating and coating-substrate of samples (a) LAHT1 (top section instead of coating-coating interface), (b) LAHT2, (c) FMHT1, and (d) FMHT2	99
Fig. 3.8. SEM images of samples after charging (a) LAHT1, (b) LAHT2, (c) FMHT1_AS, (d) FMHT1_SR, and (e) FMHT2	101
Fig. 3.9. EBSD phase maps of cold-sprayed Ti6Al4V coating layer (a) FMHT1_AS, (b) FMHT1_SR, (c) FMHT2_T, (d) FMHT2_B, and their color keys	104
Fig. 3.10. KAM maps of (a) FMHT1_SR and (b) FMHT2_B, and their (c) normal distributions of GND density.....	106
Fig. 3.11. XRD spectra of coating samples (a) before and (b) after cathodic charging	107
Fig. 3.12. Reduced modulus (a) and nanohardness (b) of samples before and after cathodic charging. AS: as-sprayed layer; SR: stress-relieved layer; T: top layer; B: bottom layer	109
Fig. 3.13 SEM/BSE images of FMHT1 (a) as-sprayed layer and (b) stress relieved coating-substrate interface, and FMHT2 (c) coating and (d) coating-substrate interface after etching...	112
Fig. 4.1. Meshing from the GB maps of cold-sprayed Ti6Al4V deposits with (a) 540°C post-spray stress relieving and (b) 750°C post-spray heat treatment.....	117
Fig. 4.2. Hydrogen concentration maps in numerical simulations of (a) SR-GB and (b) HT-GB monocrystal at $t = 0.5$ h. Comparison of analytical and numerical hydrogen diffusion profiles in monocrystal scenario of (c) SR-GB and (d) HT-GB	122
Fig. 4.3. Simulated hydrogen concentration maps across the as-characterized GB networks of cold-sprayed Ti6Al4V deposits with (a-e) 540°C stress relieving and (f-j) 750°C heat treatment at the marked time instances. Close-ups of ROIs in (a and f) were matched with their corresponding GB maps.....	124

Fig. 4.4. Simulated hydrogen diffusion profiles along the horizontal centerline in the models of cold-sprayed Ti6Al4V deposits with (a) 540°C stress relieving and (b) 750°C heat treatment at various time instances	126
Fig. 4.5. Simulated hydrogen concentration maps and diffusion profiles of cold-sprayed Ti6Al4V deposits with (a and b) 540°C stress relieving and (c and d) 750°C heat treatment in imaginary conditions containing random boundaries only.....	128
Fig. 4.6. Simulated hydrogen concentration maps and diffusion profiles of cold-sprayed Ti6Al4V deposits with (a and b) 540°C stress relieving and (c and d) 750°C heat treatment in imaginary conditions containing special boundaries only.....	130
Fig. 4.7. Simulated hydrogen concentration maps and diffusion profiles of cold-sprayed Ti6Al4V deposits with (a and b) 540°C stress relieving and (c and d) 750°C heat treatment in imaginary conditions containing grains with low H solubility	132
Fig. 4.8. Simulated hydrogen concentration maps of cold-sprayed (a-c, g-i) Al-2Cu and (d-f, j-l) Al-5Cu deposits in the study of Liu et al. [257] with (a-f) as-characterized GB fractions and (g-l) special boundaries only	135
Fig. 5.1. Small Ti6Al4V tsunami deposits	142
Fig. 5.2. (a) Stitched optical micrograph of the cross-section of the cold-sprayed Ti6Al4V tsunami, and the pore size distribution in (b) ROI 1, (c) ROI 2, and (d) ROI 3	147
Fig. 5.3. Mapping of accessible pores and isolated pores in VGSTUDIO MAX capillary pressure analysis of 2 mm thick sliced ROI on XZ-plane	148
Fig. 5.4. The 3D model and cross-sections of deposits in the permeability tensor analysis	149
Fig. 5.5. (a) Void fraction of YZ-plane at X = 541 vox along cell position in Y and Z direction; and (b) void fraction of XZ-plane at Y = 121 vox along cell position in X and Z direction	151

Fig. 5.6. (a) Mean absolute permeability of YZ-plane at X = 541 vox along cell position in Y and Z direction; and (b) mean absolute permeability of XZ-plane at Y = 121 vox along cell position in X and Z direction	152
Fig. 5.7. Permeability-void fraction (0-40%) scatter plots of YZ-plane at (a) X = 157 vox, (b) X = 541 vox, (c) X = 1028 vox, and XZ-plane at (d) Y = 121 vox, (e) Y = 400 vox, and (f) Y = 749 vox.....	154
Fig. 5.8. Permeability-void fraction (30-100%) scatter plots of YZ-plane at (a) X = 157 vox, (b) X = 541 vox, (c) X = 1028 vox, and XZ-plane at (d) Y = 121 vox, (e) Y = 400 vox, and (f) Y = 749 vox.....	156
Fig. 5.9. ROIs on the XZ-plane of the cold-sprayed Ti6Al4V tsunami with permeability and diffusivity experiment analyses in VGSTUDIO MAX.....	157
Fig. 5.10. (a) Absolute permeability-effective void fraction scatter plot, and (b) hydraulic tortuosity-effective void fraction scatter plot of ROIs in permeability analysis experiment mode	158
Fig. 5.11. (a) Mean effective diffusion coefficient of YZ-plane at X = 541 vox along cell position in Y and Z direction; and (b) mean effective diffusion coefficient of XZ-plane at Y = 121 vox along cell position in X and Z direction.....	159
Fig. 5.12. Diffusivity-void fraction (0-40%) scatter plots of YZ-plane at (a) X = 157 vox, (b) X = 541 vox, (c) X = 1028 vox, and XZ-plane at (d) Y = 121 vox, (e) Y = 400 vox, and (f) Y = 749 vox.....	160
Fig. 5.13. Diffusivity-void fraction (30-100%) scatter plots of YZ-plane at (a) X = 157 vox, (b) X = 541 vox, (c) X = 1028 vox, and XZ-plane at (d) Y = 121 vox, (e) Y = 400 vox, and (f) Y = 749 vox.....	162

Fig. 5.14. Mean absolute permeability-mean effective diffusion coefficient scatter plot of (a) YZ-plane at X = 541 vox, and (b) XZ-plane at Y = 121 vox.....	163
Fig. 5.15. (a) Effective diffusion coefficient-void fraction, and (b) formation factor-void fraction scatter plots of ROIs in diffusivity analysis experiment mode.....	165
Fig. 6.1. SEM images of Ti6Al4V feedstock powder at magnification of (a) 7520x, (b) 2380x and (c) size distribution measured at 2380x	169
Fig. 6.2. Temperature-time profiles of the MSHT-VAC and -THP settings modified from [204]	170
Fig. 6.3. Photos of the setup of the three-point bending test (a) before and (b) after the test.....	171
Fig. 6.4. Stress-strain profiles of (a) N ₂ and He cold-sprayed Ti6Al4V coatings on CP-Ti substrates, and (b) wrought CP-Ti and Ti6Al4V in as-sprayed, MSHT-VAC and -THP conditions.....	174
Fig. 6.5. Fracture morphologies of (a-c) N ₂ and (d-f) He cold-sprayed Ti6Al4V coatings on CP-Ti substrates in as-sprayed conditions	177
Fig. 6.6. Fracture morphologies of (a-c) N ₂ and (d-f) He cold-sprayed Ti6Al4V coatings on CP-Ti substrates in MSHT-VAC conditions.....	180
Fig. 6.7. Fracture morphologies of (a-c) N ₂ and (d-g) He cold-sprayed Ti6Al4V coatings on CP-Ti substrates in MSHT-THP conditions	183
Fig. 6.8. OM images of the (a-c) N ₂ - and (d-f) He-sprayed coatings in AS, MSHT-VAC and -THP conditions with porosity measurement at magnification of 200X	186
Fig. 6.9. OM images of the coating-substrate interface of (a-c) N ₂ - and (d-f) He-sprayed coatings in AS, MSHT-VAC and -THP conditions at magnification of 500X.....	188
Fig. 6.10. Vickers Microhardness of (a) coatings, (b) CP-Ti substrates and Ti6Al4V reference specimens	190

Fig. 6.11. XRD spectrum of coatings and as-received Ti6Al4V reference bar	192
Fig. 6.12. SEM images and EDS line scan profile of unetched (a-c) N ₂ - and (d-f) He-sprayed coatings in (a and d) AS, (b and e) MSHT-VAC, and (c and f) MSHT-THP conditions	194
Fig. 6.13. SEM images of the etched coating-substrate interface of (a-c) N ₂ - and (d-f) He-sprayed coatings in (a and d) AS, (b and e) MSHT-VAC, and (c and f) MSHT-THP conditions	196
Fig. 6.14. SEM images of etched (a-c) CP-Ti substrates and (d-f) wrought Ti6Al4V in (a and d) as-sprayed, (b and e) MSHT-VAC, and (c and f) MSHT-THP conditions.....	198
Fig. S4.1. Cumulative distribution of grain size measurement in (a) SR-GB and (b) HT-GB ...	207
Fig. S4.2. Hydrogen concentration maps in numerical simulations of (a) German 12 μm and (b) German 40 μm wide monocrystal at t = 0.5 h. Comparison of analytical and numerical hydrogen diffusion profiles of (c) German 12 μm and (d) German 40 μm wide monocrystal.....	207
Fig. S4.3. Hydrogen concentration maps in numerical simulations of a 12 μm wide German flag model with hydrogen properties of random boundaries (top), Ti6Al4V grains (middle), and special boundaries (bottom) at t = (a) 0.01 h, (b) 0.05 h, (c) 0.1 h, (d) 0.25 h, (e) 0.5 h, (f) 1 h, (g) 5 h, and (h) 10 h.....	208
Fig. S4.4. Hydrogen concentration maps in numerical simulations of a 40 μm wide German flag model with hydrogen properties of random boundaries (top), Ti6Al4V grains (middle), and special boundaries (bottom) at t = (a) 0.01 h, (b) 0.05 h, (c) 0.1 h, (d) 0.25 h, (e) 0.5 h, (f) 1 h, (g) 5 h, and (h) 10 h.....	209

List of tables

Table 2.1. Nanoindentation results of cold-sprayed Ti6Al4V by Garrido et al. [62]	20
Table 2.2. Tensile test results of (a) annealed and bright iron, (b) charcoal iron, (c) annealed and bright mild steel, and (d) hardened and tempered cast steel wires in as-prepared, post-immersed, and hydrogen-expelled conditions in 1875 by Johnson [75]	30
Table 2.3. Tensile properties of cold-sprayed Ti6Al4V treated with HIP and THRM [21]	82
Table 3.1. Morphologi 4 powder analysis on circle equivalent diameter and circularity	92
Table 3.2. Elemental composition by weight percentage of coatings	100
Table 3.3. Phase compositions	104
Table 4.1. Im2mesh input parameters.....	118
Table 4.2. Output mesh parameters	118
Table 4.3. Grain Size Measurement	119
Table 4.4. Material parameters in ABAQUS	119
Table 5.1. Cold spray process parameters	141
Table 5.2. Fluid properties in VGSTUDIO MAX permeability and diffusivity experiments....	144
Table 5.3. Archimedes' principle-based density and volume measurements	145
Table 6.1. Cold spray process parameters	168
Table 6.2. UFS and bending moduli of specimens.....	175

List of abbreviations and acronyms

ASI:	adiabatic shear instability
HE:	hydrogen embrittlement
HEE:	hydrogen environmental embrittlement
HRE:	hydrogen reaction embrittlement
IHE:	internal hydrogen embrittlement
HEDE:	hydrogen-enhanced decohesion
HELP:	hydrogen-enhanced localized plasticity
AIDE:	adsorption-induced dislocation emission
CSL:	coincidence site lattice
EBSD:	electron backscatter diffraction
GB:	grain boundary(ies)
GND:	geometrically necessary dislocations
KAM:	Kernel average misorientation
HAGB:	high angle grain boundary(ies)
IPB:	interparticle bonding
LAGB:	low angle grain boundary(ies)
SR-GB:	grain boundaries network in stress-relieved cold-sprayed Ti6Al4V coating
HT-GB:	grain boundaries network in heat-treated cold-sprayed Ti6Al4V coating
ROI:	region(s) of interest
TJ:	triple junction(s)
OM:	optical microscope/micrograph
SEM:	scanning electron microscope
TEM:	transmission electron microscope
XRD:	X-ray diffraction
EDS:	energy dispersive spectroscopy
SLM:	selective laser melting
LPBF:	laser powder bed fusion

DED: direct energy deposition
EBM: electron beam melting
EHP: electrical hydrogen permeation
FFT: Fast-Fourier transform
LHC: Large Hardon Collider
LH2: liquid hydrogen
MRO: maintenance, repair and overhaul
NDI: non-destructive inspection
TCP: tool centre point
UHV: ultra-high vacuum
XCT: X-ray computed tomography
HIP: hot-isostatic pressing
GIF: gaseous isostatic forging
VAC: vacuum
THP: thermo-hydrogen processing
MSHT: multi-step heat treatment
HSPT: hydrogen sintering and phase transformation
THRM: thermo-hydrogen refinement of microstructure
UFS: ultimate flexural strength
UTS: ultimate tensile strength
CTE: coefficient of thermal expansion

List of nomenclatures

Critical velocity:

$v_{\text{crit}}^{\text{th, mech}}$: critical velocity in terms of thermomechanical energy

F_1, F_2 : empirical factors

σ_{TS} : tensile strength of cold-sprayed coating

c_p : specific heat of feedstock material

ρ : density of feedstock material

T_i : impact temperature of particle

T_m : melting temperature of particle

T_R : reference temperature (293 K)

Bonding mechanism:

R : rebound energy

A : adhesion energy

m_p : mass of impact particles

v_p : velocity of impact particles

$\bar{\sigma}_Y$: mass of impact particles

ρ_p : density of particle material

E^* : elastic modulus of particle material

$a\%$: faction of bonded atoms per adhesive interface

ν : natural frequency of Eigen-oscillations of atoms in the crystal lattice

E_a : activation of energy of the chemical bonds

m_a : atomic mass of impact particles

t_c : contact time

T_c : contact temperature

e_r : recoil coefficient

k : Boltzmann constant

S_c : contact area of a single particle to substrate

N_a : total number of atoms in the unit contact plane

E_1 : mass of impact particles

Electrochemical hydrogen charging:

ρ_{GND} : density of geometrically necessary dislocations

$\Delta\theta_i$: local misorientation angle

μ : unit length equivalent to EBSD scanning step size,

b : magnitude of Burger's vector for specific metal

Simulation of hydrogen diffusion in GB networks:

Σ : coincidence site lattice index

ϕ : normalized concentration

θ : temperature

θ^Z : absolute zero temperature

c : hydrogen concentration

c_0 : initial hydrogen concentration

c_s : surface hydrogen concentration at the infinite end

D : hydrogen diffusivity

D_g : hydrogen diffusivity in grains

d_{CE} : circle equivalent diameter of grains

J : hydrogen diffusion flux

κ_p : pressure stress factor

κ_s : Soret effect factor

p : partial pressure

s : hydrogen solubility

t : time

x : distance in x-direction

Porous structure characterized by XCT

Φ_{real} : real porosity

ρ_{measured} : measured density

ρ_{Ti6Al4V} : theoretical density of Ti6Al4V

F_R : formation factor

α : pore-geometry factor

m : cementation factor

Enhancing ductility and adhesion by MSHT:

σ_f : flexural stress

ε_f : flexural strain

E_B : bending modulus

P : load

L : support span

b : cross-sectional width of the beam tested

d : cross-sectional depth or thickness of the beam tested

D : maximum deflection of the center of the beam

m : slope of the tangent to the initial straight-line portion of the load-deflection curve

Chapter 1: Introduction

1.1 Research background

Cold spray is a rapid coating deposition method with significantly reduced thermal stress and distortion compared to other thermal spray technologies. Particles are propelled with a supersonic inert gas (helium or nitrogen) jet through a de Laval nozzle and subjected to thermal softening and rapid viscoplastic deformation upon impact on a substrate and preceding deposited layers [1]. The preheated gas temperature is below the melting point of particles so that the factors of hydrogen damage like oxidation and crystalline phase transitions would be prevented with the use of cold spray [2]. This feature particularly benefits temperature-sensitive and hydrogen-susceptible materials such as titanium and its alloys, which have been broadly used in aircraft components due to their high specific strength, low density, and outstanding corrosion resistance [3]. Cold-sprayed deposits exhibit a high density of dislocations and nanograins since the particles are highly cold-worked by impact [4].

A variety of cold spray systems have been developed for a wide range of conditions, which can be categorized into very-low-pressure, low-pressure, and high-pressure systems according to the temperature and pressure of working gas [5]. Very-low-pressure systems, also known as micro-cold spray or aerosol deposition [6], are capable of consolidating submicron and nano-particles into thin film at room temperature and subatmospheric pressure. Low-pressure systems can reach up to 600 °C and 1 MPa, which are usually portable and suitable for spraying feedstock powder of soft metals such as copper and aluminum. To deposit hard metals like stainless steels, titanium and superalloys, high-pressure systems are necessary to accelerate the working gas up to 1100 °C and 7 MPa [7]. Some inherent deficiencies such as porosity brittleness require further processing to

mitigate. Numerous hybrid processes have been proposed, including laser assist, shot peening, rolling, friction stir welding, and electro-plastic treatment [8-10]. However, these methods also lead to side effects of local cracks after cooling to room temperature, increased plasticity, limited affected depth, and dimensional deformation. The instruments for hybrid processing also introduce additional installation costs and more complicated parameters, which hinder the interest of industry in adopting cold spray in practice. Therefore, the treatments for cold-sprayed deposits should be developed with reliable methods and readily available instruments such as furnace and hot-isostatic press.

Hydrogen damage is a common defect during the electroplating of metal components. The concentration of hydrogen atoms on metal surfaces in acid pickling without applied stress is indeed much higher than that in high pressure hydrogen gas environments [11]. Potential hydrogen damage in the manufacturing process is usually prevented by post-plating baking to remove entrapped hydrogen from the metal [12]. The mechanism of electrochemical hydrogen damage in the microstructure of cold-sprayed deposits is essential to investigate but obscure to date.

The HE-susceptible phase change is prevented as the spraying temperature is below the melting point of feedstock powder. This additive technology is a rapid metal deposition technique that features refined polycrystalline microstructure due to the supersonic impact and viscoplastic deformation of particles. Consequently, the extreme cold work on particles leads to poor ductility of deposits [13], where HE would not be a prioritized concern. Post-spray heat treatments are commonly used to recover the ductility of cold-sprayed deposits and assure the serviceability of repaired parts [13-17]. Some of these parts would be employed in environments with hydrogen exposure [18-25], utilizing THP to refine the microstructure further [26, 27] or even using hydrogen as cold spray carrier gas [28]. However, the mass transport and hydrogen interaction

properties of the cold-sprayed deposits and their microstructure after heat treatments have not been a concern compared to other commercialized additive counterparts to date [29-31].

The transport of hydrogen atoms is challenging to characterize due to the small size of hydrogen atoms and the perplexing relationship with microstructural features [32]. Since access to advanced hydrogen characterization instruments is costly and limited, the influence of interested microstructural features on hydrogen diffusion is usually studied with synthetic models and FEM simulation [33-37]. However, some irregular microstructures such as cold-sprayed deposits are difficult to mimic, so it would be more practical for metallography engineers to predict the hydrogen-affected zone over the service life with realistic models.

Some studies use cold spray to repair high-value and bulky components for fluid, energy and radioactive applications like hydropower turbines, gas turbines, natural gas pipelines, thin-walled pressure vessels, UHV chamber in LHC, nuclear waste containers and water pipes in nuclear plants [18, 25, 38-45]. Porosity has been seen as a quality indicator of cold-sprayed coatings. The porosity in hydropower and gas turbines reduces strength, fatigue performance and efficiency [46-48]. Natural gas or hydrogen leakage leads to explosion hazards if the cold-sprayed coatings are not gas-tight [39, 40]. The interconnected pores in the metal coating of the UHV chamber increase the outgassing rate and deteriorate the beam lifetime [41, 49]. More catastrophic consequences including corrosion, cooling water and radioactive leakage would occur in nuclear plants or waste repositories if cooling water or ground water permeates through the cold-sprayed deposits [18, 43-45]. On the other hand, the intended porous structure may fabricate functional coatings such as transpiration cooling, high-electrocatalytic-activity electrodes and self-lubrication [23, 50, 51]. Hence, understanding the porosity characterization and control is critical to fabricating fluid-tight or functional porous deposits.

Cold spray is gaining traction in aerospace and military sectors due to its sustainability benefits and ability to additively repair and manufacture components. Its features of solid-state consolidation and supersonic jet benefit the reserve of composition and high deposition rate, but the bond strength and geometric precision are difficult to control. Aviation industries prefer conventional machining, casting, forming, and powder metallurgy for critical components over metal additive manufacturing methods due to safety concerns. Since the process was developed by Papyrin and his colleagues back in the mid-1980s [52], the near-zero ductility has remained as the critical challenge. This limits the applications of cold spray to functional coatings, light corrosion and wear repairs, but not for structural purposes [53-55].

1.2 Research objectives

Based on the research background introduced above about cold-sprayed Ti6Al4V and concern of hydrogen embrittlement, the objectives of this thesis are as follows:

- (1) To probe the hydrogen damage on cathodic charged cold-sprayed Ti6Al4V coatings.
- (2) To create a framework for macroscopic simulation of hydrogen diffusion across the grain-boundary networks in cold-sprayed Ti6Al4V.
- (3) To unravel the statistical correlation between porosity, permeability and diffusivity of cold-sprayed Ti6Al4V.
- (4) To explore the feasible treatments on cold-sprayed Ti6Al4V coatings to achieve structural ductility and adhesion.

1.3 Outline

This thesis is composed of 7 chapters. Chapter 1 briefly introduces the research background and objectives. A comprehensive literature review of the previous studies is presented in Chapter 2

presents a systematical review on cold spray, hydrogen damage, electrolytic hydrogen interaction in cold-worked microstructure, simulation strategy for hydrogen diffusion, fluid transport in porous structure, heat treatment strategies to enhance the ductility of Ti6Al4V including thermo-hydrogen processing. Chapter 3 examines the hydrogen influence of cold-sprayed Ti6Al4V by cathodic charging the samples in as-sprayed, stress-relieved, and recrystallization heat-treated states. Chapter 4 describes the image-based realistic modeling method to simulate hydrogen diffusion across the grain boundary (GB) networks of cold-sprayed Ti6Al4V after stress-relief and recrystallization heat treatments. Chapter 5 reveals the porosity deviation of porous cold-sprayed Ti6Al4V in different characterization methods, as well as correlates porosity with permeability and diffusivity of liquid hydrogen by utilizing micro-XCT reconstruction and simulation. Chapter 6 demonstrates superior ductility enhancement on cold-sprayed Ti6Al4V coatings on CP-Ti substrates and elucidates the cause of failure in other setups with potential solutions. Chapter 7 provides overall conclusion and suggestions to navigate future development.

Chapter 2: Literature Review

2.1 Principle of cold spray

Cold spray originated from the study of meteorites striking on space vehicles by Alkhimov et al. in the 1980s [56]. The metal powder used as mockup of meteorites accumulated on the shield of space vehicles, which inspired the Soviet researchers utilizing this phenomenon to fabricate metal coatings and thick deposits. The core feature of cold spray is propelling feedstock powder in solid-state throughout the process, in other words, under the melting point of feedstock materials. To achieve successful deposition with thermal energy constraint, the feedstock powder must acquire ultra-high kinetic energy. Therefore, a supersonic jet is used to accelerate the powder to the velocity that can deposit on the substrate. While the design of cold spray systems may vary by the models and manufacturers, the layouts of system units are similar. A typical cold spray system is illustrated schematically in **Fig. 2.1** [57]. There are four main units in cold spray system: gas supply unit, gas-preheating unit, powder feeder, and cold spray gun. The working and idling gas cylinder pallets are connected to the gas pressure controller then adjusts to the preset pressure value. General gas types include helium, nitrogen and air. Nitrogen is usually used as idling gas to warm up and cool down the cold spray system, which saves expensive helium for powder spraying. After the hot and compressed gas passing through the throat of de Laval nozzle, as known as converging-diverging nozzle, the gas accelerates to supersonic velocity upon expansion. When powder is fed through a coaxial gas stream, this supersonic jet carries the powder to impact on substrate.

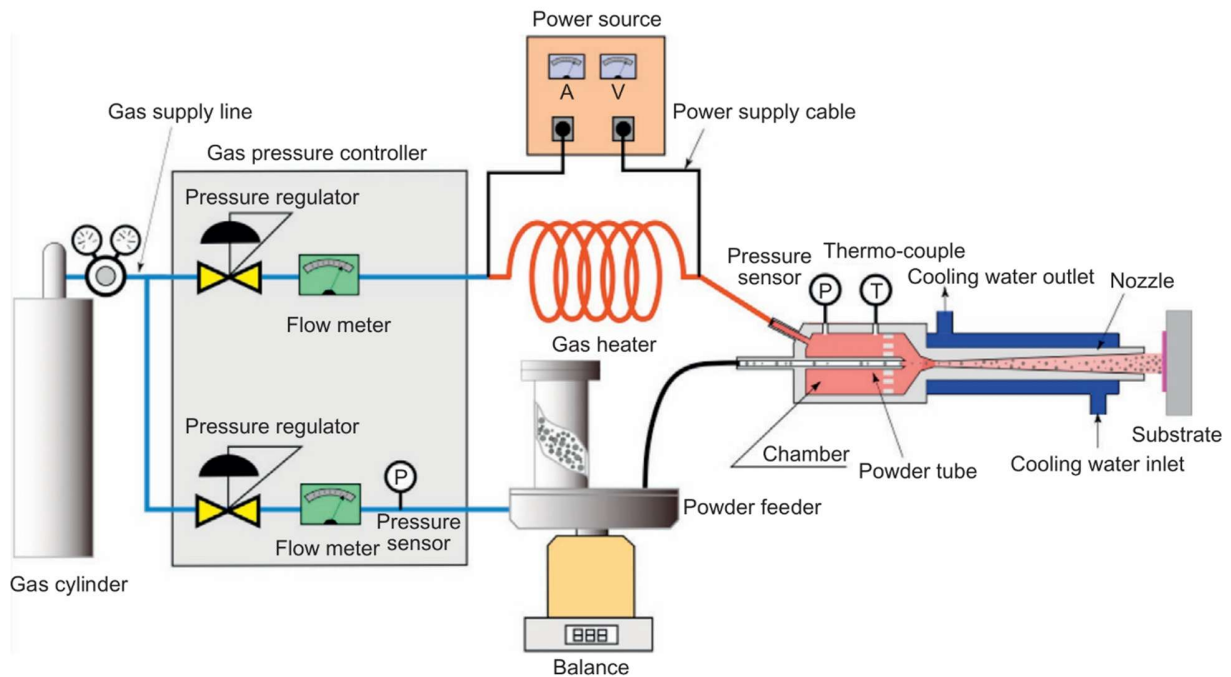


Fig. 2.1. Schematic diagram of typical cold spray system [57].

2.1.1 Bonding mechanisms

The solid-state bonding mechanism of cold spray can be seen as cold welding of metal microparticles. There is a thin oxide layer on every metal powder and substrate. Upon the collision of powder on substrate, the plastic deformation compresses and stretches the interfacial region. The oxide layers are then broken up and thus the fresh metallic surfaces are exposed and contact tightly with each other, as shown in **Fig 2.2** [1]. This phenomenon allows bonding to form without intense heating, fusion or mechanical interlocking. However, the oxide layer may not break up if it is too strong or too thick. The insufficient surface preparation of substrate, and contamination of powder during atomization or storage are possible causes. Although cold welding works around room temperature instead of few hundred °C in cold spraying, it is still a comparable illustration as a mechanical solid-state process without using electrical or chemical energy source.

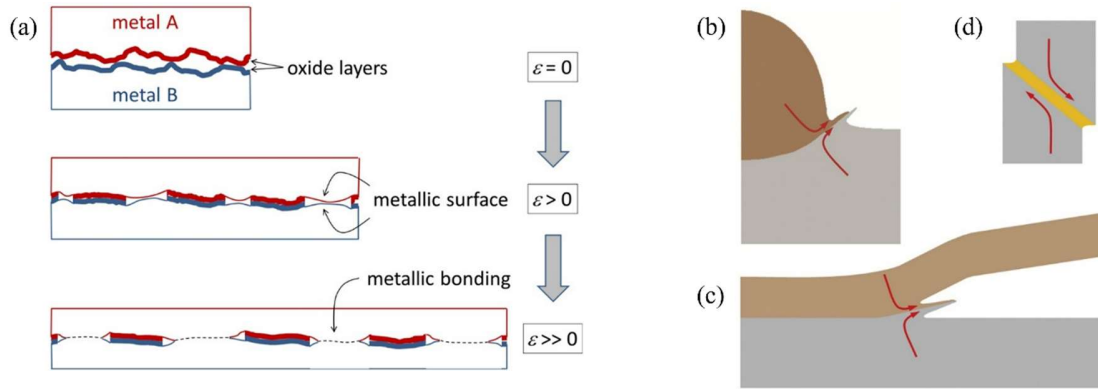


Fig. 2.2. Schematics of (a) interfacial plastic deformation resulting in cold welding, (b) deformation localization due to shear instability in particle impact in cold spraying, (c) explosive and/or magnetic pulse welding, and (d) shear banding under compression, resulting in breakup and failure [1].

The contact of fresh metal surfaces is a prerequisite for the bonding. Adiabatic shear instability (ASI) is considered as a major contributor to cold spray bonding. Similar to explosive welding and magnetic pulse welding, the shear banding and failure under dynamic loading of high-velocity impact result in material jetting and bonding, as shown in **Figs. 2.2b, c and d** [1]. The formation of re-entrant jet is considered as a prerequisite for successful welding but not compulsory for cold spray. Vortex shedding analogy can elucidate the bonding morphology of fluid-like metals at high pressure levels or high strain rates. The confluence of powder (flyer stream) and substrate (parent stream) in the vicinity of the stagnation point produces a plane flow of viscous fluid around a cylindrical obstacle [58]. The bond interface is flat when the flow around jet is laminar at low Reynolds number. Contrarily, the interface becomes wavy due to vortex formation following unstable flow separation at high Reynolds number.

On the other hand, there is viewpoint of hydrodynamic plasticity being the major bonding mechanism of cold spray instead of ASI. Shockwave is formed as a highly compressed state of matter from the impact center to the contact edge, as shown in **Fig 2.3** [59]. The particle flattens

and expands the interfacial area. In the beginning, the speed of shockwave is slower than that of matter. However, the strain hardening effect decelerates the flow of material, while the velocity of shock wave is stable in the same material. The shock wave is able to detach from the edge of particle when the contact edge outward velocity becomes slower than that of shock wave. The free surface with zero-pressure zone is then formed upon the cracking of edge. The high hydrodynamic stresses exceed the flow strength of the material. The large pressure gradient accelerates the material, releases the pressure and undergoes a localized tension to form jet lips. Such jetting and its subsequent large interfacial strain facilitate the contact of clean metal surfaces to form bonding.

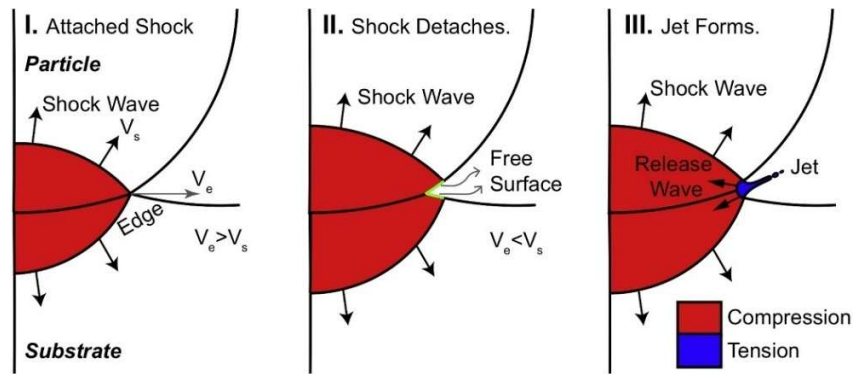


Fig. 2.3. Schematic representation of jetting in cold spray: Stage I. Impact induces a shock wave.

Stage II. Shock detaches from the leading edge. Stage III. Jet forms on the basis of pressure releases [59].

Vortex-like intermixing is a special phenomenon at some coating-substrate interfaces. Yin et al. [60] propose that low deposition efficiency and material properties are the critical factors to trigger intermixing interfaces. After the successful deposition of the first-layer particles, the succeeding particles rebound rather than deposit on the first layer. The continuous peening flattens the first layer of particles, then breaks the particles and eventually buries some of the fragments into the substrate, as shown in **Fig. 2.4a**. Intermixing occurs at low preheating gas temperature, which implies there are less thermal softening and less pre-expansion heat for kinetic energy conversion

through de Laval nozzle. Hence, intermixing is reduced along with the increase of gas temperature and deposition efficiency, as shown in **Fig. 2.4b**. From the perspective of materials, the feedstock powder has to be harder than substrate to trigger intermixing. There is more kinetic energy in particles with higher density to induce severe plastic deformation of substrate for intermixing. Therefore, intermixing is observed in the hard coating-soft substrate combinations of Cu-Al, Ni-Al, SS304L-Al, and Cu-Mg at gas temperatures of 100 and 200 °C. However, intermixing is not triggered if the materials are reversed, such as Al-Cu. Ti alloys are considered to be hard compared to Mg, Al, and Cu. Thus, intermixing is not observed in their coatings and substrates, as shown in **Fig. 2.12** in **Section 2.1.4**. ASI and hydrodynamic plasticity dominate the bonding mechanisms in cold-sprayed Ti alloys, which decide their physical properties including mechanical strength and fluid transport properties.

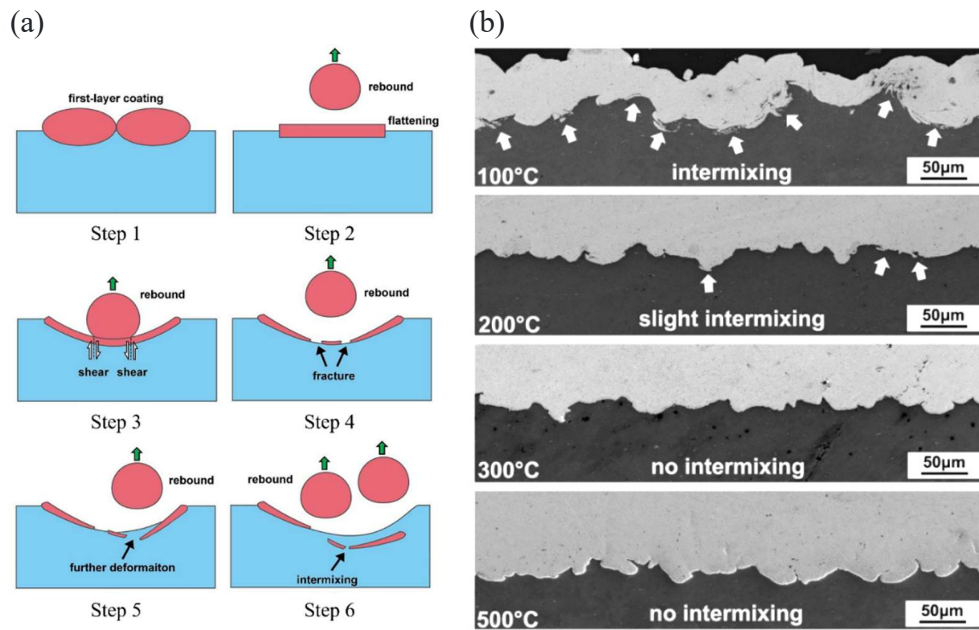


Fig. 2.4. (a) Schematic of the intermixing interface formation mechanism. (b) Microstructure of the Cu coating-Al substrate interfaces deposited at various gas temperatures [60].

2.1.2 Deposition velocity window

Critical velocity refers to the appropriate impact velocity that feedstock powder needs to be accelerated to form bonding. It depends on the material properties and process parameters, i.e. temperature, specific heat, thermal conductivity, density, and strength. The equation by Schmidt et al. [61] is expressed as:

$$v_{\text{crit}}^{\text{th, mech}} = \sqrt{\frac{F_1 \cdot 4 \cdot \sigma_{TS} \cdot \left(1 - \frac{T_i - T_R}{T_m - T_R}\right)}{\rho} + F_2 \cdot c_p \cdot (T_m - T_i)} \quad (2.1)$$

The equations for estimating the critical velocity include mechanical (F_1) and thermal (F_2) calibration factors based on experiments. The erosion velocities are calculated by substituting higher values of calibration factors. Some factors including particle size, strain rate and purity are not considered in Eq. (2.1). Despite the estimations being rough due to excess uncertainties, the particle impact-temperature and velocity can be correlated. **Fig. 2.5a** presents the deposition velocity window over impact temperature. The window refers to the particle velocity above the critical velocity but below the erosion velocity. Particles cannot be deposited, and slight erosion occurs if they are under the critical velocity. On the other hand, exceeding the erosion velocity results in no deposition and strong erosion. Both the critical and erosion velocities decrease along with the rise of particle impact temperature. However, there is no deposition if the particle temperature is too low, regardless of the velocity. Feedstock materials exhibit brittle behavior without sufficient thermal softening. The optimal particle impact conditions are chosen within the deposition window slightly above the minimum deposition temperature, which complies with the initiative of cold spray to reduce the thermal residual stress. Schmidt et al. [62] later calculated the window of deposition for a variety of materials by assuming a particle size of 25 μm and an impact temperature of 20 $^{\circ}\text{C}$, as shown in **Fig 2.5b**. The theoretical deposition window for Ti6Al4V is

between 900-2450 m/s at these assumed conditions, which is way above the velocity range of commercial cold spray systems without heating. Thus, preheating the carrier gas is required to reduce the velocity of deposition window besides accelerating the gas stream to supersonic speed.

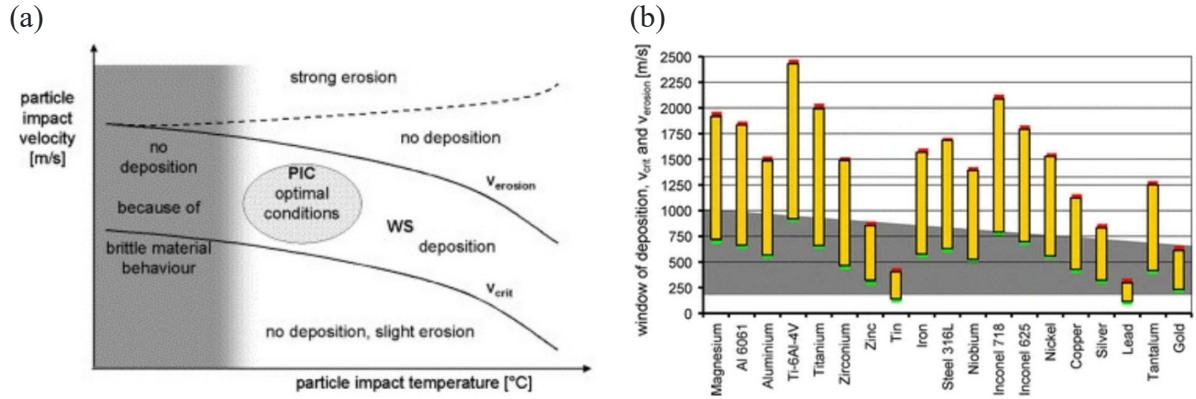


Fig. 2.5. Windows of sprayability (WS) in terms of particle velocity over (a) particle temperature [61] and (b) metals at room temperature [62].

It is noted that the velocity and temperature profiles of gas and particles are not identical throughout the propulsion process. Huang and Fukanuma [57] illustrate the velocity (**Fig. 2.6a**) and temperature (**Fig. 2.6b**) profiles of particles and gas along the symmetrical centerline of nozzle in Plasma Giken cold spray system. The heat of gas-solid-flow is accumulated before entering the throat of de Laval nozzle. Their temperatures slightly drop to the same level at the throat regardless of N_2 or He gas. After passing through the throat, the heat converts to kinetic energy rapidly upon expansion to supersonic speed. He gas is accelerated to much faster exhaust speed at ~ 2600 m/s than that of N_2 at ~ 1100 m/s due to its lighter molecular mass (He: 4.002602 g/mol; N_2 : 28.0134 g/mol). Consequently, the velocity of particles propelled by He (~ 1250 m/s) is much faster than that by N_2 (~ 700 m/s). This indicates He carrier gas providing more kinetic energy for particles deformation and bonding than N_2 . Contrarily, the exhaust temperatures of gas (~ 190 °C) and particles (~ 20 °C) in He jet are much lower than that of N_2 gas (~ 500 °C) and its particles (~ 140 °C).

In other words, N₂ facilitates slightly better thermal softening effect and eases deformation than He. Moreover, the quality of cold-sprayed deposits emphasizes the balance between impact velocity and temperature for each material rather than focus on a single parameter.

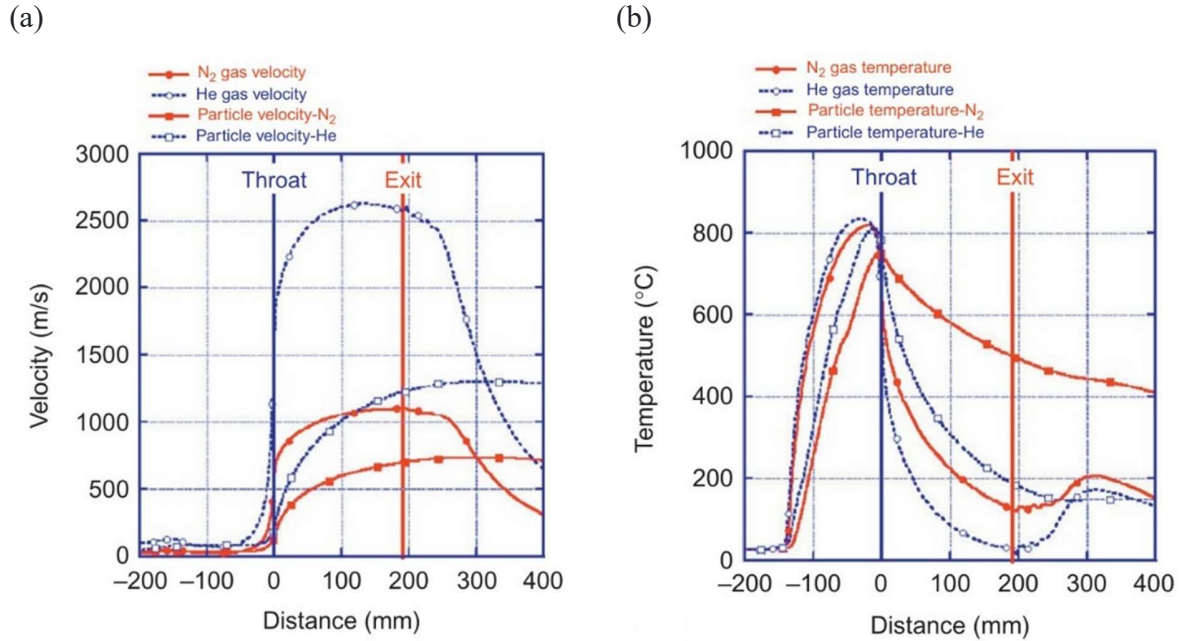


Fig. 2.6. (a) Velocity and (b) temperature profiles of particles and gases across cold spray nozzle in simulation [57].

The deformation morphology of particles at different impact velocities affects the overall quality of the deposit. Wu et al. [63] cold-sprayed Al-12Si powder with mean size of 25 μm on the mild steel substrate. The pressure of N₂-He mixture gas varies from 0.3 to 3.0 MPa at fixed temperature of 400 °C to obtain a wide range of particle velocities. The study evaluates the deposition efficiency by considering the fraction of deposited particles to total impacted particles in the regions of interest (ROIs), which is named as the ratio of bonds. **Fig. 2.7** summarizes the overall morphology of substrate surfaces and particles deposited at different impact velocities. The ratio of bonds for particles deposited at 500, 700, and 1000 m/s are 30, 70, and <10 %, respectively. The impacted spots without bonding can be recognized with craters, where deep dents are also

found on substrate surface for particles impacted above erosion velocity. **Fig. 2.7a** shows a closer look on moderate deformation of particle impacted at 500 m/s, where the bottom of particle spreads out to a diameter of $\sim 50\ \mu\text{m}$ with little jetting. The particle further deforms to $\sim 88\ \mu\text{m}$ wide with more severe jetting with impact velocity of 700 m/s (**Fig. 2.7b**), which is considered to be nearly optimal. Raising the impact velocity to 1000 m/s results in most particles rebounded and few deposited particles with a morphology of “bullet blossom” but without further increase in diameter (**Fig. 2.7c**). The excess kinetic energy deforms the particle to very flat and fractures on its edge. The over deformation near erosion velocity hinders the buildup of coating.

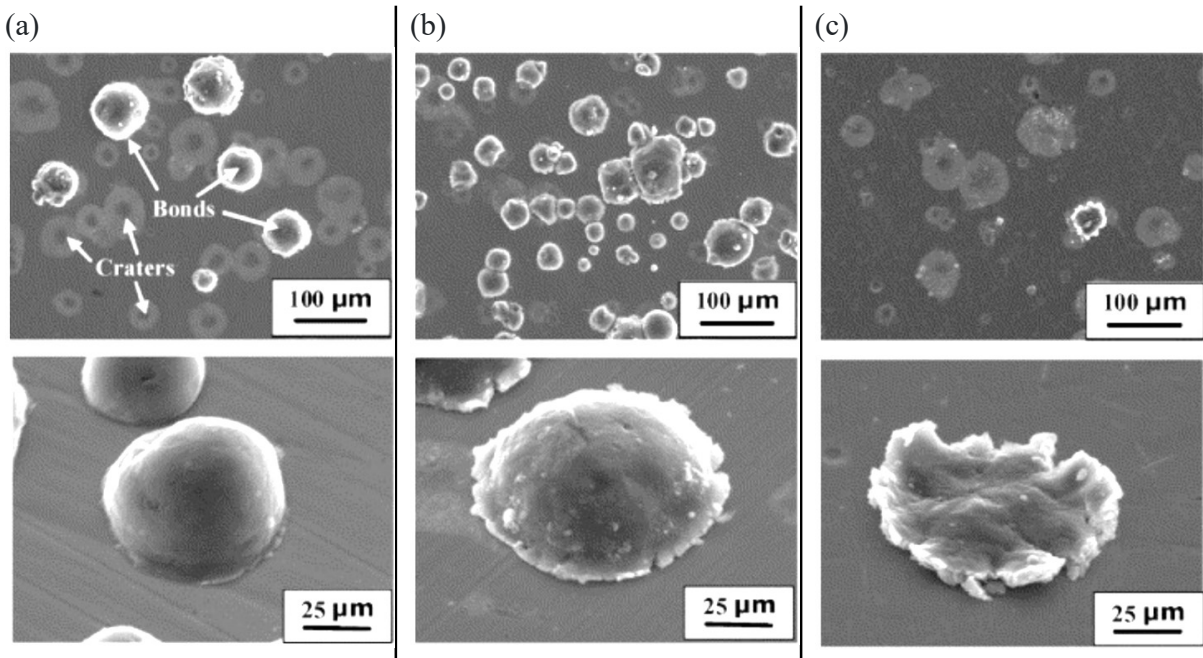


Fig. 2.7. SEM micrographs of the substrate surfaces (top view) and the attached Al-12Si particles onto the mild steel substrate (45° angle tilting view). Impact with a mean particle velocity of (a) 500 m/s, (b) 700 m/s and (c) 1000 m/s [63].

Wu et al. [63] suggest that the cold spray deposition is a competition between rebound energy (R) and adhesion energy (A), where their equations are expressed as follows:

$$e_r = 11.47 \left(\frac{\bar{\sigma}_Y}{E^*} \right) \left(\frac{\rho_p v_p^2}{\bar{\sigma}_Y} \right)^{-\frac{1}{4}} \quad (2.2)$$

$$R = \frac{1}{2} \cdot e_r \cdot m_p \cdot v_p^2 \quad (2.3)$$

$$a\% = 1 - \exp \left\{ -v t_c \exp \left[\frac{-E_a}{kT_c + (1-e_r)m_a v_p^2 / 2} \right] \right\} \quad (2.4)$$

$$A = a\% \cdot S_C \cdot N_a \cdot E_1 \quad (2.5)$$

The window of deposition velocity indeed refers to the velocity range where adhesion energy is higher than rebound energy, as shown in **Fig. 2.8**. The optimal particle velocity is approximately located at the point of maximum displacement between the two energy curves. However, there are some factors neglected in the above equations. The contact temperature is assumed to be the He gas process temperature of 400 °C instead of the particle impact temperature mentioned previously in **Fig. 2.6**. The different properties of particles and substrates are not considered, such as atomic mass, elastic modulus and density. Particle contact time is critical to calculate adhesion energy, but the exact value is not mentioned. Despite these uncertainties, the calculated optimal velocity matches experimental observation. Nevertheless, the optimal velocity for each combination of powder and substrate still needs to be tested to achieve high deposition efficiency and coating quality.

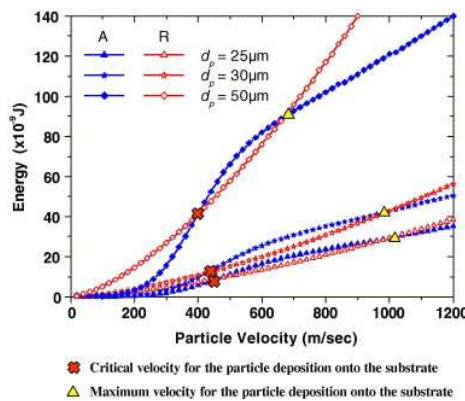


Fig. 2.8. Calculated adhesion energy and rebound energy for various sized Al-Si feedstock impacting onto a mild steel substrate [63].

2.1.3 Mechanical Properties

Near-zero ductility is the critical shortcoming of cold-sprayed deposit in as-sprayed condition due to severe deformation with high strain rate [64]. Tan et al. [65] test the tensile loaded flexural strength of cold-sprayed Ti6Al4V coatings on Ti6Al4V substrates with multiple coating thicknesses of 0.1, 0.5, 1, and 3 mm. The fracture morphologies of three-point bending specimens are summarized in **Fig. 2.9**. All coatings exhibit cohesive failure without necking. Hairline cracks are formed on the 0.1 and 0.5 mm thin coatings. The number of cracks on Ti6Al4V coating reduces along with the increase in thickness, so as to maintain integrity. There is only a single crack on the 1 and 3 mm thick coatings which is parallel to the bending load. However, there is more severe local delamination with a larger bending radius. In addition to the change of fracturing behavior, this also indicates that the adhesion of thick coatings is strong enough to withstand the stress release upon the brittle fracture. The stress-strain curves of bending test specimens are plotted in **Fig. 2.10**. The brittleness of the coating becomes more significant than the plasticity of the substrate beyond a thickness of 0.5 mm. The fracture strains of thin coatings are about 6 %, but the 1 and 3 mm thick coatings fracture at strains of 0.7 and 1.1 %, respectively. It is noted that the flexural stress drop upon fracture drastically increases when the thickness of coating increases from 1 mm to 3 mm, which are 550 to 450 MPa, and 519 to 190 MPa, respectively. This reflects the residual stress in cold-sprayed deposits is accumulated along with the buildup, which may slowly bend the substrate or shock-damage the substrate upon coating failure.

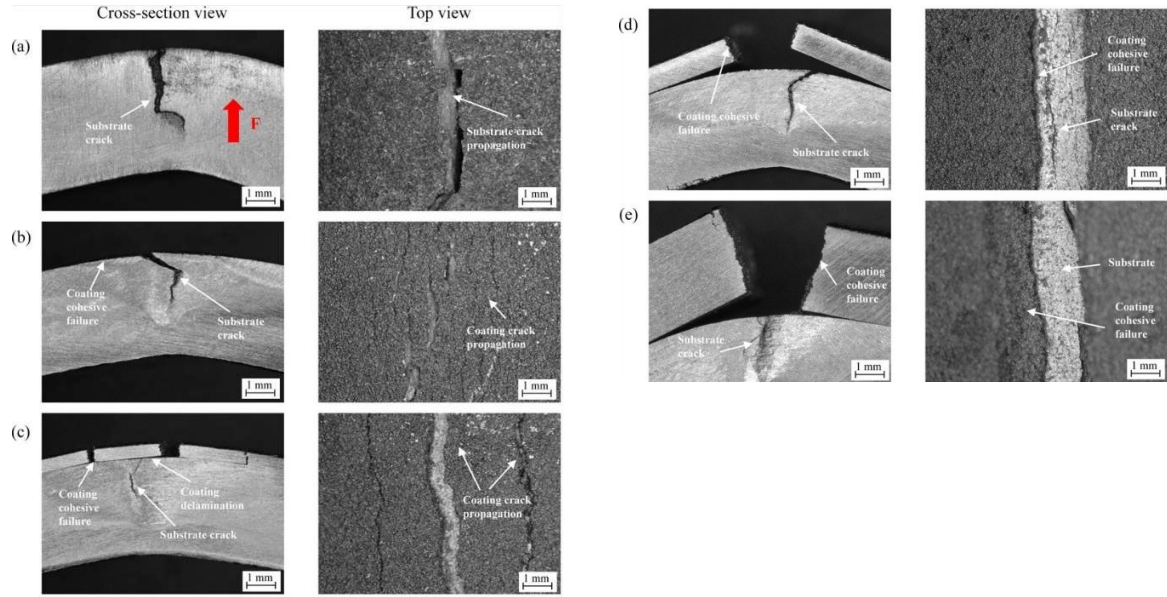


Fig. 2.9. Side and top views of cold-sprayed Ti6Al4V samples at crack locations after bending test: (a) bare substrate and (b to e) coated samples with coating thicknesses of (b) 0.1 mm, (c) 0.5 mm, (d) 1 mm and (e) 3 mm thick [65].

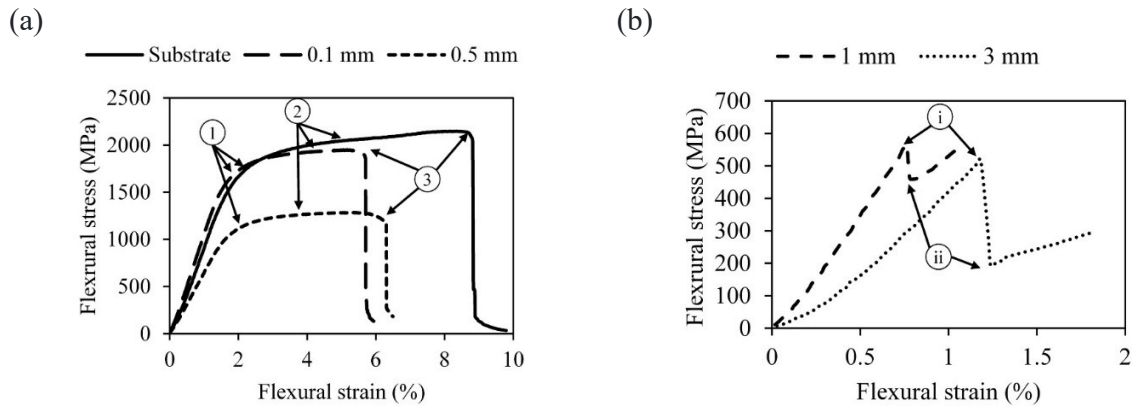


Fig. 2.10. Stress-strain curves as a function of coating thickness: (a) bare substrate and coated samples with 0.1 mm and 0.5 mm thin coatings and (b) coated samples with 1 mm and 3 mm thick coatings [65].

Cold-sprayed deposits have distinctive performance in different loading directions. Ogawa et al. [66] use four-point bending test in both compressive and tensile loading directions to evaluate the performance of low-pressure cold-sprayed Al coatings on Al substrates. The thickness of coatings

and substrates is 2 and 3 mm, respectively. The photos and results of specimens after the bending test are summarized in **Fig. 2.11**. There is no cracking or delamination in the compressively loaded cold-sprayed Al coating throughout the crosshead displacement of 1 mm, which also has a strength double that of the cold-rolled Al specimen. On the other hand, tensile-loaded bending induces a vertical crack that initiates from the coating surface, propagating to the coating-substrate interface. This crack then delaminates the coating. The cold-sprayed Al coating fractures brittly at a tensile load of 0.6 kN and 0.2 mm of displacement, where the substrate is subjected to 0.3 kN loading right after losing the support of the coating. It is considered that there is strong adhesion between coating and substrate, but the cohesion between particles is weak. Compressive loading compacts the particles, while tensile loading disconnects the weak interparticle boundaries (IPB). Thereby, the specimens undergo a recrystallization heat treatment at 270 °C for 9 hours. The heat-treated specimen has a slightly lower elastic modulus than the as-sprayed one upon compression, since the work-hardening effect is reduced by recovery and recrystallization. On the contrary, the heat-treated specimen exhibits significant improvement under tensile loading with an ultimate load of 1.1 kN at a displacement of 1.2 mm. This demonstrates that heat treatment can enhance the ductility of cold-sprayed coatings and mitigate the anisotropy. The next section introduces the detailed mechanisms and parameters of heat treatment for cold-sprayed Ti6Al4V coating.

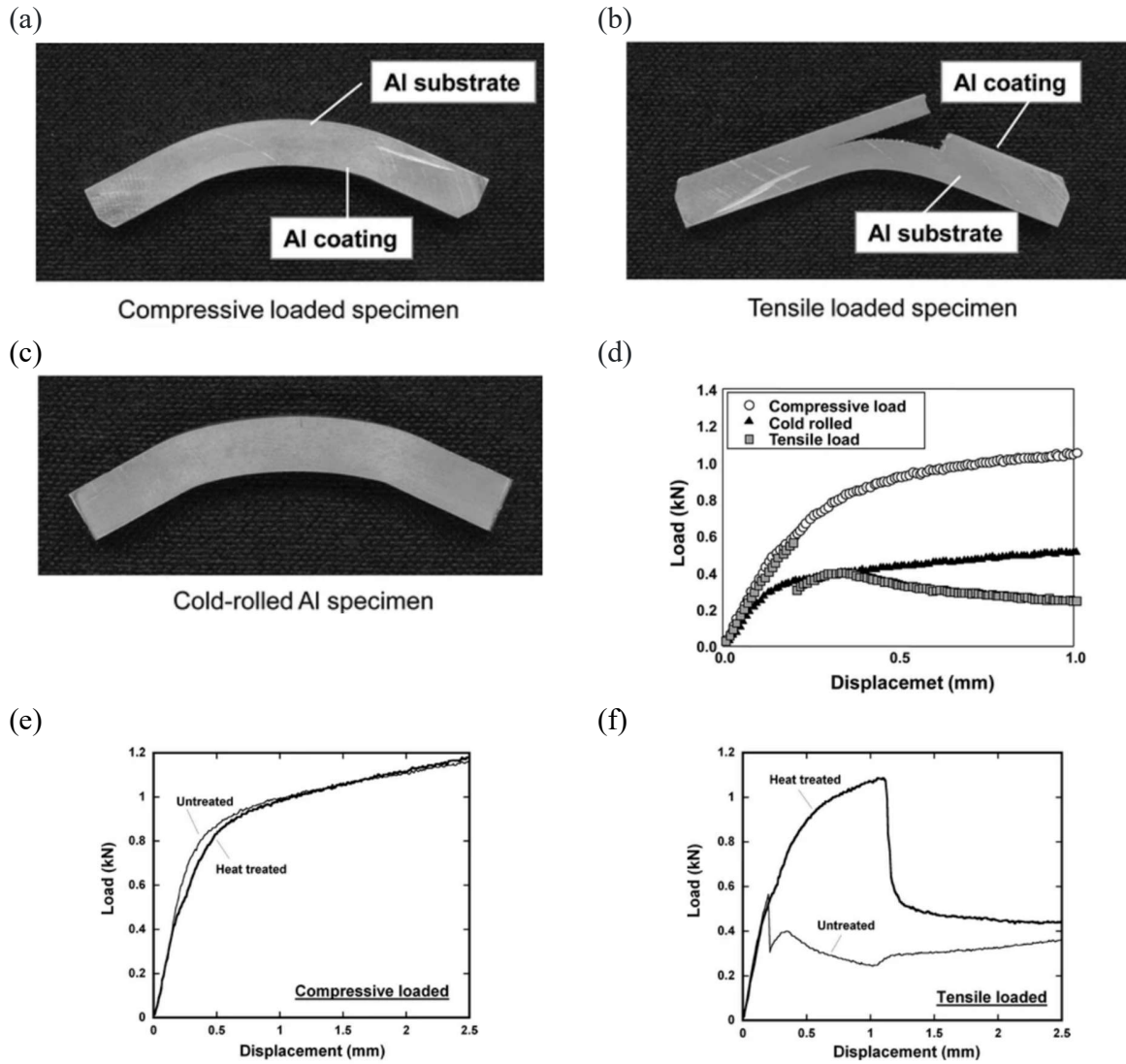


Fig. 2.11. Images of (a) compressive loaded, (b) tensile loaded, (c) cold-rolled specimens after four-point bending tests and their corresponding load-displacement curves in (d) as-sprayed and (e and f) heat-treated conditions [66].

2.1.4 Microstructure evolution during heat treatment

The process methods and parameters with various microstructures of wrought Ti6Al4V have been well studied last century [67]. However, it is challenging to implement the exact heat treatment to cold-sprayed coatings since there are excess porosity and particle deformation to be annihilated. Garrido et al. [68] prepare cold-sprayed Ti6Al4V coatings on Ti6Al4V substrates with N₂ gas in

two sets of parameters: (1) 800 °C and 4 MPa; (2) 1100 °C and 5 MPa. A part of specimens sprayed at 1100 °C are heat-treated at 1000 °C for 1 hour in high vacuum followed by argon quenching to room temperature, then proceeds with precipitation heat treatment at 537 °C for 4 hours followed by furnace cooling. The optical micrographs of the coatings and interfaces are displayed in **Fig. 2.12**. Raising the spray temperature from 800 to 1100 °C effectively reduces the porosity from 18.1 to 3.83 %, which is likely contributed by better thermal softening effect. The heat treatment further reduces the porosity of coating sprayed at 1100 °C to 1.37 %. It is aware that the porosity near coating surface does not eliminate as remarkable as the interface region. Furthermore, there is intense phase change in both coating and substrate, which is counter to one of the purposes of using cold spray. Moreover, the equiaxed microstructure and disappearance of IPB near the interface are signs of ductility and strength enhancement. The nano-indentation results are summarized in **Table 2.1**. The influence of heat treatment on the mechanical performance is limited despite the apparent change of microstructure. Thus, it is essential to understand the evolution of pores structure and grain-boundaries during heat treatment to improve the post-spray treatment for cold-sprayed coatings.

Table 2.1. Nanoindentation results of cold-sprayed Ti6Al4V by Garrido et al. [68].

Ti6Al4V cold-sprayed coatings	Reduced modulus (GPa)	Nanohardness (GPa)
Ti6Al4V-800	99.3 ± 5.9	3.53 ± 0.26
Ti6Al4V-1100	107.2 ± 3.4	3.94 ± 0.36
Ti6Al4V-1100-HT	117.0 ± 4.9	3.86 ± 0.33
Particles	94.5 ± 5.4	3.01 ± 0.40
Substrate	110.8 ± 3.6	3.34 ± 0.15

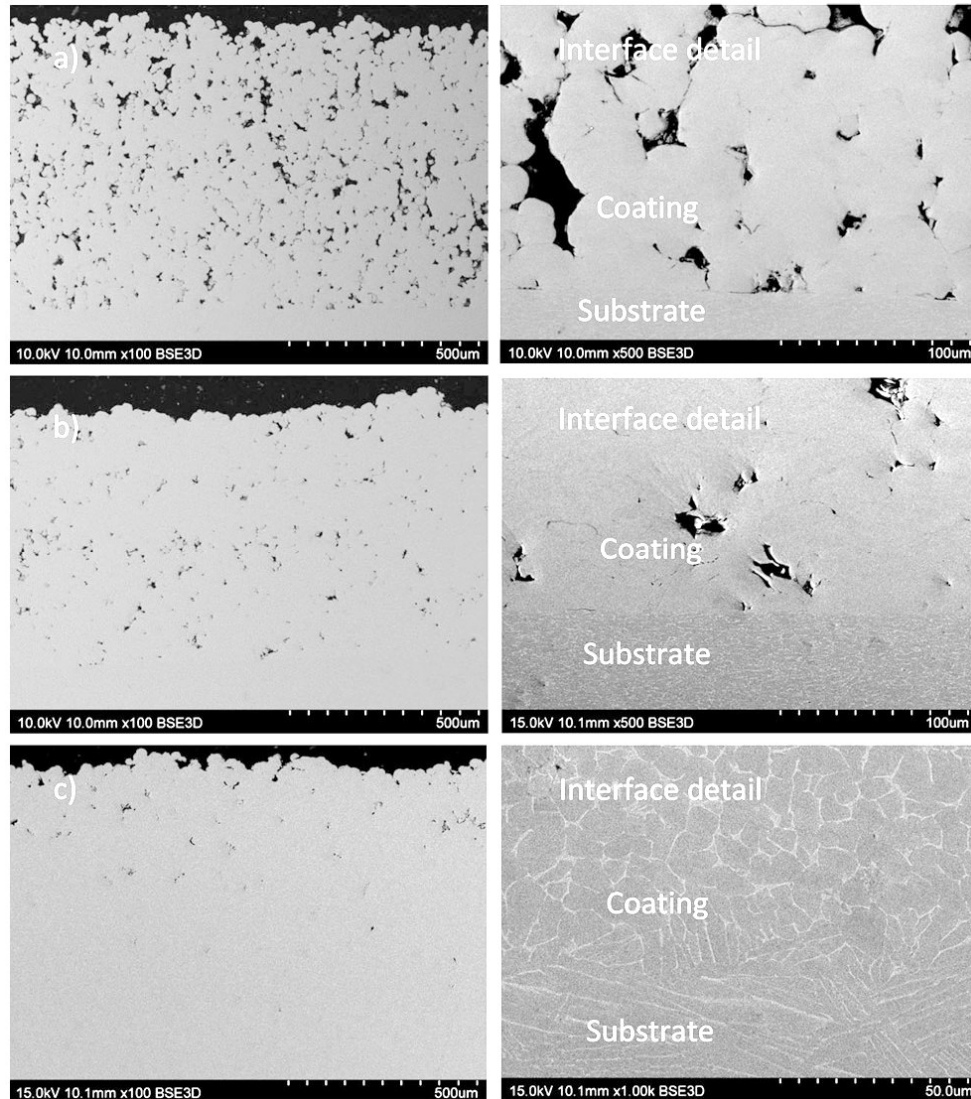


Fig. 2.12. Coating and interface: (a) sprayed at 800 °C; (b) sprayed at 1100 °C; (c) sprayed at 1100 °C with subsequent heat treatment [68].

Huang et al. [13] compared the pore structure evolution of coatings during heat treatment, as shown in **Fig. 2.13**. The hardness of the feedstock material plays a crucial role in defining dense or porous coating. Dense coating is usually sprayed with soft metal powder like Cu, where hard metal like Ti is consolidated into porous coating. When the coatings are heat-treated at lower temperature, slight diffusion is triggered between particles. The compactly connected IPB become obscure, which does not occur on the weakly bonded and unbonded particles in porous coating. The

temperature at this stage does not remove the work hardening effect or trigger recrystallization. Hence, low temperature heat treatment can slightly strengthen the dense coating but the influence on ductility is very limited. Raising the heat treatment temperature to the recrystallization temperature further encourages the interparticle diffusion, which gradually removes the work hardening effect, the marks of the boundary, as well as severe plastic deformation. Deformed grains are recrystallized into fine grains, which contribute to enhanced strength and ductility to near-bulk level for dense coating. Further diffusion in still a porous coating that closes the small pores and strengthens the compact interparticle bonding; however, the coating remains brittle due to the remaining large pores. The previously recrystallized fine grains grow to larger sizes as the heat treatment temperature increases further. The grain growth decreases the strength of dense coatings as a compromise for extended elongation. For porous coating, pores become diminished and spheroidized in addition to grain growth. However, the deterioration of strength in porous coating due to grain growth is not as significant as dense coating since the recovery of defects is prioritized. Moreover, there is no apparent grain growth in cold-sprayed CP-Ti after heat treatment at 1000°C for 4 hours. For bulk CP-Ti, grain size is decided by the amount of work and annealing temperature, but grain growth does not start until recrystallization is completed [69]. There are excessive microstructural defects in cold-sprayed deposits of Ti and its alloys. Heat treatment with prolonged time and dynamic pressure control need to be considered to complete the recrystallization stage and recover the performance of deposits to near wrought.

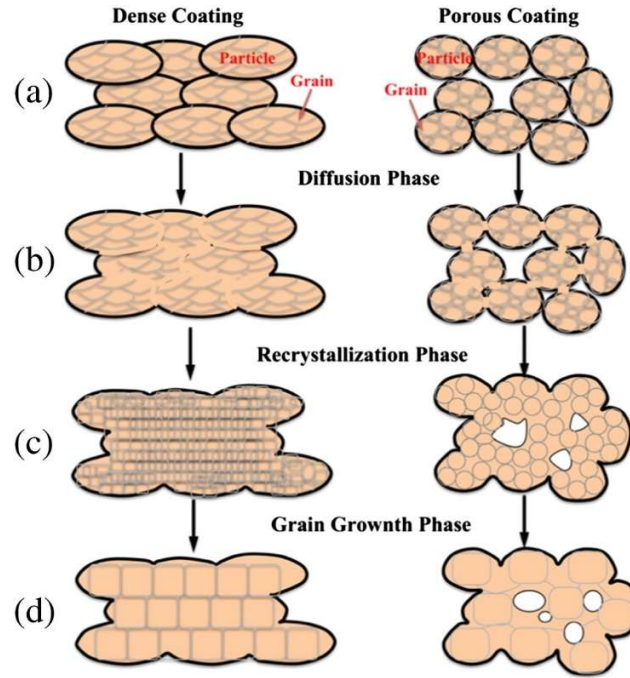


Fig. 2.13. Schematic illustration of the evolving cold-sprayed coating during heat treatment from (a) as-sprayed condition to phases of (b) diffusion, (c) recrystallization, and (d) grain growth [13].

Zhou et al. [70] suggest that heat treatment triggers both shrinkage and expansion of pores in cold-sprayed Ti6Al4V coating, as shown in **Fig. 2.14a**. The atomic diffusion at compact IPB strengthens the metallurgical bonding and results in necking. The irregularly shaped pores become spheroidized, shrink progressively, and disappear eventually. On the other hand, some of the weakly bonded interfaces separate upon stress relief during heat treatment. Since particles shift to accommodate neck growth at strong bonding, the weak interfaces detach then result in the growth or even merging of neighboring pores. The pores near the weak interfaces still vanish with sufficient heat treatment time. **Fig. 2.14b** shows that the evolution of pores can be divided into four stages: (1) inoculation stage with little change, (2) rapid quasi-free contraction during recrystallization, (3) arrested contraction rebound caused by weak interface detachment, and (4) free contraction as diffusion overwhelmingly close pores. Coating deposited at higher

temperatures with better thermal softening contains more and stronger metallurgical bonds that suppress rebound, so the porosity reduces continuously. However, the porosity evolution would fluctuate more if there are excess weak bonds due to lower spraying temperature or other issues such as powder feeding instability.

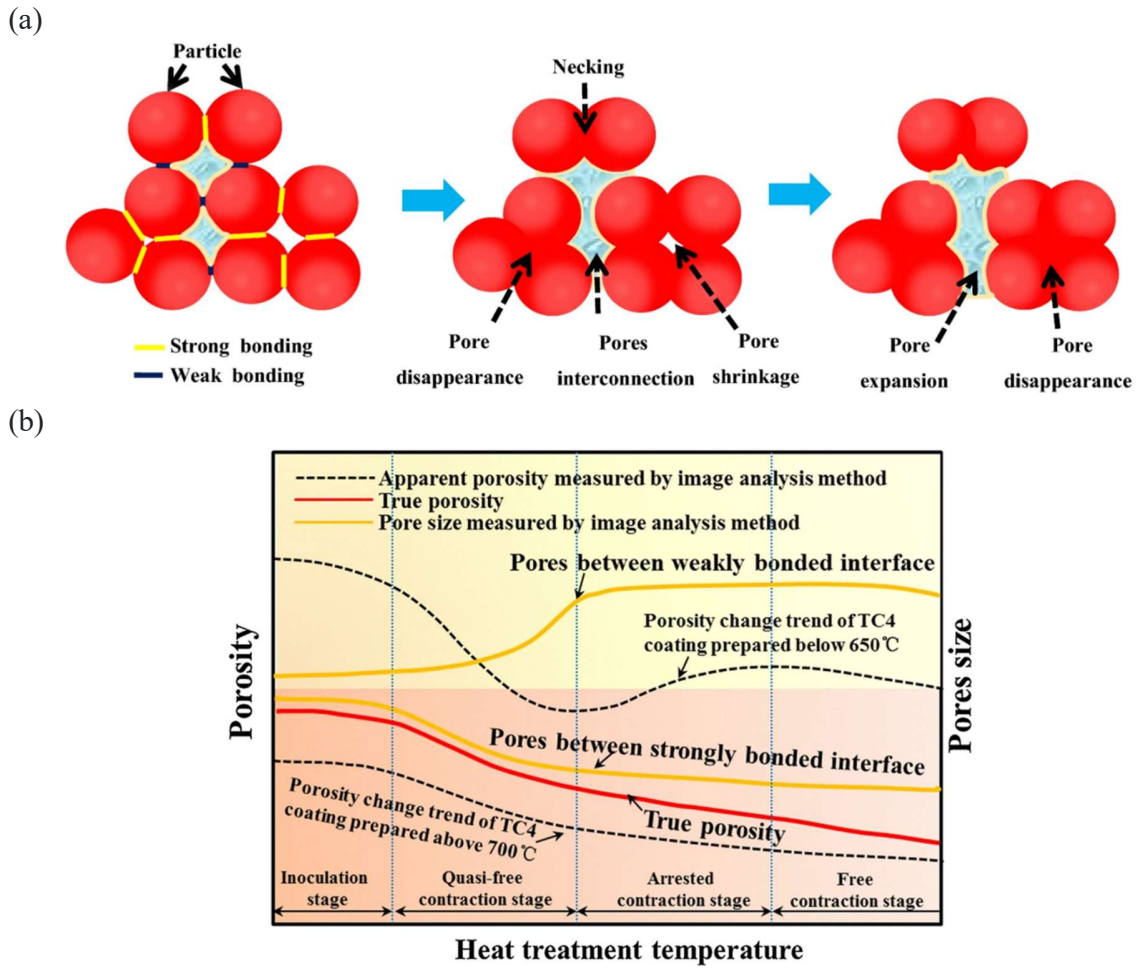


Fig. 2.14. Pores shrinkage and expansion mechanism along with heat treatment in (a) schematic illustration, and (b) porosity profile [70].

The grain-boundary evolution during heat treatment elucidated by Yang et al. [16] is presented in **Fig. 2.15**. There are three regions in a pair of bonded particles: (1) as-atomized powder microstructure with little deformation, (2) IPB with nanograins, and (3) deformation transition

layer adjacent to IPB. The Ti6Al4V powder in martensitic microstructure is prepared by plasma rotating electrode process atomization, and thus the deformed layer is composed by nano-laths. The deformed layer accumulates more dislocations and internal stress than the IPB as the stored energy at IPB is consumed for dynamic recrystallization into nanograins. Upon non-phase-change heat treatment at 850 °C for 1 hour, the nanograins at IPB grow into submicron grains with equiaxed microstructure and diffusion bonding. Meanwhile, the nano-laths and subgrain boundaries in deformation transition layer transform into nanograins and equiaxial ultra-fine grains, respectively. The heat treatment parameters above result in an inhomogeneous growth of the interfacial grains, which subsequently deteriorate the average reduced modulus of cold-sprayed Ti6Al4V by 16 %. Therefore, the appropriate heat treatment parameters for cold-sprayed Ti6Al4V are explored in **Section 2.6** and implemented in **Chapter 6**.

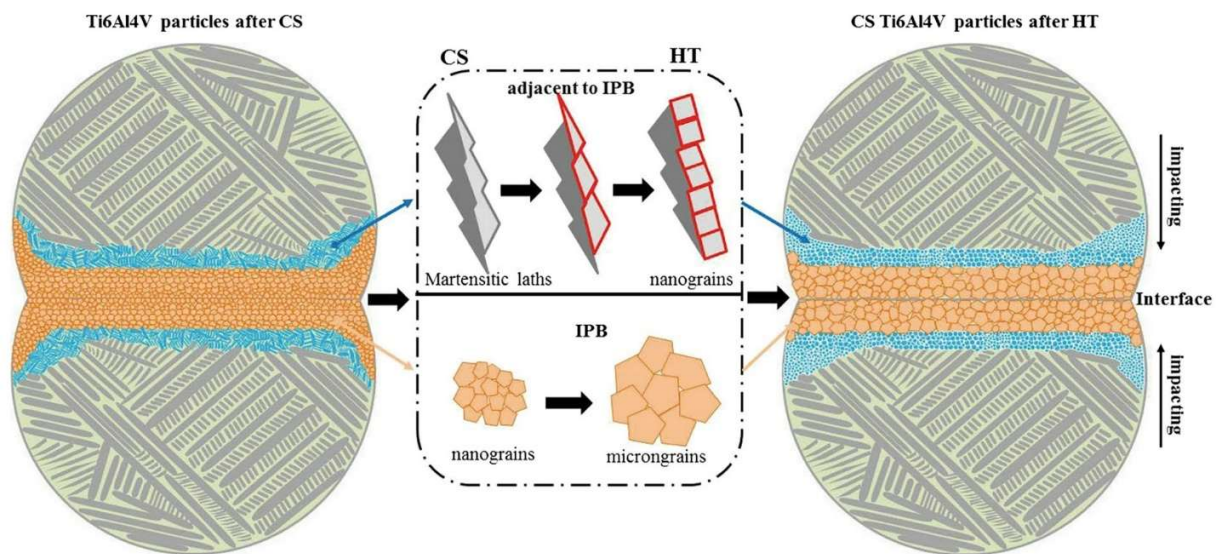


Fig. 2.15. Evolution of microstructure of deformed Ti6Al4V particles at IPB of CS deposits after HT [16].

2.1.5 Applications

Although most cold spray studies aim at implementation in aerospace, the most popular application of cold spray nowadays is cookware. Plasma Giken and Hitachi [53] apply cold-sprayed steel coating on aluminum rice cooker inner pot for induction heating, as shown in **Fig. 2.16a** [71]. The thin ferromagnetic layer at the bottom of the pot has a high electrical resistance to be heated up by eddy currents, then the generated heat is distributed quickly and uniformly across the thermal conductive aluminum main body. The mass production of the rice cooker inner pot demonstrates the reliable deposition of steel coating on aluminum substrate, which can be adopted in aerospace, such as de-icing, engine preheating, and electromagnetic interference shielding with both wave reflection and absorption [72]. Such bimetallic capability also enables depositing materials locally for weight optimization based on component requirements. NASA and ASB Industries cold-spray NASA HR-1 onto a LPBF GRCop-84 subscale chamber, as shown in **Fig. 2.16b** [73]. The project evaluates the deposition quality of cold spray, DED and laser hot wire cladding for the particular thrust chamber application and optimize post-processing parameters.

Since new technologies require about two decades of proper testing and analysis to be safely adopted in aviation [55], the testing and verification are conducted by the OEMs and certified service providers. The first GE component tested with cold spray repair is the accessory gearbox of GE90 engine by Avio Aero and Polytechnic of Bari in 2017, as shown in **Fig. 2.16c** [74]. The working process also involves digital scanning, damage recognition, and toolpath planning. The studied feedstock materials include steel, Al, Mg, Ti, and TiAl alloy. However, laser deposition is preferred for TiAl rather than cold spray since the material is used in high precision engine parts, which cannot be achieved by cold spray. In addition to industry and academia, the service shops for military aircraft provide more technological proving grounds for cold spray repair. COC

Aerospace develops a long-reach nozzle and controls the rotation speed of turntable to cold spray Ni-based powder on the inner-wall of main-landing-gear cylinder of Northrop F-5, as shown in **Fig. 2.16d** [75]. The deposit is needed since the cylinder would be too thin to hold hydraulic pressure after machining off the scratches and gouges. It is claimed that the cold spray repair saves over 70% of new production and reduces the turn-around time to 90 days. Another example is the cold spray dimensional restoration of aircraft fuel flow proportioner by ES3, as shown in **Fig. 2.16e** [76]. The corrosion damage is restored by the Al alloy deposit with improved corrosion and wearing resistance. To prevent secondary corrosion after restoration, corrosion resistance has been considered an essential factor to evaluate the performance of cold-sprayed deposits. Researchers in the US defense companies and institutes have in-depth investigations on the corrosion resistance of cold-sprayed Al, Cu, Fe, Ni, Ti alloys and the potential addition of ceramic such as CrC, B₄C and BN_x [54, 77-80]. Nevertheless, a metal degradation that is well known for Ti but has been undermined among studies of cold spray: hydrogen damage.

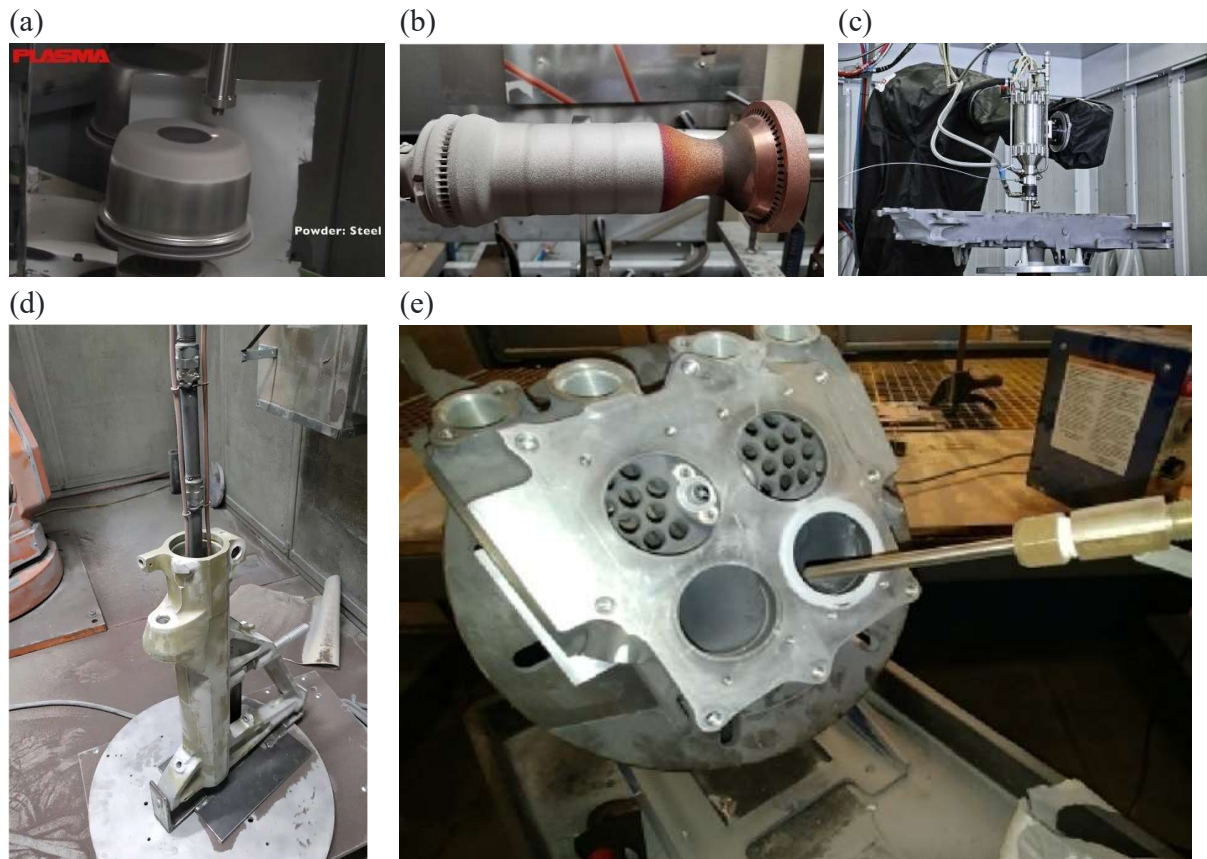


Fig. 2.16. Applications of cold spray: (a) cold-sprayed steel coating on rice cooker inner pot for induction [71], (b) cold spray of NASA HR-1 onto a LPBF GRCop-84 subscale chamber [73], (c) cold spray repair the accessory gearbox of GE90 engine in Boeing 777 [74], (d) cold spray inside of main-landing-gear cylinder of Northrop F-5 [75], and (e) cold spray dimensional restoration of aircraft fuel flow proportioner [76].

2.2 Hydrogen damage

The first study of hydrogen embrittlement was in 1875 by Johnson [81-83]. The British metallurgist used strong hydrochloric and very dilute sulfuric acids to remove surface rust from iron wire before drawing it. He found that iron wire became brittle after immersing it into acid for few minutes. When the specimen was still hot due to the heat generated by the fracture, and the fracture surface was moistened, bubbles kept being released for 30 to 40 seconds. To further

investigate the phenomenon, the wires of annealed and bright iron and mild steel, charcoal iron, as well as hardened and tempered cast-steel were selected to perform tensile test in the conditions of as-prepared, post-immersed, and heated for hydrogen-expulsion. However, the immersion time of different specimens varied widely with unspecified concentration of acids, plus the naming and unit of parameters deviated from modern standard, i.e. breaking-strain and elongation were used in the study, as shown in **Table 2.2**. Therefore, the result values might not be compared fairly with those in state-of-art studies. Diminution of some specimens in acid also hindered the evaluation of post-immersed and hydrogen-expelled conditions with as-prepared state. Leastwise, the behaviors across various iron and steel in acid immersion and subsequent hydrogen expulsion were revealed. Hydrogen expulsion by heating recovered the tensile strength of most iron and steel from the post-immersed state, which was most significant on charcoal iron with low carbon content. The tensile strain of bright mild steel, high carbon content hardened and tempered cast steel even surpassed the as-prepared strain after hydrogen expulsion heating. Johnson also observed distinctive hydrogen diffusion behaviors between iron and steel. The hydrogen embrittled length in iron with fibrous structure was traced up to 17 cm away from the immersed section, where bubbles released from the center of the moistened fracture surface. In contrast, hydrogen only spread 2 to 3 cm in the non-immersed section of steel with a non-fibrous structure. Unfortunately, Johnson did not publish follow-up articles, possibly due to the limited characterization technology at the time, or his works were lost over the last 151 years. Henceforth, his discoveries have inspired research in hydrogen embrittlement with respect to compositions, microstructures, and diffusivity.

Table 2.2. Tensile test results of (a) annealed and bright iron, (b) charcoal iron, (c) annealed and bright mild steel, and (d) hardened and tempered cast steel wires in as-prepared, post-immersed, and hydrogen-expelled conditions in 1875 by Johnson [81].

(a)

	Break- ing- strain.	Mean error in breaking- strain.	Elongation.	Mean error in elongation.	Number of experiments of which each result is mean.
Annealed iron wire when containing H...	100	per cent. ± 1.16	per cent. 20.5	per cent. ± 1.12	12
Annealed iron wire, H expelled	100.487	± 1.37	21.3	± 1.71	12
Bright iron wire when containing H	100	± 2.57	2	± 0.66	3
Bright iron wire, H expelled	100.274	$\pm .47$	2.83	± 0.64	3

(b)

	Break- ing- strain.	Mean error in breaking- strain.	Elongation of length tested.	Mean error in elongation.	Number of experiments for each result given.
Charcoal-iron wire con- taining H occluded in H ² SO ₄	100	per cent. ± 1.33	per cent. 1.3	per cent. ± 0.23	6
Charcoal-iron wire, H expelled by heat	106.62	± 7.10	4	± 0.33	6
Charcoal-iron wire con- taining H occluded in H Cl	100	± 0.3	1.41	± 0.41	6
Charcoal-iron wire, H expelled by heat	105.35	± 1.1	4.6	± 0.33	6

(c)

	Break- ing- strain.	Mean error in breaking- strain.	Elongation.	Mean error in elongation.	Number of experiments for each result given.
Annealed mild steel containing H	100	per cent. ± 5.08	per cent. 20.1	per cent. ± 0.61	9
Annealed mild steel, H partially expelled by heat	104.77	± 3.81	15.4	± 1.2	9
Bright mild steel be- fore immersion in H Cl	104.03	± 10.1	1.66	± 0.44	6
Bright mild steel con- taining H	100	± 9.2	2.8	± 0.46	6
Bright mild steel, H partially expelled by heating 12 hours	108.68	± 1.5	2.16	± 0.38	6
Bright mild steel, H completely expelled by heating 7 days ...	114.29	± 8.4	3.42	± 0.75	6

(d)

	Break- ing- strain.	Mean error in breaking- strain.	Elongation.	Mean error in elongation.	Number of experiments for each result given.
Steel before immersion in acid	123.79	per cent. ± 2.7	per cent. 2.16	per cent. ± 0.27	6
Steel immersed in H ² SO ₄ 12 hours	100	± 4.9	1.916	± 0.416	6
Steel, H expelled by heating 10 days to from 100° to 200° ...	122.53	± 6.09	2.66	± 0.55	6
Steel before immersion in H ² SO ₄	100.27	± 1.28	3.75	± 0.25	2
Steel after immersion in H ² SO ₄ 1 hour ...	100	± 2.19	3.75	± 0.25	2
Steel heated 24 hours to 100°-200°, to ex- pel H	105.49	± 2.9	2.75	± 0.25	2

2.2.1 The classification of hydrogen embrittlement

Lee in NASA [12] has categorized hydrogen embrittlement into three main types: hydrogen environmental embrittlement (HEE), internal hydrogen embrittlement (IHE), and hydrogen reaction embrittlement (HRE). The significant factors contributing to hydrogen embrittlement include hydrogen environment, applied stress and material type. **Fig. 2.17.** illustrates the types of hydrogen embrittlement and their corresponding factors. Both HEE and IHE result in the formation of solid solutions of hydrogen in metal. HEE occurs in a high-pressure hydrogen gas environment, such as hydrogen vessels and Jupiter [84, 85]. The surface defect or notch tip are usually the crack initiation sites. Constant static tensile loading well below the yield strength is sensitive to HE, but

cyclic or dynamic loading even at high cycle is not. Although IHE shares the same region with HEE, the hydrogen source for IHE is not from a high-pressure environment. The hydrogen absorption of IHE occurs during electroplating, corrosion, cathodic charging, thermal charging, or moisture absorption during welding, casting, and solidification. External applied stress is required after hydrogen absorption to trigger the time-delayed embrittlement. Different from the two previous types, stress is not necessary to activate HRE. At certain conditions, hydrogen atoms diffuse into metal and react with its elements and compounds to form metal hydride or gas.

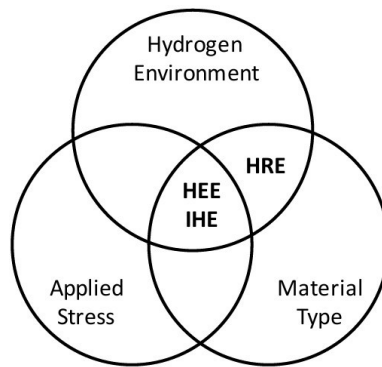


Fig. 2.17. Classification of HEE, IHE, and HRE types based on hydrogen, stress, and material factors [12].

Ustolin et al. [86] elucidate the HRE into three forms depending on the combinations of metal and environment: hydrogen attack, blistering, and metal hydride formation, as illustrated in **Fig. 2.18a-c**. Firstly, Hydrogen attack refers to the embrittlement of carbon and low-alloy steels in hydrogen gas at elevated temperature and pressure for a prolonged time. Hydrogen reacts with carbon in steel to form methane, creating pores and cracks that result in loss of ductility and strength, as shown in **Fig. 2.18d** [87]. This mechanism is also known as high-temperature hydrogen attack, decarburization or methane formation. Secondly, blistering occurs in low-strength alloys such as steel, Cu, and Al being exposed to corrosive environment. Hydrogen atoms gather at

microstructural defects then recombine into hydrogen molecules. The recombination of hydrogen gas generates high local pressure, which expands the defects into blisters or shatter cracks, **Fig. 2.18e** [88]. The last mechanism is metal hydride precipitation, which occurs commonly in metal and alloys of Nb, Ta, Th, U, Zr, V, and Ti. Hydrogen can be introduced into metal during heat treatment, welding, melting, corrosion, or irradiation [89-91]. **Fig. 2.18f** shows hydrides formation in heat-treated laser-powder-bed-fused (LPBF) Ti6Al4V by electrochemical hydrogen charging for 96 hours [29]. Pressure can encourage the formation of metal hydride, where the FeH_x and CoH_x need to be prepared under high hydrogen or hydrostatic pressure [92]. Although these brittle metal hydrides undermine structural integrity, they can be used for other specialized functions including hydrogen storage, alkaline fuel cell, catalysts, reducing agents, isotope separation, neutron moderators, and heat pumps.

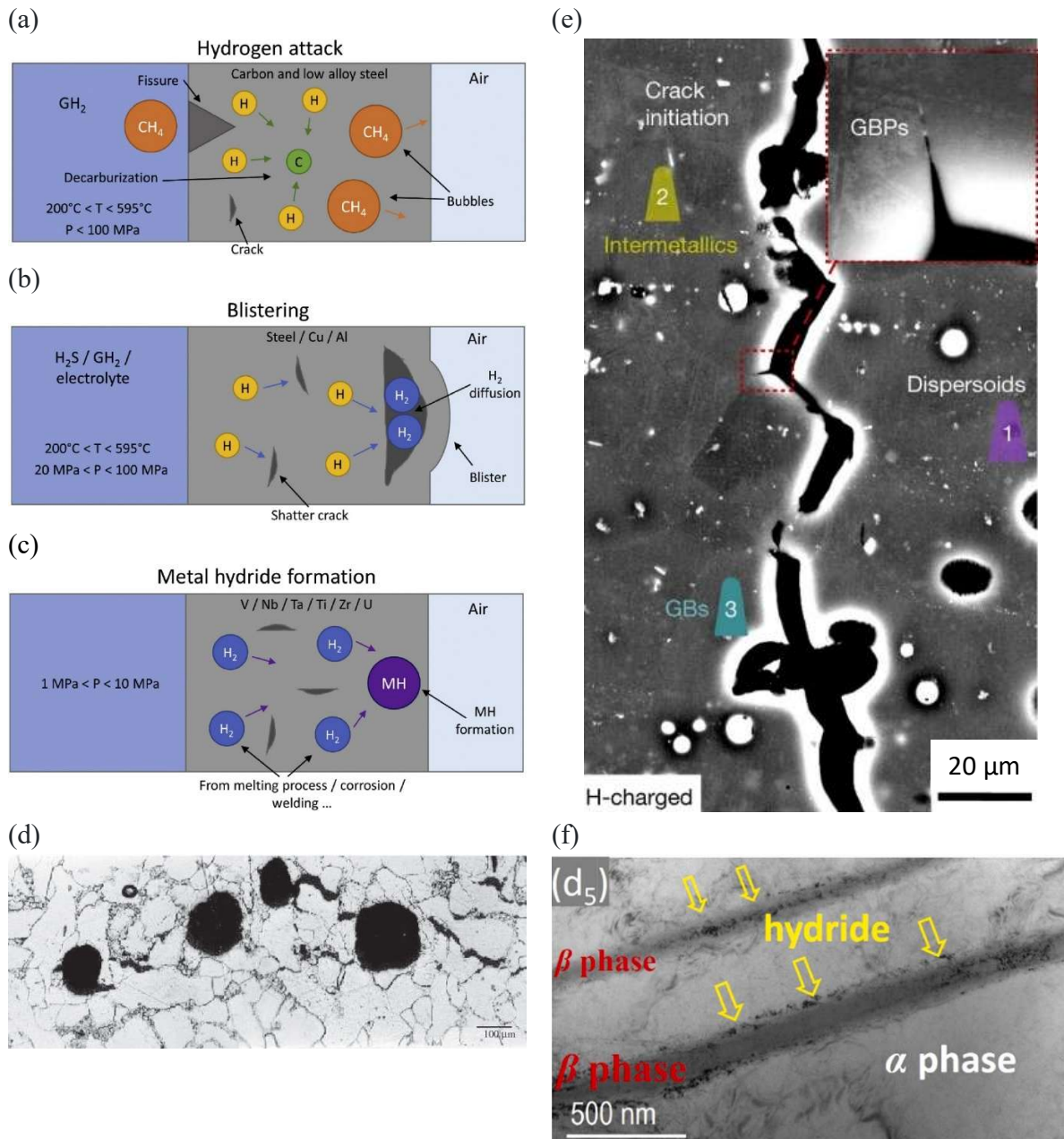


Fig. 2.18. Schematic of (a) hydrogen attack, (b) blistering and (c) metal hydride formation phenomena [86]. (d) Voids formed by methane in a carbon steel exposed to a hydrogen atmosphere at high temperature [87]. (e) Backscattered electron imaging of an intergranular crack of the H-charged Al 7XXX alloy subjected to tensile fracture [88]. (f) TEM image of 96 h H-charging heat-treated LPBF Ti6Al4V [29].

2.2.2 Hydrogen absorption scenarios

Hydrogen absorption during manufacturing process primarily contributes to the hydrogen embrittlement in metallic parts of aircraft. Rossmann [89] explains the absorption scenarios in detail, as shown in **Fig. 2.19**. Moisture is the source of hydrogen atoms when hydrogen gas is not used at high-temperature process. Hydrogen atoms are generated on the surface of molten metal and absorbed into the interior, which leads to severe cracking upon solidification or during operation. The moisture in welding comes from electrodes, shielding gas, or the parts [93-95]. If moisture source is humid ambient air, argon may be contaminated during feeding or storage through the leaks. The electrodes may be moistened due to improper storage or insufficient drying before use. Likewise, the condensation on part surfaces harms the weldment even if it is thin as a film. An example is the hydrogen embrittlement in weld seams of old compressor and turbine housings made of low alloy steels. Similar to welding, hydrogen dissociates from the moisture or organic binder in casting mold upon contact with molten metal and is absorbed rapidly due to high diffusivity at high temperature [96-98]. Additionally, pores are also formed due to the evaporation of moisture which further deteriorates the casting product. Since cold spray is a solid-state process, the hydrogen absorption mechanism in molten metal is not applicable to its deposits.

On the other hand, cold sprayed-deposit may need processing bath or heat treatment that may concurrently absorb hydrogen. Hydrogen ions are created during galvanic baths, chemical baths, and some corrosion processes [29, 99-101]. Hydrogen gas molecules are recombined at cathode or cathodic zone. However, some atomistic hydrogen diffuses into metal lattice, which can be enhanced with addition of hydrogen recombination inhibitor such as thiourea or arsenic compounds [29, 102, 103]. It is noted that hydrogen embrittlement can occur if Ti alloys are operating with aviation hydraulic oil above 130 °C as acid forms at this temperature. A specific β -

Ti alloy TIMETAL 21S is used to be immune to this damage [89, 104, 105]. The other post process method, heat treatment, can lead to hydrogen absorption if there is intense contact between a hydrogen-charged piece and an uncharged piece. Some studies about diffusion bonding of Zr and Ti alloys utilize hydrogen to lower the bonding temperature and enhance the interfacial bond strength [106-109], where further desorption heating is required to prevent the embrittlement by hydrides.

The aforementioned decarburization is one of the mechanisms of hydrogen embrittlement, but hydrogen absorption can also occur during carburization. Hydrocarbon gases, hydrogen-carbon monoxide mixture, and nitrogen-alcohol mixtures are commonly used in carburizing atmosphere for case hardening [89, 110, 111]. Upon heating to carburization temperature around 1000 °C, hydrogen atoms decompose from the carburization material and diffuse into the steel workpiece. The carburization induced lattice defects act as hydrogen trapping sites and thus hinder hydrogen desorbing to pre-carburization level even tempering at 180 °C. Although the hydrogen atoms effuse out slowly at room temperature, a surface region with low defect density and tempering in vacuum can accelerate the desorption for operations readiness. Alternative hardening methods such as plasma ion nitriding are available to prevent the presence of hydrogen atoms [112].

Finally, hydrogen can be dissociated and absorbed in metal by catalytic effect as known as hydrogen spillover [113-121]. The wide GB and moderate density of defects in microstructure after deformation have very low potential barriers for quantum transition, so that the ends of GB at metal surface act as catalytic pockets for hydrogen dissociation and further diffusion [113]. However, the activation energies for dissociation and diffusion are inversely proportional to each other. Pozzo and Alfe [114] have calculated the activation energies of transition metals-doped Mg surfaces with density functional theory, nudged elastic band method, as well as the bulk properties

including lattice constant, modulus, valence, and core radius. The result shows that Ag has the highest activation energy of 1.18 eV for hydrogen dissociation and allows easy diffusion of hydrogen molecules. Pt and Pd would have even higher diffusivity than Ag [115]. On the other hand, Ti, V, Zr, and Ru do not have any dissociation energy barrier, but their high activation energies of diffusion lead to slow diffusion and strong binding [114]. Fe, Co, Rh, and Ni have stroked a balance between dissociation and diffusion for better catalytic effect. This indicates Mg or CNT doped with these transition metals would be ideal for hydrogen storage and release [115]. On the contrary, Ti, V, Zr, and Ru are not suitable for speedy hydrogen charging and discharging due to slower diffusion rates than their counterparts [114]. The alloys of Ti, V, and Zr can be used for structural purposes in hydrogen environment at low temperature and moderate pressure, however, regular inspections and hydrogen desorption baking are necessary to prevent the accumulation of hydrides and subsequent embrittlement.

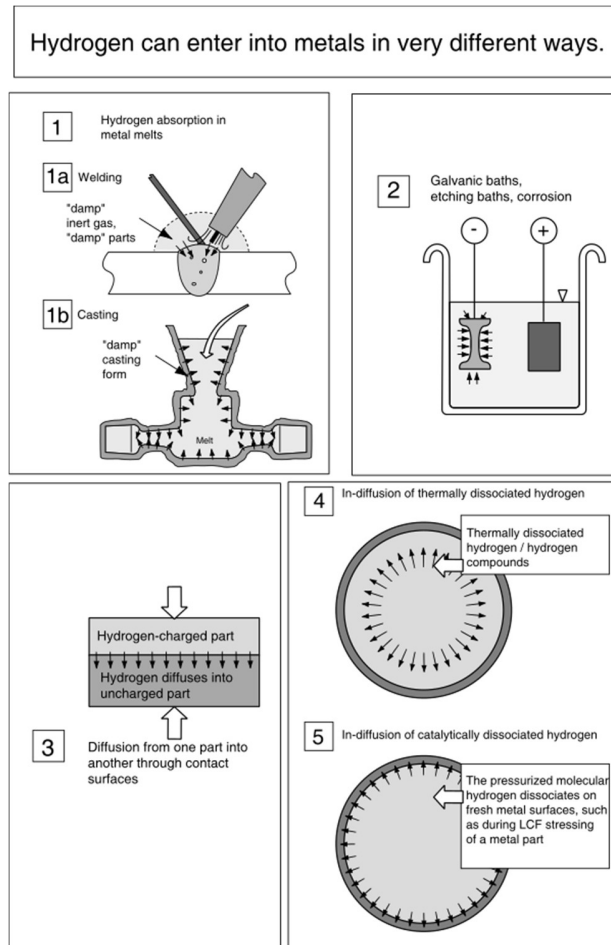


Fig. 2.19. Hydrogen absorption scenarios in manufacturing process and operation [89].

2.2.3 Hydrogen in metal microstructure

Hydrogen trapping sites and transport routes in metal microstructure can be categorized with a multiscale perspective from surface to interior of the material, as shown in **Fig. 2.20** [122]. On the metal surface, hydrogen is adsorbed at oxides, cracks, and valleys of roughness profile [123-127], then segregates and diffuses to deeper regions of metal. These surface defects can be either promoter or barrier for hydrogen diffusion depending on the density and material properties. Once hydrogen diffuses to the subsurface region, it can concentrate at internal crack tips and voids [128], or further diffuse due to concentration gradient. If the metal is consolidated from powder with excess defects, hydrogen or other fluid may diffuse rapidly through particle interfaces [41, 129].

When the scale is magnified to grain structure, the mechanism of deciding hydrogen to be bound or transported at a sped-up pace becomes more apparent. The potential trapping sites include GB, GB triple junctions (TJ), phase boundaries, precipitates and their interfaces [122]. Nonetheless, the defects need more refined categorization as they exhibit varying properties. For example, the hydrogen flux at LAGB is lower than that at HAGB [130]. It is challenging to simply conclude whether hydrogen is trapped or accelerated by these sites. At atomistic scale, hydrogen trapping occurs in the forms of vacancy decoration or hydride formation at dislocations [122]. Hydrogen atoms fill the lattice vacancies partially or fully depending on the migration and binding enthalpies of vacancy complexes with different hyperfine fields and nuclear quadrupole coupling frequencies [131, 132]. This nature is also utilized to detect vacancies in semiconductors [133]. The presence of GB indicates the increases of critical stress for dislocation generation as well as critical hydrogen concentration [134]. Thus, hydride-like cylinder volumes are formed at the edge dislocations as a cubic distortion around a hydrogen atom [135].

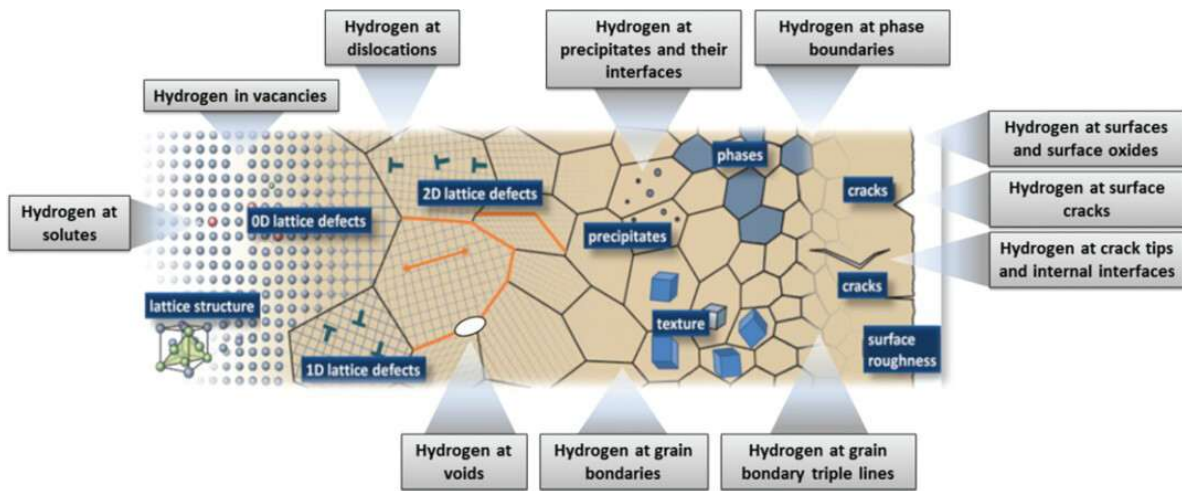


Fig. 2.20. Schematic diagram of hydrogen trapping and transport sites in metals [122].

On the other hand, these defects are not compulsory for hydrogen entry and hydride formation since there are interstitial sites to accommodate hydrogen atoms as solid solution. Fukai [136] uses

Fig. 2.21 to illustrate the octahedral and tetrahedral interstitial sites occupied by hydrogen atoms in FCC, HCP, and BCC crystal structures. Hence, there are four possible types of interstitial sites in dual-phase Ti6Al4V with HCP and BCC structures. In addition to the matrix metal, the structures of hydrides also depend on pressure, temperature, and concentration of hydrogen. The hydrides formed at higher parameters include TiH_2 , VH, and VH_2 in FCC structure. Hydrogen atoms occupy tetragonal sites in the HCP with limited terminal solubilities, then dihydrides form along with further hydrogenation. The β phase with BCC structure tends to accommodate hydrogen atoms with tetrahedral sites randomly at low concentrations. However, V-H systems tend to accommodate hydrogen atoms with sublattice octahedral interstitial sites at high concentration and low temperature, which results in slight lattice elongation. There is severe lattice strain in the cold-sprayed deposit due to supersonic impact, and thus the availability for hydrogen occupation and lattice elongation is questionable [137]. Although it can be reduced drastically by heat treatment, the overall metal-hydrogen interactions along with other defects in both as-sprayed and heat-treated conditions have not been investigated yet. The consensus on hydrogen solubilities of phases in Ti6Al4V is that the α phase has a much lower solubility than that of the β phase based on hydrogen concentration measured by thermal **desorption** [138-141]. On the contrary, the addition of Al in α phase should increase hydrogen solubility by facilitating supersaturation with [142], where V in β exhibits opposite effect by becoming a stronger exothermic occluder and precipitating hydrides at higher concentration [143]. It is also noted that BCC structure has smaller lattice parameter than HCP, so that the activation energy for diffusion in β phase is also lower. Hence, Ti6Al4V needs to prevent hydrogen damage by reducing the β phase, where CP-Ti is considered to be hydrogen-safe and comprehends with the NASA guideline by Lee [12].

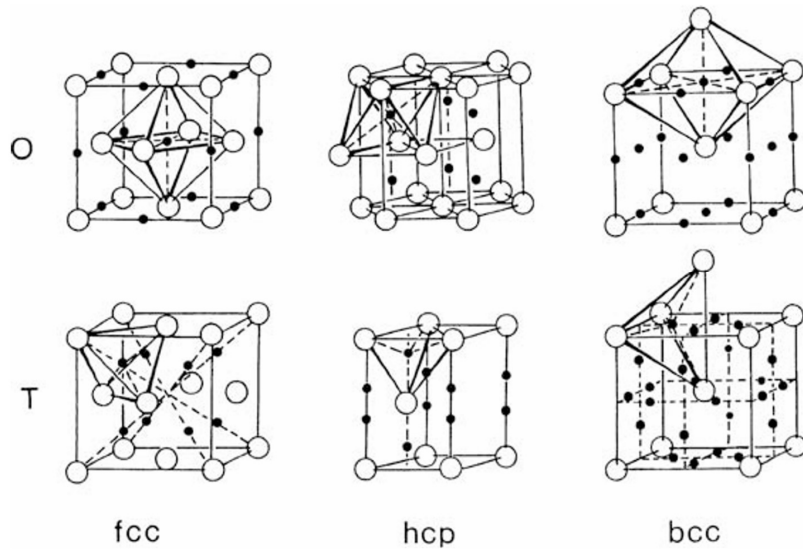


Fig. 2.21. Interstitial octahedral (O) sites and tetrahedral (T) sites in FCC, HCP, and BCC lattices [136].

2.2.4 Evolution of hydrogen embrittlement

Lynch [144] has summarized the evolution of different hydrogen embrittlement mechanisms in **Fig. 2.22**. The mechanisms include hydride formation and fracture, hydrogen-enhanced decohesion (HEDE), localized plasticity (HELP), and adsorption-induced dislocation emission (AIDE). The other forms of hydrogen damage including blistering and hydrogen attack as hydrogen reaction embrittlement have been well introduced in previous paragraphs and thus are omitted here. Formation of hydrides occurs in susceptible metals such as Ti, V, Zr, Nb, and Ta under high stress or high concentration, as shown in **Fig. 2.22a** and previously in **Fig. 2.18c**. Hydrogen atoms first gather at crack tips to induce the formation and growth of hydrides upon reaching the solubility limit of grains, then the cracks develop along cleavage planes in hydrides. The interface between hydrides and metal matrix temporarily arrests the propagation of cracking until hydrogen concentration raises to the precipitation level and repeats the process. HEDE in **Fig. 2.22b** alludes to hydrogen weakening the bonds between metal atoms and thus leads to sequential

tensile separation of atoms. Accumulation of hydrogen and subsequent decohesion can occur at few locations: (1) atomically sharp crack tips due to adsorbed hydrogen, (ii) several tens of nanometers ahead of cracks where tensile or hydrostatic stress reaches maximum due to dislocation shielding effects, (3) particle-matrix interfaces ahead of cracks, which results in intergranular fracture. In the HELP mechanism, the high hydrogen concentration and stress at the crack tip induces the motion of stationary dislocations and increases the nucleation rate of dislocations. Subcritical crack growth occurs by localized microvoids-coalescence process, as shown in **Fig. 2.22c**. The locally high hydrogen concentrations within grain interiors or adjacent to GB decide the crack paths to be transgranular or intergranular. In contrast, AIDE in **Fig. 2.22d** is the most complicated among these mechanisms. The crack growth under increasing stress involves high dislocation emission from crack tips, nucleation and growth of microvoids at second-phase particles, slip-band intersections, or other sites in the plastic zone ahead of crack tips. Dislocation emission from crack tips primarily contributes to crack growth, where coalescence of microvoids also reshape crack tips with small opening angles.

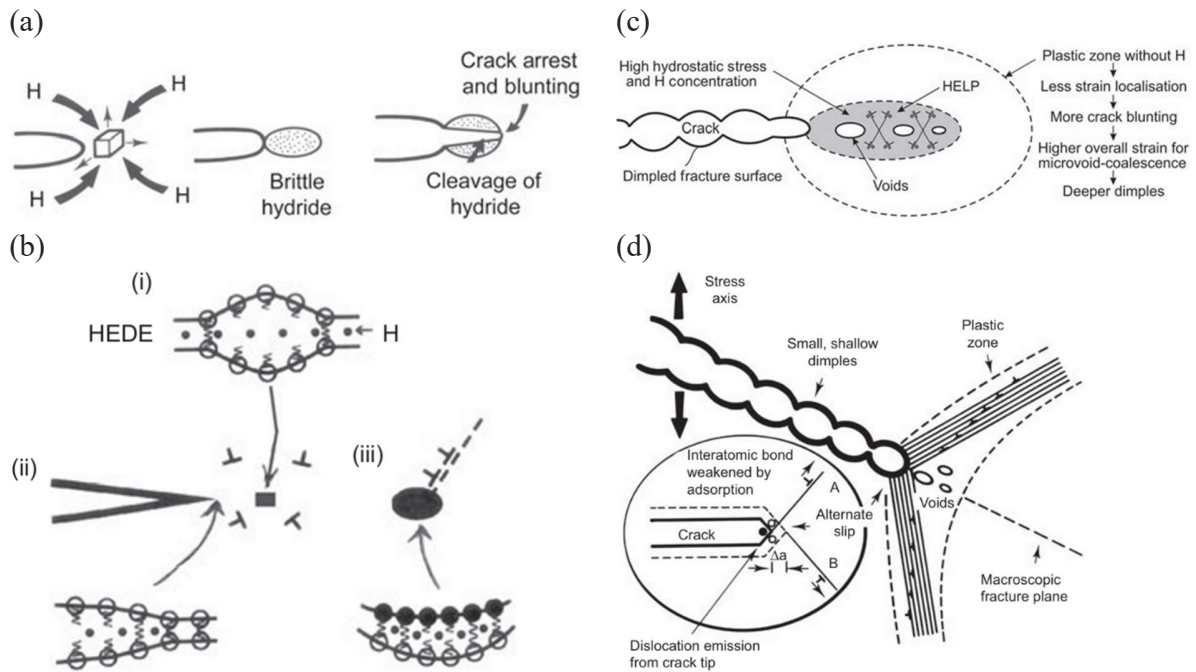


Fig. 2.22. Schematic diagrams of HE mechanisms: (a) hydride formation and fracture, (b) HEDE, (c) HELP, and (d) AIDE [144].

2.2.5 Hydrogen damage scenarios

Fig. 2.23 displays some examples of hydrogen damage in real-world engineering. The steel pipe in **Fig. 2.23a** is subject to blistering under high hydrogen fugacity without external stress [145]. This usually occurs in oil and gas pipes with abundant H_2S and hydrogen gas, which attracts NETL to consider repairing and corrosion protection with cold spray [39]. In aviation, hydrogen-related failures often stem from the production of parts. **Fig. 2.23b** shows a fractured nut with beach marks extending away from the nut bearing face [146]. The nut is one of the fractured nuts from the clutch assembly of R22 Beta helicopter prompting a precautionary landing. The Australian Transport Safety Bureau concludes that the premature nut failure is likely caused by embrittlement of residual hydrogen generated during cadmium electroplating process applied during manufacture. The manufacturer of this MS21042L-series nuts has issued a bulletin addressing detailed

procedural improvements to reduce the potential for hydrogen-related failures. Particularly, there are numerous reports about potential hydrogen embrittlement in aircraft parts that involve cadmium plating.

In 2018, Southwest United Industries conducted cadmium-titanium plating on a batch of slat tracks which had later failed a quality test indicating the presence of hydrogen embrittlement, as illustrated in **Fig. 2.23c** [147-149]. Additionally, the required protective coating over the part identification mark was not applied. These defective slat tracks were installed on 178 Boeing 737 MAXs and 133 Boeing 737 NGs. Federal Aviation Administration issued an Airworthiness Directive mandating inspections and replacement of these slat tracks, followed by proposing USD 10.1 million in penalties. Hence, it is necessary to develop alternatives to cadmium plating for eliminating the risk of hydrogen embrittlement and assuring the airworthiness from technical perspective.

On June 29, 2018, the Korean Airlines HL7573 Boeing 777 safely landed at Narita International Airport but had its right main landing gear aft axle fractured during taxiing, as shown in **Fig. 2.23d** [150]. The aircraft was delivered in 2000 and flew for 69,674 hours. The investigation report suggests that the fractured axle was probably attributed to the stress corrosion cracking that originated from the corrosion on the pivot bore and propagated during ongoing operations. Furthermore, the corrosion on the pivot bore was probably contributed by water penetration due to the torn fillet seal by rotation of the bushings as well as the absence of corrosion inhibitor coating during overhaul. It was noted that the main landing gear overhaul in 2009 applied grease BMS-3-33 according to the manual, but the manual was updated in 2012 to use corrosion inhibitor BMS-3-38 to bushings of pivot. During the stress corrosion process, hydrogen atoms diffuse into the metal around the crack tip and facilitate the dissolution rate of metal [151]. This catastrophic failure

reflects the essentiality of water proofing and corrosion inhibitors to prevent hydrogen-related damage on aircraft components in addition to the aforementioned acid in heated hydraulic oil.

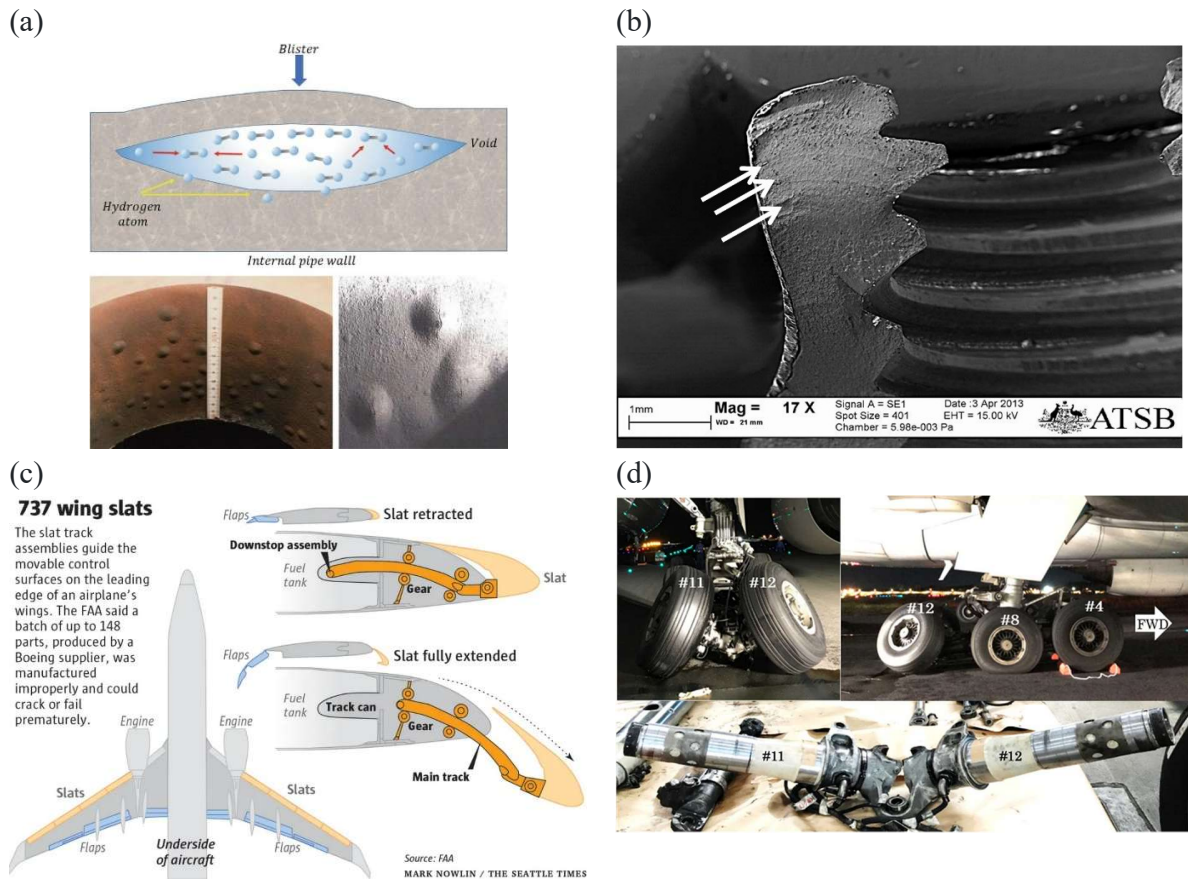


Fig. 2.23. Hydrogen damage (a) blistering phenomena in steel pipe [145], (b) fractured nut in clutch of R22 Beta helicopter with beach marks extending away from the nut bearing face [146], (c) Boeing 737 slat tracks failed a quality test indicating the presence of hydrogen embrittlement [147], and (d) fractured axle of right main landing gear in Korean Airlines HL7573 Boeing 777 associated with stress corrosion cracking [150].

2.2.6 Hydrogen in future aviation

At end of 2024, FAA has published a safety and certification roadmap for hydrogen-fueled aircraft roadmap [152]. Fuel cells and combustion engines (**Fig. 2.24**) are considered potential power

plants for hydrogen-fueled aircraft. However, the near-term application of fuel cell is limited to smaller aircraft due to unproven reliability such as electrical hazards under high voltage, membrane damage upon reactant flow instabilities, and lower water boiling point at high altitude. On the contrary, combustion engines are considered to be capable of generating sufficient propulsion for medium and long-range transport. Likewise, the reliability and safety of modified combustion engines for hydrogen fuel are speculative. Firstly, fire hazards and internal detonation during the start and relight of engine have to be contained, otherwise it would result in serious explosions. Clemen et al. [153] in Rolls-Royce have demonstrated stable hydrogen combustion with modified Pearl 15 turbofan engine, where future studies will focus on reducing the NO_x level, long-term operation tests, and implanting in larger turbofans. Next concern is hydrogen in fuel systems and proposed cryogenic heat exchangers possibly leaking into the cabin through the engine bleed lines and reaching to flammable level without prior detection. The incidents of fume entering cabin air supply have been reported occasionally due to failures of an engine oil seal or recirculation fan bearings [154]. Boeing 787 has adopted a bleedless design with two variable-frequency electrical generators for each engine to eliminate this issue [155], which would be applicable to the hydrogen-powered aircraft. However, it is noteworthy that the influence of hydrogen leakage on the titanium parts in compressors cannot be neglected. Moreover, the cryogenic heat exchangers are facing ice build-up on external surfaces open to environment, as well as flow blockage due to debris or ingestion of air. These challenges require extensive work to implement experience from the single-use rocket turbopumps into the workhorse turbofan engines. Hence, the conditions of as-built and repaired materials throughout the operation period with hydrogen require in-depth understanding from extensive studies.

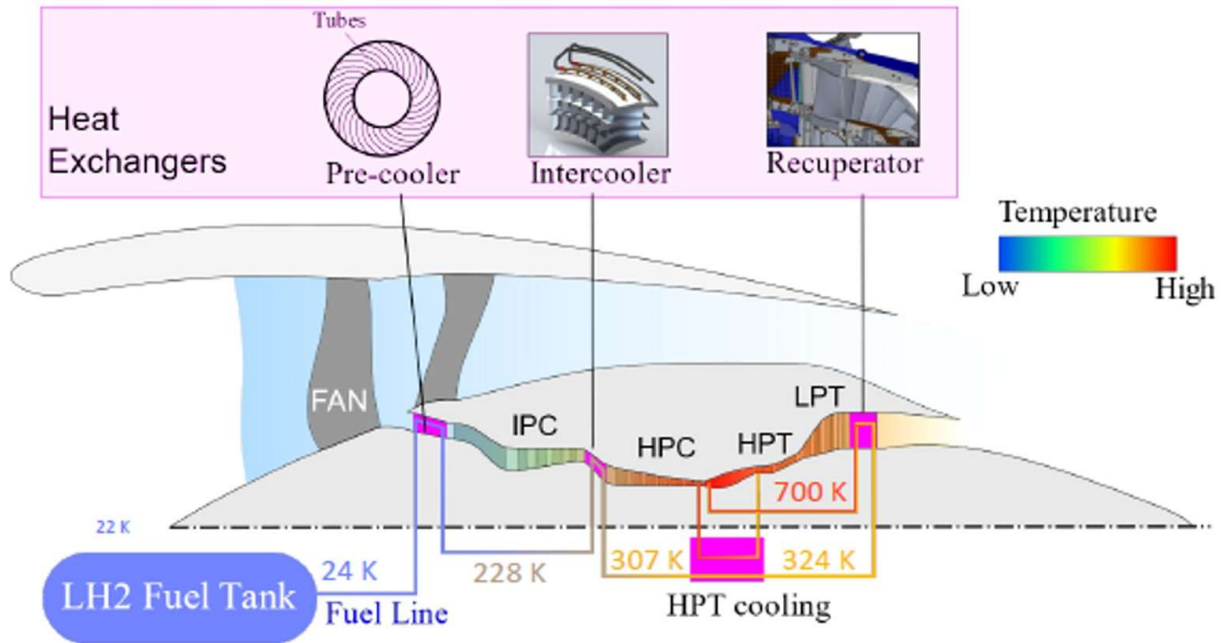


Fig. 2.24. Schematic diagram of large turbofan hydrogen combustion engine [152].

2.3 Electrolytic hydrogen interaction in cold-worked microstructure

2.3.1. Hydrogen concentration and ductility

Hydrogen embrittlement in electrolytic process is the primary issue to be addressed in order to promote cold spray for aircraft repair. Furthermore, electrochemical hydrogen charging proposed by Devanathan and Stachurski in 1962 [156] has been the economic option to study metal-hydrogen interaction, so that the literature about hydrogen and cold-worked metals provide valuable insights into cold-sprayed deposits. Huang and Shaw [157] have revealed the relationship between ductility and hydrogen concentration in cold-rolled 1020 low-carbon steel. Hydrogen diffusion and concentration are measured by a mercury-filled eudiometer and a barnacle electrode with 0.2 M NaOH electrolyte, Ni-NiO cathode and steel anode. The results show hydrogen diffusion coefficient decreases when subjected to higher intensity of cold work, where the decline becomes stabilized at 30-40% cold work, as shown in **Fig. 2.25a**. Cold work increases dislocations,

voids and GB as hydrogen trapping sites, which eventually mitigates hydrogen diffusion. On the other hand, **Fig. 2.25b** indicates both cold work and exposure time are directly proportional to hydrogen concentration. In other words, steel with cold work has smaller hydrogen affected zone but higher susceptibility to form hydride especially after accumulation for prolonged time, vice versa. Fracture toughness decreases upon strain hardening by cold-rolling, which degrades further after electrochemical hydrogen charging. The drastic drop in fracture toughness of both non-immersed specimens and those immersed for 72 hours occurs at 20% cold work followed by steady decline hereafter, as shown in **Fig. 2.25c**. This indicates 1020 steel undergoing ductile-brittle transition around 20% cold work, where the ductility loss throughout the cold work range attributes to hydrogen absorption. **Fig. 2.25d** reveals the fracture strain deterioration in tensile test and hydrogen concentration along with exposure time. The ductility losses of non-rolled and 30% cold-rolled steel are 37% and 70% after 75 and 30 hours of immersion, respectively. Despite the deterioration of ductility coming to a halt after certain hydrogen exposure time, hydrogen concentration continues to elevate. Under these circumstances, the results imply that cold-sprayed particles with flattening ratio >20% would have lost most of their ductility but the hydrogen would not stop accumulating. On top of that, wrought Ti6Al4V is considered harder than 1020 steel but the performance can be varied by microstructures and thus Ti6Al4V in cold-sprayed microstructure may exhibit distinctively.

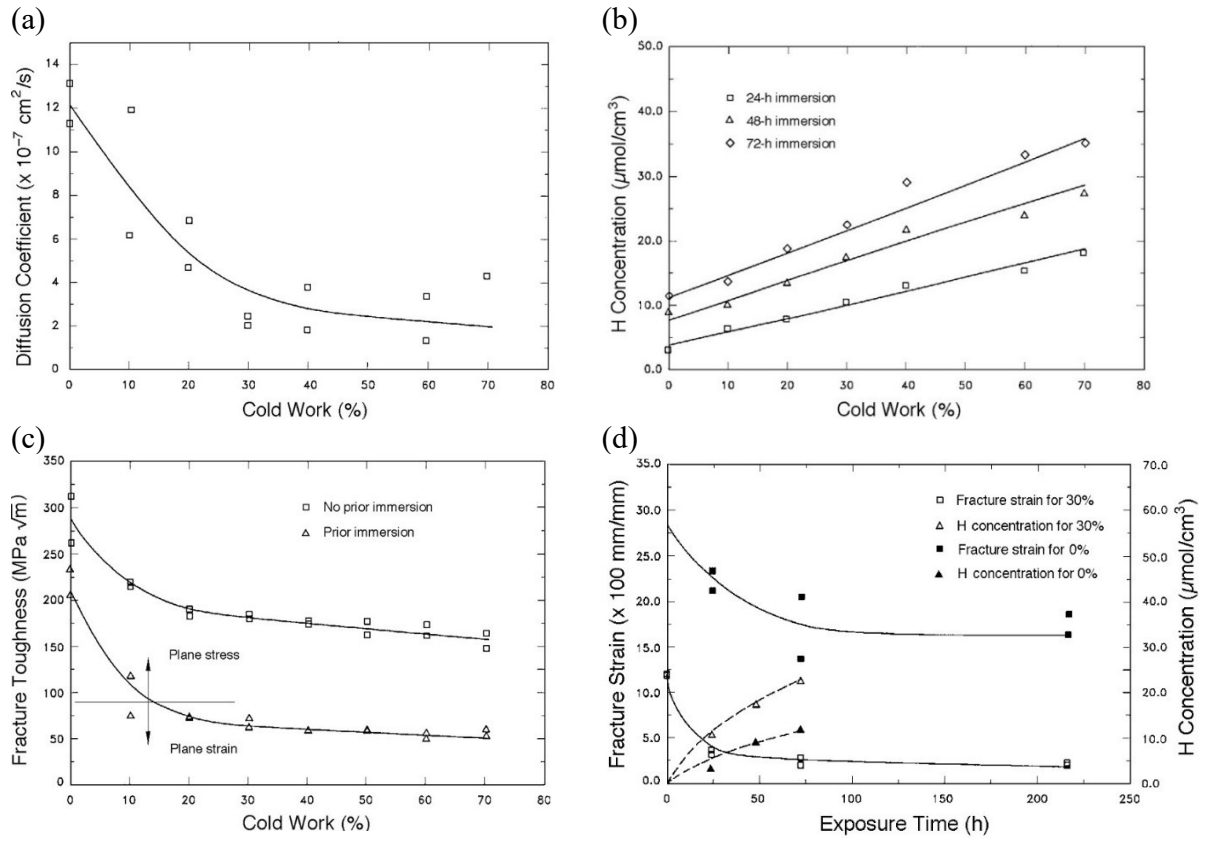


Fig. 2.25. Relationship between cold work versus (a) hydrogen diffusivity, (b) hydrogen concentration, (c) fracture toughness, and (d) fracture strain [157].

2.3.2. Effect of cold-worked microstructure

The experiment by Yazdipour et al. [158] used annealing to prepare X70 steel samples with various grain sizes and found that the cathodic-charged hydrogen diffusion coefficients were 20×10^{-10} , 8×10^{-10} and $6 \times 10^{-10} \text{ ms}^{-1}$ at grain size of 46, 32 and 15 μm , respectively. This trend fits with the observation by Huang and Shaw [157], which also reflects the high concentration of hydrogen in ultra-fine-grained structure so as high susceptibility of hydrogen damage. Controversially, there are some studies suggesting that surface cold works, such as peening and roughening, can suppress hydrogen embrittlement since the trapping sites at the cold-worked surface layer hinder further hydrogen diffusion and subsequent damage [123, 159-162]. In fact, the enhancement of the

hydrogen diffusion coefficient by grain refinement is limited to a certain range of grain size. Ichimura et al. [163] suggest once the grain size is smaller than the optimum point with maximum hydrogen diffusion coefficient, it would drop drastically due to the GB cross effect, as shown in **Fig. 2.26a**. The cross effect refers to the two contrary effects: (1) rapid diffusion along straightforward GB; and (2) suppressed diffusion by trapping at GB junctions. In other words, it is competition between highways and crossroads to affect the diffusion dynamics. Meanwhile, solubility decides the amount of hydrogen that can be stored in the material. The thermal gas charging and vacuum hot-extraction method has also measured hydrogen solubility of aluminum. Hydrogen solubility is independent of GB and size, but it is enriched by voids. Micro-void is categorized as a 3D volume defect for extrinsic-physical trapping, while GB is a 2D surface defect for extrinsic-physical trapping and also contributes to intrinsic-chemical trapping, e.g. diffusion, interstitial occupation, and hydride formation.

On top of these defects, cold-worked metals also need to account dislocations as 1D line defects for physical trapping. For example, Kim et al. [123] reveals the potential of utilizing dislocations induced by surface roughening to enhance the hydrogen resistance of bimodal Ti6Al4V. In an electrochemical cell with diluted sulfuric acid and ammonium thiocyanate, the rough surface consists of dense dislocations as hydrogen trapping sites and induces a large concentration gradient across the metal-electrolyte interface, as shown in **Fig. 2.26b**. This feature of rough surface contributes to recombination of most adsorbed hydrogen atoms and returns to electrolyte, while very few absorbed hydrogen atoms are contained between the subsurface and interior by internal stress. Instead, polishing results in lower electrochemical activity on surface and sparse trapping sites at subsurface, which eventually leads to deep diffusion and formation of hydrides. Another study carried out by Lopez-Suarez [164] proves that the trend is also applicable to globularized

Ti6Al4V upon thermal hydrogenation at 650 °C for 2 hours. However, the barrier effect of roughness fades out upon each absorption-desorption cycle. Compared to surface roughening with limited effective depth, cold-sprayed coating would have much thicker hydrogen trapping layer as long as the particles continue to deposit. The aforementioned hydrogen embrittlement in wrought Ti6Al4V during the plating process may not occur on as-sprayed Ti6Al4V based on this assumption. Nevertheless, the hydrogen resistance of cold-sprayed Ti6Al4V after heat treatment and microstructural evolution during thermal hydrogenation are more complicated to estimate.

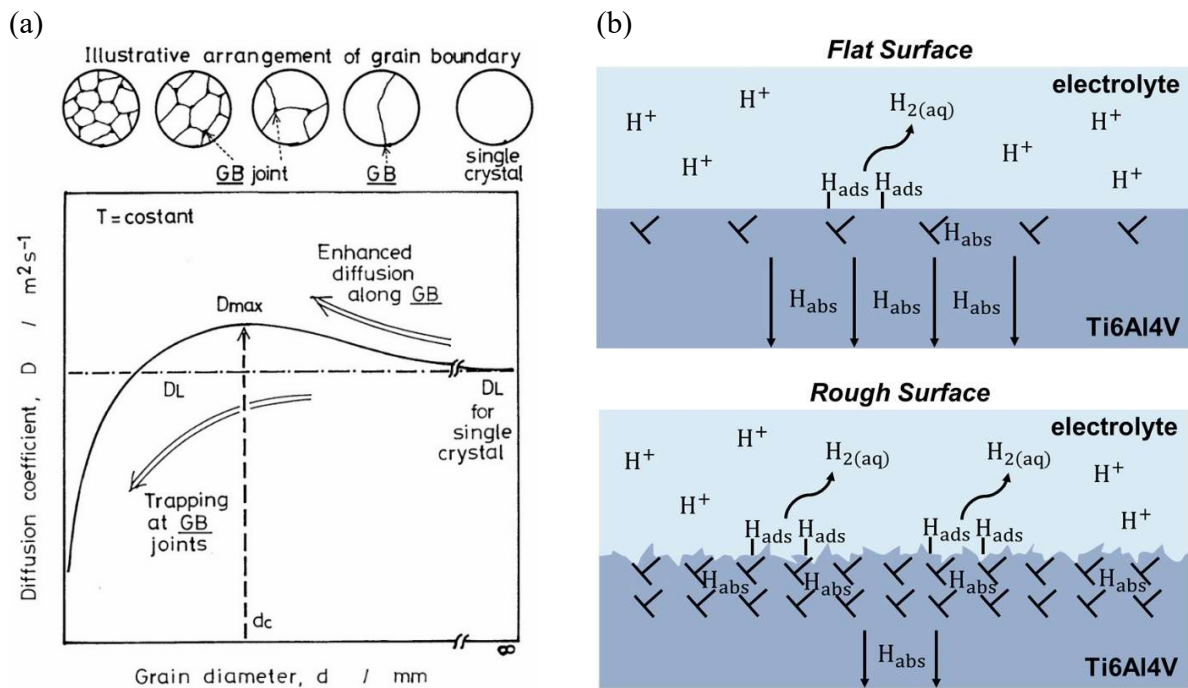


Fig. 2.26. Hydrogen diffusivity models based on (a) the “GB cross effect” [163], and (b) dislocations density near surface [123].

For the cold-sprayed Ti6Al4V, Yang et al. [16] suggested more than half of the hexagonal grains were nano-scaled before heat treatment. Electron backscatter diffraction (EBSD) revealed the nanograins at the interparticle bonding (IPB) area grew into micron-equiaxed grains after heat treatment at 850 °C in argon atmosphere for 1 hour, while the dislocation entanglement led to

martensite laths adjacent to IPB transforming into nanograins, as shown in **Fig. 2.27**. The non-uniform growth mechanism was considered as the factor deteriorating the nano-mechanical properties after heat treatment, except oxidation and high porosity. Oxidation can be prevented by selecting feedstock powder with lower oxide content, as well as storing and handling feedstock and deposits in an environment with low oxygen concentration, controlled temperature and humidity. The coating density can be increased by switching carrier gas from nitrogen to helium, where the feedstock powder can impact at a higher velocity with more intense plastic deformation. However, it would also result in excess nanograins due to dynamic recrystallization [14], increase the non-uniformity of grain growth during heat treatment, and eventually change the GB cross effect to barricade hydrogen. It is uncertain to determine whether the hydrogen diffusivity of such random microstructure results in a high concentration for hydride formation or an ultra-high concentration for recombination on surface. Thus, the hydrogen resistance of nanocrystalline structure in cold sprayed deposits and the effect of grain growth by heat treatment are investigated in **Chapter 3**. Since Ti6Al4V cannot withstand hydrogen uptake at elevated temperatures and prolonged time [164], thermal hydrogenation is studied as a solution to enhance ductility of cold-sprayed Ti6Al4V comprehensively in **Section 2.6** and **Chapter 6**.

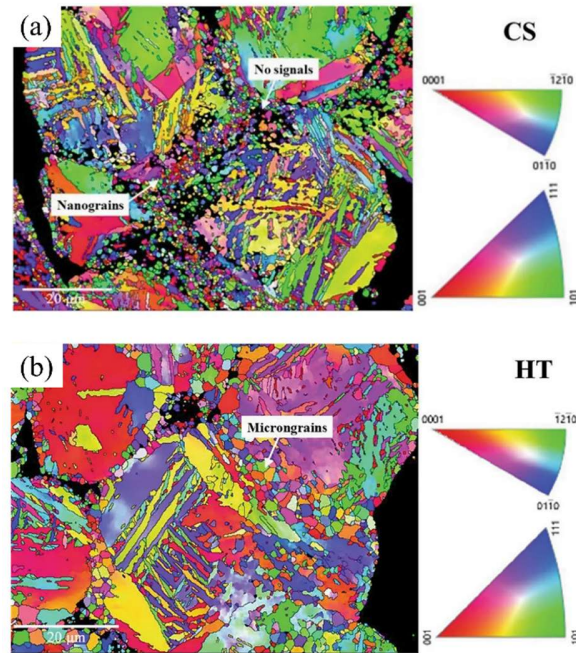


Fig. 2.27. EBSD images of the cross-sectional microstructure of CS and HT Ti6Al4V deposits: grain orientation of (a) CS sample, and (b) HT sample [16].

2.4 Simulation of Hydrogen Diffusion across the Grain-boundary Networks

2.4.1 Modeling of grain-boundary networks

The GB network is a significant feature for evaluating the hydrogen diffusion mechanism across cold-sprayed deposits on a macroscopic scale. The simulation in **Fig. 2.28a** by Jaseliunaite et al. [37] claims that diffusion in a polycrystalline GB network was accelerated depending on the morphological features (typical solid, bi-modal, and semi-lamellar), but the potential role of GB as a hydrogen trap was not considered. The semi-lamellar microstructure with the densest GB does not exhibit Ichimura's [163] GB cross-effect across the hydrogen displacement. A possible cause is the method relies on varying the diffusivity ratio of grain and GB; however, the solubility and types of GB are ignored.

Since the correlation between GB diffusivity and geometrically necessary dislocations (GND) density would be invalid for misorientation $>15^\circ$ with a complex GB network, Oudriss et al. [165, 166] have proposed the approach of coincidence site lattice (CSL) index for a wide misorientation range. According to the results of EBSD and ToF-SIMS on cold-drawn pure Ni, GB are categorized into low misorientation ($\Sigma 1$) and special boundaries ($\Sigma 3^n < 29$) which trap hydrogen atoms and suppress further diffusion, as well as high-angle random boundaries ($\Sigma > 29$) accelerate the hydrogen diffusion with “short-circuit diffusion effect”. Special boundaries exhibit properties with low interfacial energy, low solute diffusivity, low susceptibility to segregation and GB corrosion, since these boundary properties are exceptionally low at low misorientation angles [167, 168]. Special boundaries can disrupt the interconnected random boundaries so as crack propagation. The principle of GB engineering is promoting a high proportion of special boundaries by reducing the grain size. Hoch et al. [33] in the same group as Oudriss have developed a 2D model with three phases (grains, special and random boundaries) to study the influence of the GB network towards the effective hydrogen diffusivity, as shown in **Fig. 2.28c**. The virtual model has been improved to a 3D continuum network, but some features like TJ are still under investigation to further advance the simulation accuracy [169]. If the model for cold-sprayed deposit is only required to be 2D, the challenge falls on how to create a model for diffusion simulation.

Perhaps realistic modeling is a feasible strategy to overcome the complexity of cold-sprayed microstructure. Adair and Johnson [170] use spectral descriptors to compare the diffusion through the synthetic GB networks with different cluster lengths and morphologies (**Fig. 2.28b**), then implement into the realistic models generated from the EBSD data of Ni in reference and GB engineered states by Randle et al. [171]. The results have showed the diffusion in both reference and GB engineered Ni being dominated by HAGB, even though the fractions of LAGB and $\Sigma 3$

GB are at least 50%. Conversely, the diffusion through grains and the solubilities of the GB are not considered. Li et al. [24] suggest the high fraction of special boundaries in the cold-sprayed pure Cu could improve the localized corrosion resistance in used nuclear fuel containers, where the grain size effect on corrosion resistance would be negligible. The absence of GB cross effect in the simulation by Jaseliunaite et al. [37] may attribute to omission of special boundaries. Hence, the special boundaries in cold-sprayed deposits are key study objectives in GB engineering to resist corrosion, HE and other metal degradation mechanisms.

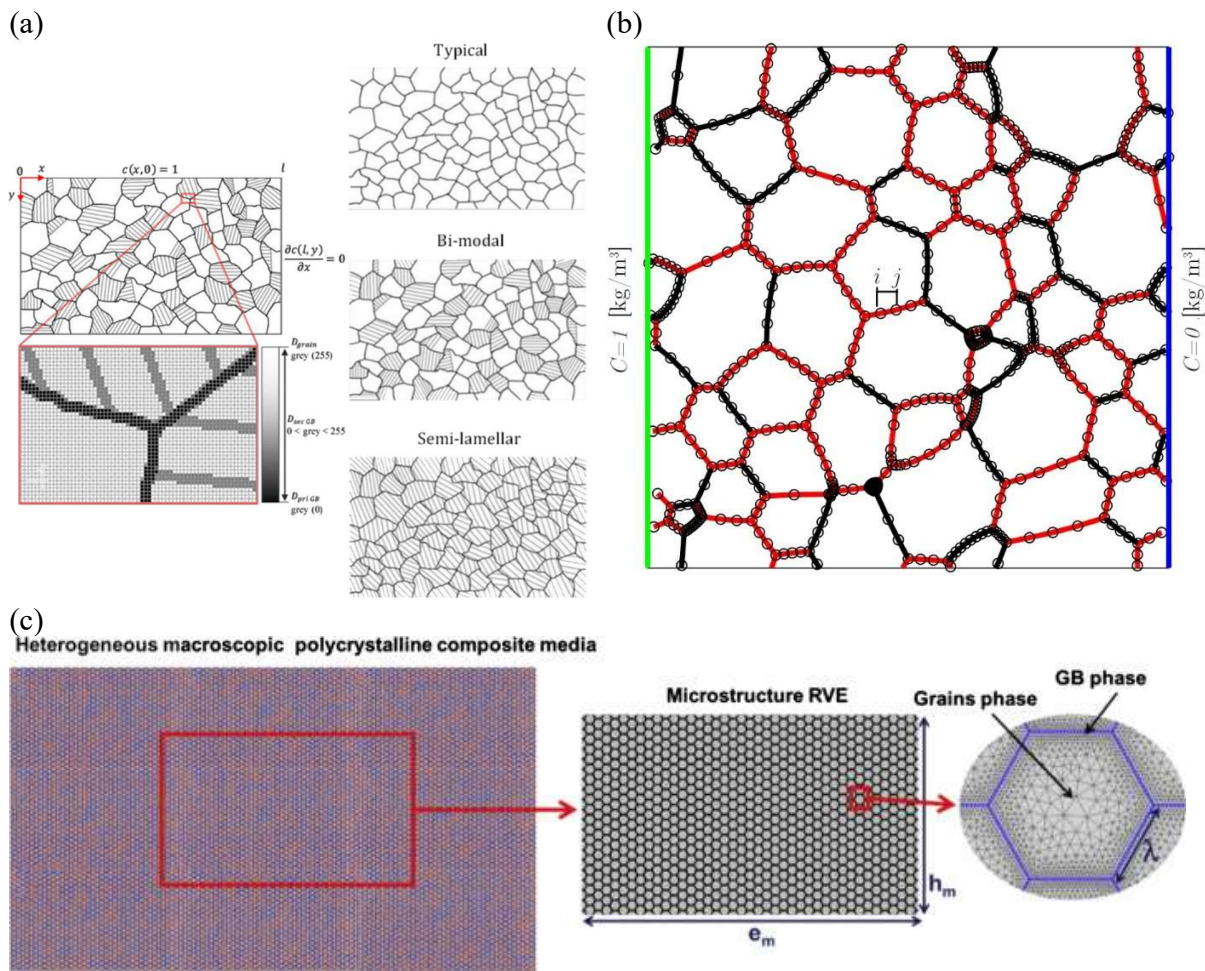


Fig. 2.28. Virtual GB network modeling methods of (a) heterogeneous grains and homogeneous boundaries [37], (b) heterogeneous boundaries only [170], and (c) homogeneous grains and heterogeneous boundaries [33].

2.4.2 Simulation parameters

In addition to the effective hydrogen diffusivity, hydrogen solubility and the mode of diffusion are essential to assess the hydrogen transport behavior and affected zone in metals [158]. Hanson et al. [172] attempted to describe the capability of GB blocking chemical transport with the degree of hindrance in synthetic models of solid oxide fuel cell and nickel manganese cobalt cathode, which indeed could be represented by solubility. The GB networks of cold-sprayed deposits exhibited localized refined grains at IPB, which evolved into different phases depending on the heat treatment parameters [13-17]. Thus, heat treatment of cold-sprayed deposits has to be under the phase change temperature if HE is a concern in the employing environment. The hydrogen diffusion behavior in cold-sprayed deposits with the GB network approach highly depends on the following points: (1) the hydrogen diffusivity and solubility of grains and boundaries, and (2) the ratio of grains to random and special boundaries after different heat treatments. These concerns are addressed systematically in Chapter 4 with a realistic modeling method to convert the microstructures of cold-sprayed Ti6Al4V and assign hydrogen transport properties for diffusion simulation.

2.5 Permeability and diffusivity of porous structure

2.5.1 Porous structure of cold-sprayed deposits

Correlating the porosity and fluid transport properties has been widely adopted in petrophysics [173-175], geology [129, 176, 177], and powder metallurgy [178, 179], which has the potential to be employed in cold spraying for fluid applications. Chapter 4 uses realistic modelling with EBSD GB maps to simulate hydrogen diffusion across the dense cold-sprayed Ti6Al4V deposits, but the method is not applicable to the fluid-tightness problem of porous deposits on the particle-pore

scale. Weiller and Delloro [51] compared the simulated porosity of Al and Al-Al₂O₃ deposits in multi-particle impact simulations with the measured porosity of real deposits on 2017A-T4 substrates by XCT scans. The simulated porosity was about 13-19%, whereas the measured porosity was only about 1-2%. The authors suggested that the simulation had not been able to estimate the experimental values due to the limited volume of particles, neglected hammering effect, mesh size issues, and the choice of the material model. Weiller et al. [41] also sprayed Al and Al-Al₂O₃ powders on 2017A-T3 substrate with numerous sets of spraying parameters for the UHV chamber, where a sample SEM image of deposit sprayed at 2.5 MPa, 350 °C, 20% of Al₂O₃ is shown in **Fig. 2.29a**. It was observed that helium leakage through the nanochannels in some samples could not be detected by micro-XCT. The voxel size of 0.325 µm was insufficient to detect porosity below 1.3 µm for accurate percolation assessment. **Fig. 2.29b** showcases the white percolating porosity of Al deposit sprayed at 3 MPa and 300 °C having an experimental leak rate of 3E-5 mbar/s, where another sample with similar leak rate could not indicate any percolating porosity in reconstructed model. Overestimating percolation level is another issue attributable to limited voxel resolution. **Fig. 2.29c** reconstructs a structure with high but discrete porosity in the same deposit as **Fig. 2.29a**, however, the model indicates an interconnected cluster lying on the edges of ROIs. This kind of error results in the variation of 2 orders of magnitude between the calculated and measured permeabilities, as shown in **Fig. 2.29d**. Therefore, the leak test with working fluid must be conducted in addition to quantitative micro-XCT inspection for a comprehensive assessment.

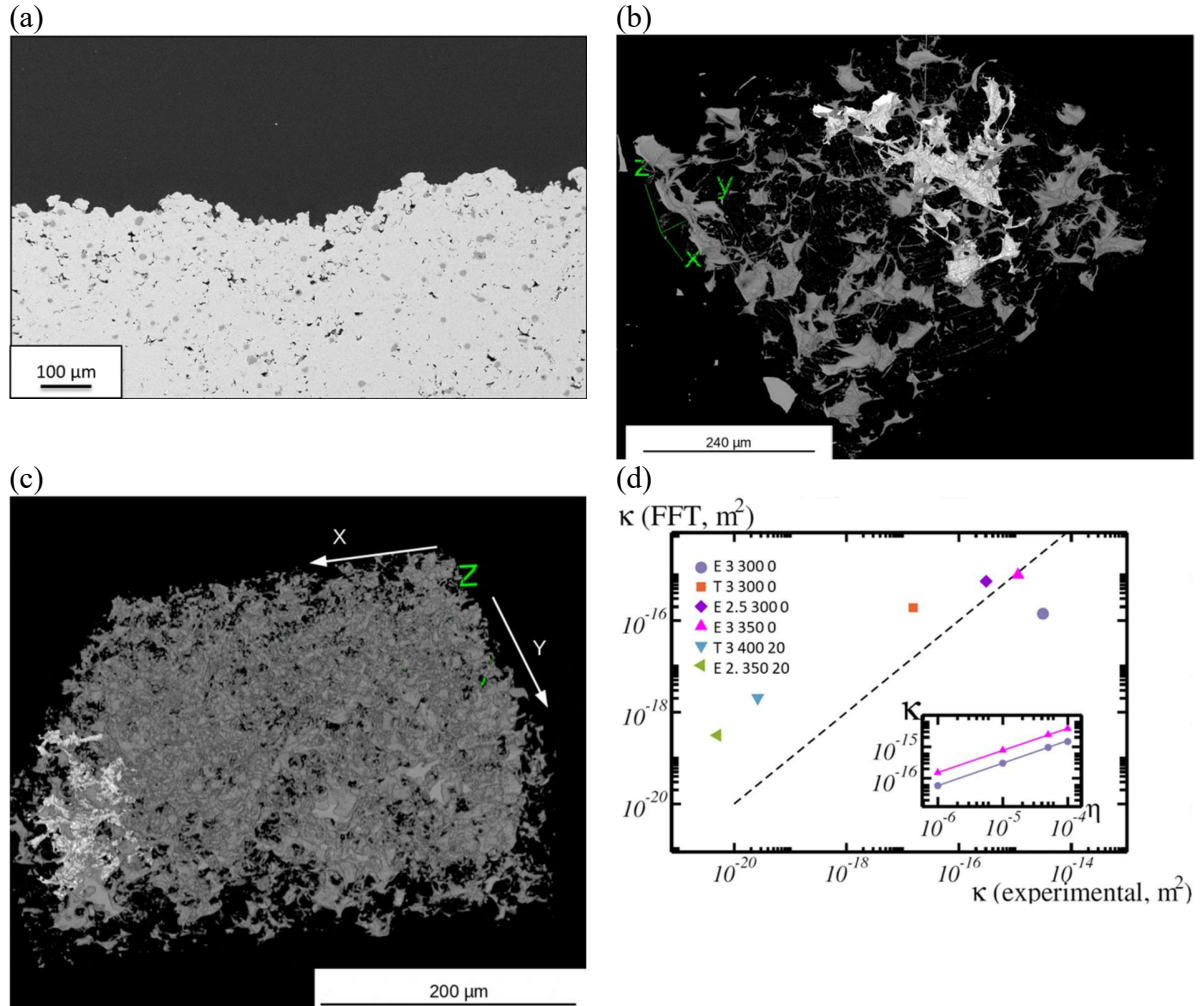


Fig. 2.29. Porous structure characterized by (a) SEM-BSE, and XMT at regions of (b) low porosity and (c) high porosity. Percolating porosity and non-percolating porosity clusters are in white and gray, respectively. (d) FFT-predicted vs. experimentally measured permeability [41].

2.5.2 Traverse speed induced porosity

Controlling the traverse dynamics of nozzle with a supersonic consolidation stream into design porosity is challenging. Tan et al. [180] used SiC nozzle to spray Ti6Al4V with N₂ at 4.5 MPa and

1000 °C, 30 mm away from Ti6Al4V substrates. The analysis on **Fig. 2.30** suggests slowing down nozzle traverse scanning speed from 500 to 100 mm/s could reduce porosity of coating from 3.2 to 0.5%, because of extra hammering by particles and excess thermal softening by heat accumulation. From this point of view, this cold spray setup and parameters with 100 m/s of traverse speed is ideal for fabricating gas-tight deposits to withstand hydrogen flow. Even so, the slow traverse speed sacrifices the coating-substrate interface consequently. Authors pointed out there was a 24 μm thick shattered substrate subsurface layer leading to severe delamination (**Fig. 2.30a**), which might actually be shattered first-layer powder due to over-deformation. Furthermore, interparticle cracks were spotted at multiple regions of the coating possible due to unevenly accumulated stress from non-uniform thermal expansion and shrinkage. Despite having lower porosity, the coating sprayed at 100 mm/s ended up with interfacial failure at 2.5 MPa while the adhesion of both counterparts exceeded the glue strength of 60 MPa. Similar to the GB cross effect, there is also optimum traverse speeds for porosity and other properties.

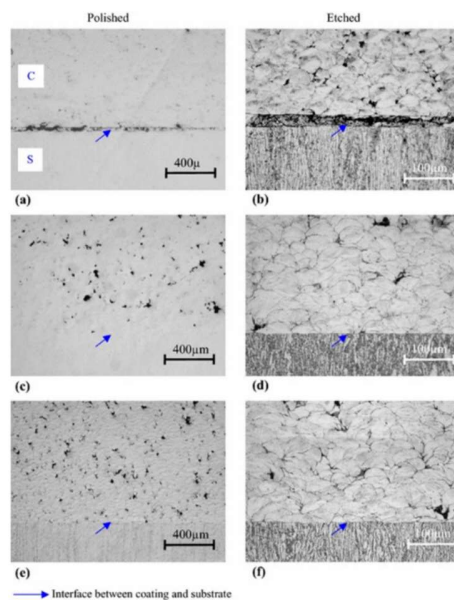


Fig. 2.30. Optical micrographs of polished and etched cross sections of cold-sprayed Ti6Al4V with traverse speed at (a and b) 100 mm/s, (c and d) 300 mm/s, and (e and f) 500 mm/s [180].

Percoco et al. [181] attempted cold spraying Al-based powder on Al-based substrate with constant traverse speeds ranged from 40 to 2 mm/s. The porosity increased from about 2% to 12% along the reduction of traverse speed (**Fig. 2.31**), while the coating thickness per layer increased from 0.18 to 1.8 mm. The hypotheses of authors include smaller particle size, lower orthogonal velocity of outermost powder in the jet, and the effect of bow shock. On the other hand, the traverse speed optimization in cold spray can be seen as the pitch distance optimization in paint spray to prevent striping defects, as shown in **Fig. 2.32** [182]. This way, the volume, distribution and thickness profile of deposits are controlled by the combination of pressure, feed rate, and robot velocity. Such optimization becomes challenging when the powder is accelerated to supersonic speed, which needs advanced dynamic control and inspection method to assure the quality of deposits.

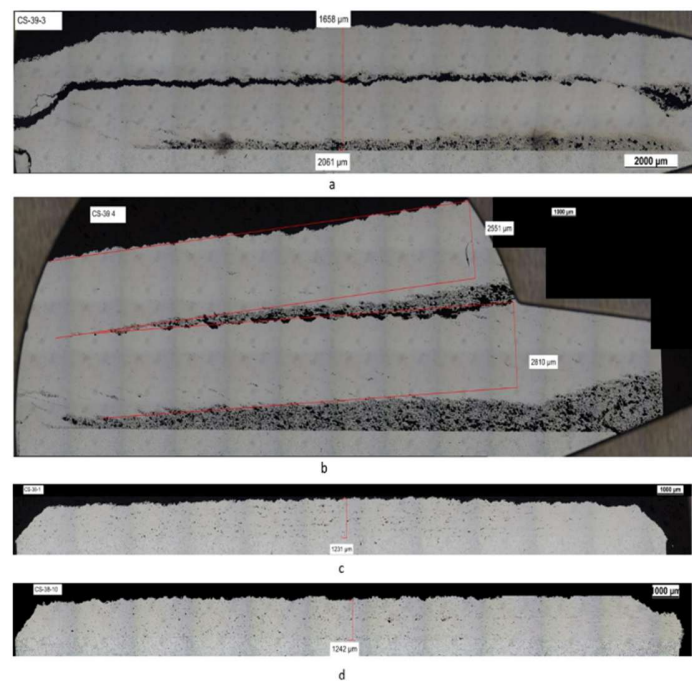


Fig. 2.31. Cross sections of all the deposited beads [181].

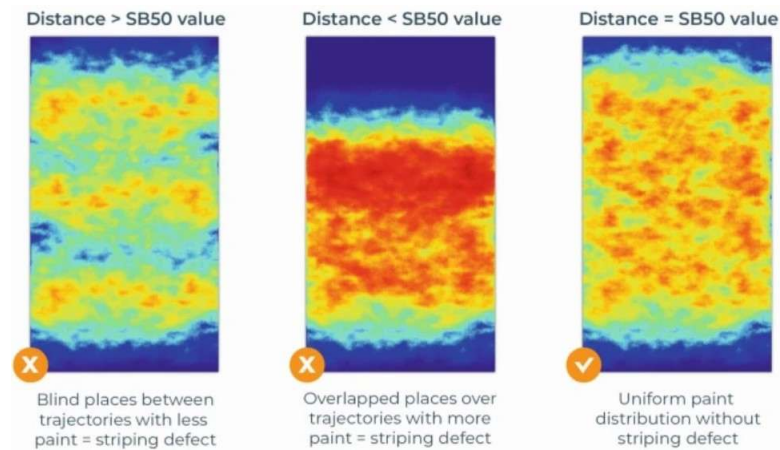


Fig. 2.32. The optimization of pitch distance for the trajectories can be derived from the dynamic pattern [182].

2.5.3 Dynamic control of spraying

Vaz et al. [183] demonstrated spraying Al, Cu, Ti, Ti6Al4V, and 316L powder into complex geometry with metal knitting strategy (**Fig. 2.33**), but the description of robot velocity only stated the higher velocity resulting in thinner layer. The metal knitting cold-sprayed deposits had about double porosity under optical microscope and one-third of tensile strength compared with those of traditional snake pattern. These early toolpath studies reflected the limitations of non-adaptive nozzle control on the quality of cold-sprayed deposits.

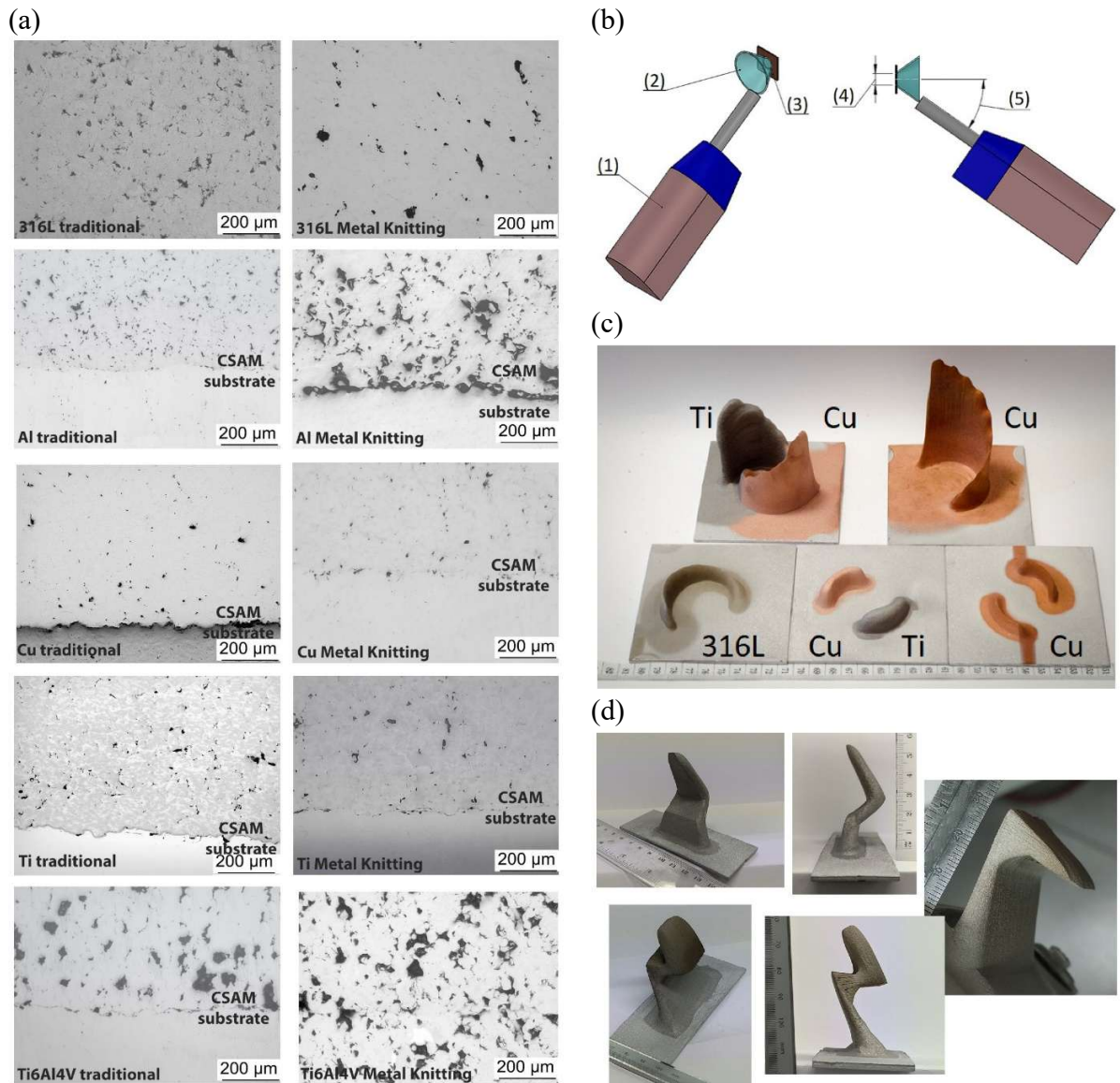


Fig. 2.33. (a) Cold-sprayed microstructures of 316L, Al Cu, Ti, and Ti6Al4V in traditional and metal knitting strategy. (b) Metal knitting strategy scheme elements of (1) cold spray gun, (2) virtual frustum of cone path, (3) substrate, (4) radius, and (5) angle. (c) Cold-sprayed curved parts made by the Metal Knitting strategy. (d) Cold-sprayed 316L complex geometries made by the metal knitting strategy [183].

Vargas-Uscategui et al. [184] in CSIRO have developed 3D toolpath generation based on the geometry and porosity of cold-sprayed straight Ti walls and square corners. The nozzle was tilted

35° for spraying most samples to well control the formation of vertical structures and avoid tapering effect in single track spraying. From the geometry perspective, the corner deposited at higher traverse speed results in overbuilt structure while larger corner radius leads to underbuilt structure, as shown in **Fig. 2.34a**. The different morphologies reflect the instant deceleration and acceleration during turning the corner. It is notable that the corner profiles vary in different planes, as shown in **Fig. 2.34b** and **c**. Therefore, the toolpath needs to adjust the traverse speed and corner radius to prevent misshape in multiple orientations. In addition to the overbuilt sections that need to be machined off, the porous shell on deposit also has to be accounted as oversized zone in the design profile. The reconstructed micro-XCT scan in **Fig. 2.34d** shows a layered “fishbone” pattern of porosity in the Ti deposit at traverse speed of 25 mm/s and a corner radius of 0.3 mm. The “fishbone” pattern refers to porosity at the edge or shell (20-30 %), interlayer (10-15 %), and intertrack (5-10 %) along the build direction. Although the porous shell can be machined off, heat treatment is required to reduce interlayer and intertrack pores. This reflects that cold spray works better with depositing evenly distributed layers on pre-formed substrates rather than free-forming on flat plates. The disparity of structural performance between these two strategies becomes more apparent when the geometry of deposit is convoluted.

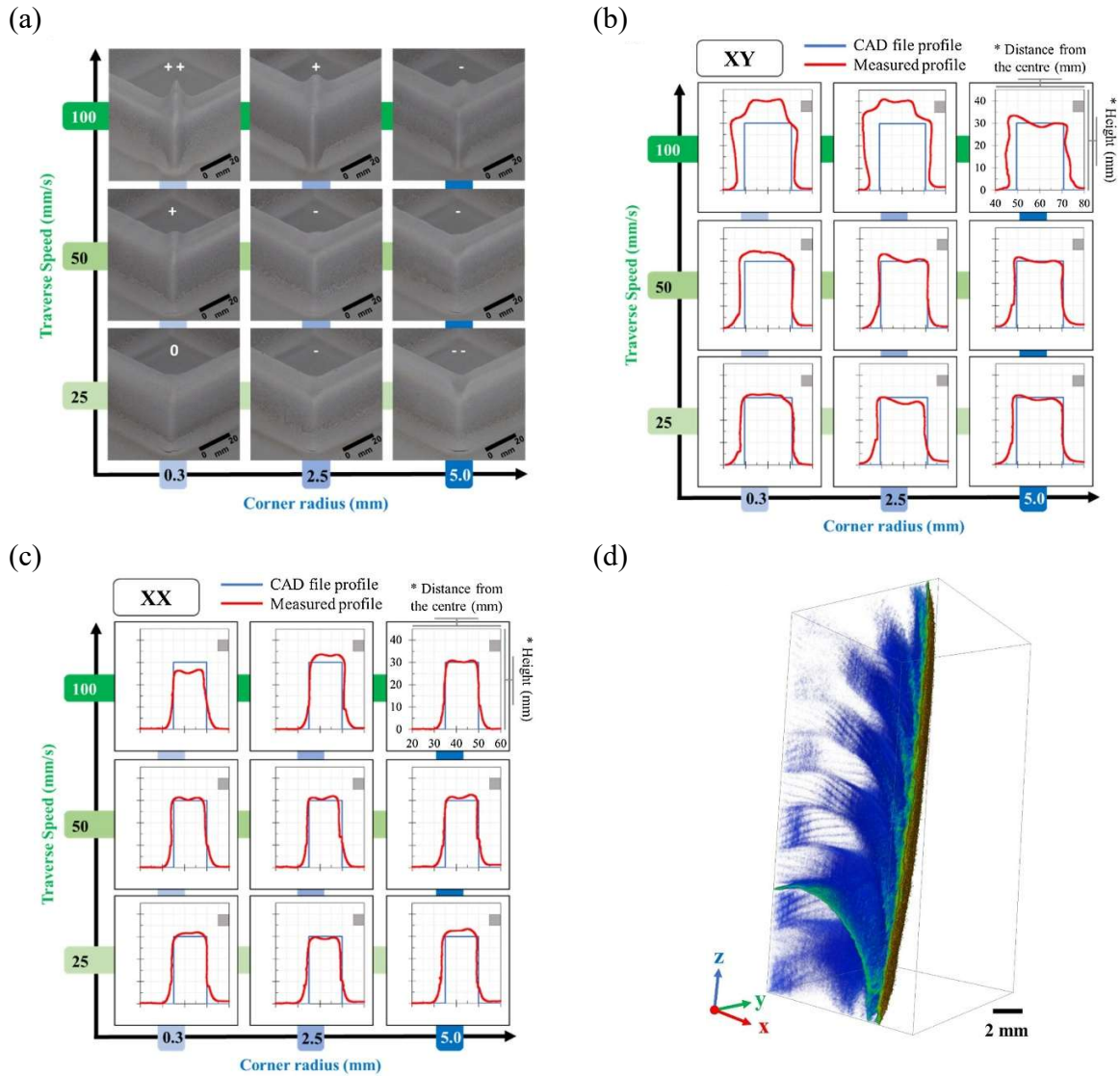


Fig. 2.34. Influence of traverse speed vs. corner radius on the presence of defects at the corner of the square frame: (a) photographs of the corner region, (b) profile along the XY direction measured by laser scanning, and (c) profile along the XX direction measured by laser scanning. (d) Porosity distribution of Ti deposit at traverse speed of 25 mm/s and a corner radius of 0.3 mm [184].

To enhance formability and microstructure, in-process cold spraying control has become popular. Lomo et al. [185] in RMIT utilized geometry optimization, XCT scan of reference samples, and 3D toolpath generation software Continuous3D by CSIRO to form a Ti-6.1TiC composite jet

engine bracket onto flat Al substrate, as shown in **Fig. 2.35a**. The top ring was misshapen due to an improper powder feed rate, as shown in **Fig. 2.35b**. Concave shape was formed instead of convex surface due to the side walls were deposited faster than the middle of rings. This kind of defect is attributed to aforementioned overbuilt structure during instant deceleration which had not been overcome. There was also cracking on the feet, possibly because the porous shell region failed to withstand thermal residual stress upon cooling, as shown in **Fig. 2.35c**. However, the microstructure of cold-sprayed bracket was unknown since only visual inspection was described.

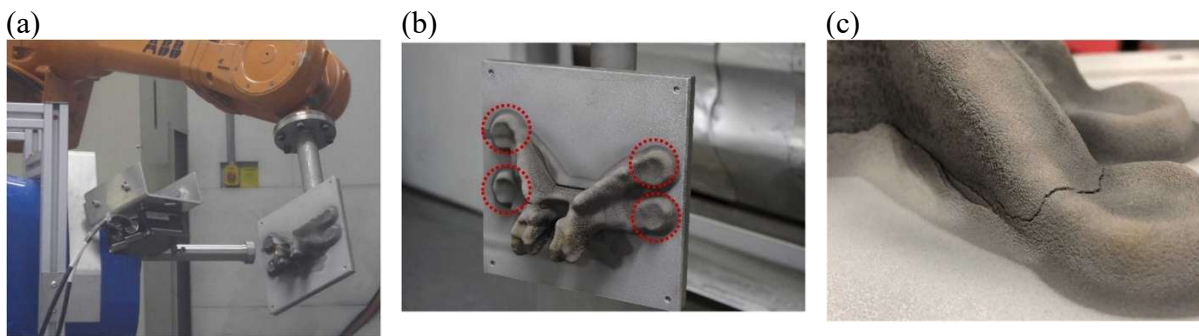


Fig. 2.35. (a) The spraying session of the optimized jet engine bracket using the PCS-1000 L (Plasma Giken, Japan). (b) Finished optimized jet engine bracket on the substrate. The dotted red circles represent the bolt holes to be drilled through. (c) Cracking occurred around the bolt holes interface 30 min after spraying and cooling to room temperature 20 °C [185].

Visual inspection is indeed the most basic method in practice. Later, Chew et al. [186] in the same group improved spraying control with real-time 4D reconstruction to deposit CP-Ti cube, blade, and bracket without observable surface cracking. Their hardware setup is displayed in **Fig. 2.36a**. The multi-camera and multi-marker vision system was composed of three RGB-D cameras and eight planar fiducial markers. The markers were claimed to solve alignment problems and reduce the computation load on feature extraction and captures matching in conventional point clouds method. **Fig. 2.36b** illustrates three steps in real-time reconstruction: (1) ROIs segmentation and

spatial registration, (2) substrate tracking and temporal 3D registration, and (3) 3D fusion and updating of growing object. The final deposits were scanned with high-resolution laser and compared to the camera-reconstructed models by CloudCompare software. The averaged root-mean-squared errors of cold-sprayed cube, blade, and bracket were small as 0.713, 0.733, and 0.963 mm, respectively. However, there was 6.67 % of layer height error by comparing the laser-scanned model and the CAD design. The porosity was measured to be about 7.4 % with optical micrographs in **Fig. 2.36c**. Despite such tolerance being acceptable, the influence on porosity by geometry and corresponding nozzle motion remained unclear without specifying which deposit was characterized.

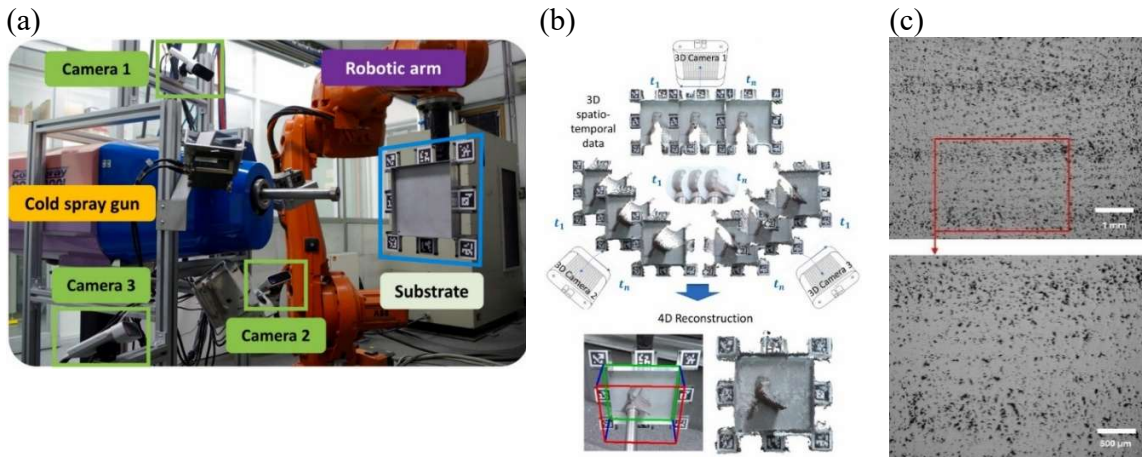


Fig. 2.36. Real-time 4D reconstruction for cold spray robot control: (a) hardware setup, (b) computation routine, and (c) microstructure of the cold-sprayed CP-Ti [186].

The local defects related to the nozzle motion were explored thoroughly in a study by Wu et al. [187] in Helmut-Schmidt-Universitat, who developed the cold spray toolpath generating algorithm to form a 33 mm tall multi-feature freestanding part with pure Al powder and compressed air-argon mixture. There were sharp peaks formed on the top of the part (**Fig. 2.37a** and **b**), which were caused by the instantaneous fluctuations of TCP speed from input speed 50 mm/s to almost zero (**Fig. 2.37c**). Detailed observations found that small peaks formed at the bottom section of the

part, where offline simulation indicated the TCP speed fluctuating between 50 to 40 mm/s around the peaks. Similar to other dynamic systems, it is more difficult for the robot at higher speed to readjust motion against its inertia. In this case, the fluctuation was more serious during height adjustment after spraying every planar circle. Comparatively, the U-turns of parallel strokes at bottom section only led to 10 mm/s fluctuations. Hence, the geometric accuracy of cold-sprayed deposits requires dynamic motion smoothing or other strategies such as masking. Although the machined part did not exhibit any visual defects on both top and bottom sections of the part, the detailed internal defects were not investigated with XCT or sample cuts under a microscope.

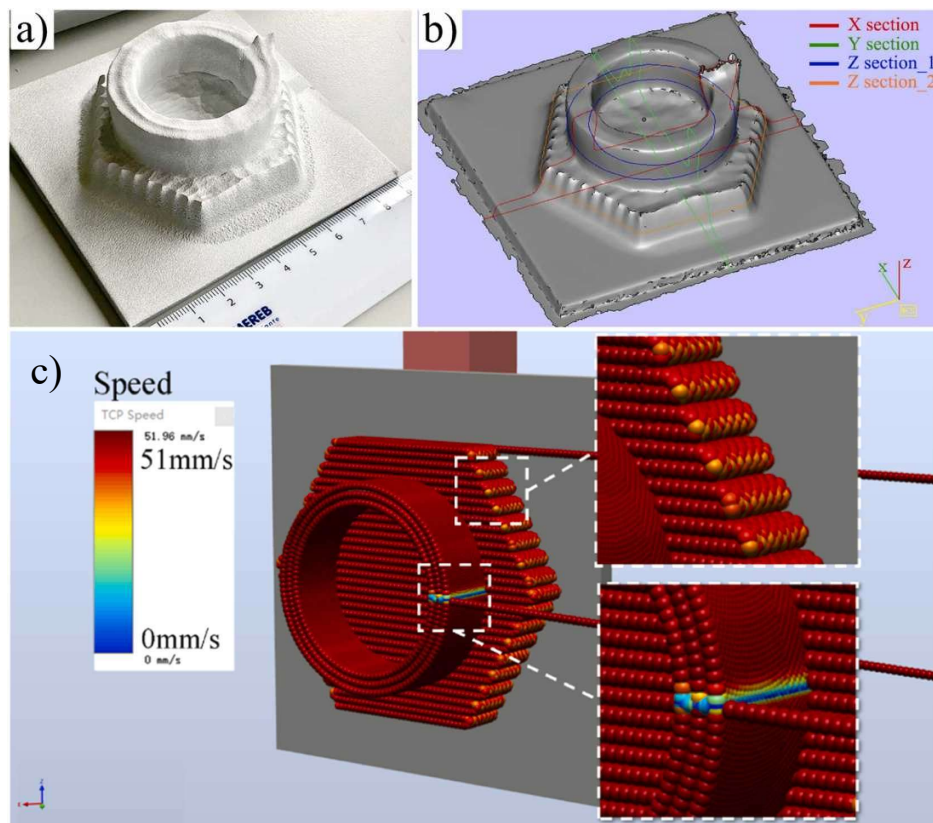


Fig. 2.37. Local defects due to fluctuation of nozzle traverse speed during cold spray: (a) real part, (b) 3D scanned part, and (c) comparison with TCP speed variation of toolpath [187].

Lewke et al. [188] in the same group later improved the speed fluctuation range from 500-25 mm/s to 280-50 mm/s, which produced a 1.91 mm thin Al-6061 deposit. Admittedly, there was a 4.48 mm tall peak at the center of the deposit which added the effort of post-machining. The overbuilt peak was likely caused by the minimized loop perimeter, or the time delay between the robot arm completing the toolpath and stopping powder feeder. However, the comparison of speed fluctuations between these two studies might not be fair enough due to their different sizes. Furthermore, the configuration in their previous free-form study [187] was substrate-on-robot with fixed-nozzle but that was reversed in the automation study [188]. The most significant contribution of the automation study was demonstrating the workflow of inspection (**Fig. 2.38a** and **d**), pre-machining (**Fig. 2.38b** and **e**), and cold spraying (**Fig. 2.38c** and **f**) with tools-switching capability on a single robot arm.

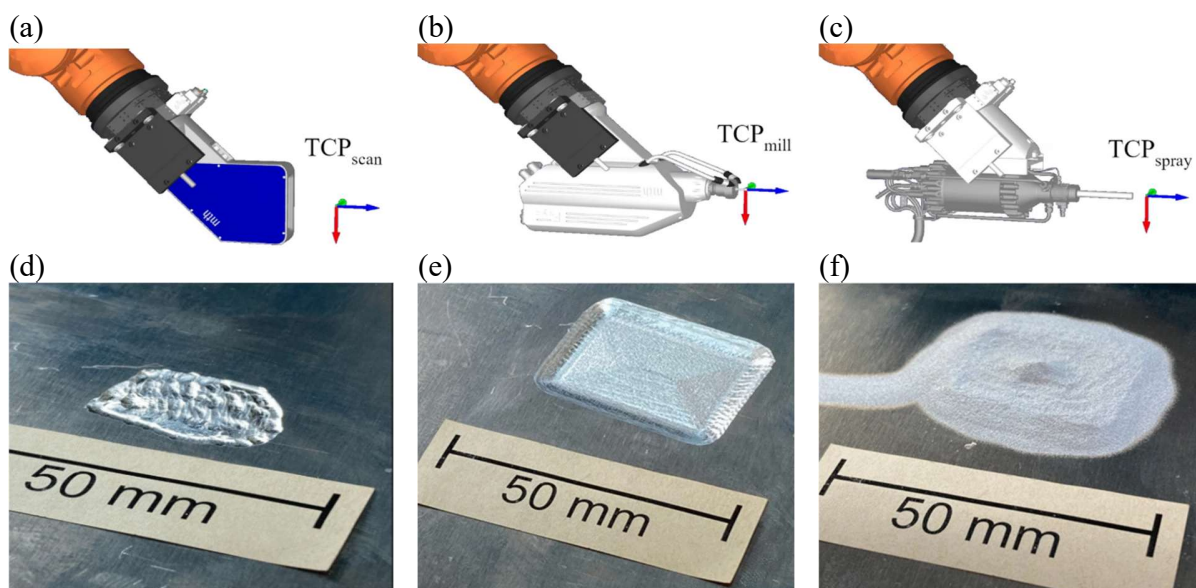


Fig. 2.38. Tool center points of the respective tools, (a) sensor for scanning, (b) milling tool, (c) cold spray gun in the automated repair system. (d) Damaged area, (e) pre-machined area, (f) cold-sprayed Al6061 deposit on the Al6061 component [188].

Indeed, the substrate-on-rotary with linearly traversing nozzle-on-robot, i.e. radial-axial, has been considered as the most reliable setup to fabricate dense deposits such as test coupons, rice cooker inner pots and pressure vessels [13, 40, 53]. Nonetheless, the influence of the instantaneous fluctuation of nozzle speed on porous structure and fluid transport properties has not been reported to date, where the required skill to cold spray with faster helium gas and harder Ti6Al4V powder is even more demanding.

As there are many uncertainties varying the porosity and fluid transport properties in the in-lab cold spraying and inspection, it is more difficult for operators on-site to achieve the deposition with in-lab quality [189]. Qualitative and quantitative data are necessary to develop comprehensive guidelines for quality control of cold spraying. However, the detailed process parameters and constraints of on-site trials, especially the dynamics of the nozzle, often remain confidential since the projects are affiliated with the US Department of Energy or Department of Defense [39, 40, 54, 190]. The current technical threshold for cold spray is exorbitant for most technicians in the aviation, energy and manufacturing industries. Statistical correlation is a straightforward method for operators evaluating the fluid transport properties of deposits, and thus, the quantitative database needs to be prepared. Shorinov et al. [191] in Kharkiv Aviation Institute and Motor Sich JSC also demonstrated using regression equations based on experimental data to optimize handheld spraying parameters for adhesion and deposition efficiency of Ni-Al₂O₃ coatings on VT3-1 substrate, which was targeted to be adopted in mass-produced aircraft engines. Furthermore, the use of XCT is limited by long scanning time, the capacity of the sample holder and its immobility. Therefore, statistical references are crucial to develop automated toolpath generation and correlate the on-site NDI results with detailed XCT scans and subsequent fluid transport

properties. This approach would narrow the knowledge gap of operators and eventually achieve the goal of sustainable MRO.

2.6 Ductility enhancement by heat treatments

2.6.1 Hot-isostatic pressing

Some recent studies have achieved ductile cold-sprayed soft metals, including pure Cu, pure Zn, Al2024 and Al6061 alloys, in their as-sprayed conditions or followed by post-spray deformation processing [192-195]. However, modifying cold-sprayed hard metals, such as Ti alloys, to be ductile requires much harsher conditions. Twenty years ago, Blose et al. [196, 197] reported using hot isostatic pressing (HIP) to reduce the porosity to wrought level and enhance the 10 mm thick cold-sprayed Ti6Al4V coatings to ultimate tensile strength (UTS) of 890 MPa at strain of 7% and fracture stress of 620 MPa at strain of 14%, as shown in **Fig. 2.39a**. The micrographs of as-sprayed and HIPed coatings are presented in **Figs. 2.39b** and **c**, respectively. However, later studies were unable to replicate such ductile cold-sprayed Ti6Al4V with HIP [27, 198-200]. The airworthiness of cold spray repair could not be approved due to these inconsistent results. Blose et al. [197] also revealed that the cold-sprayed coating with 2.7% of porosity and coating-substrate gap in **Fig. 2.39d** could be healed after heat treatment at 954°C for 8 hours instead of using HIP, which facilitated globularized and lamellar microstructures in coating and substrate, respectively, as shown in **Fig. 2.39e**. However, the details of their mechanical performance were not provided. Moreover, heat treatment for eight hours was considered impractical from a cost perspective, and thus heat treatment above beta transition temperature was targeted. Unfortunately, there had not been updated publications from Blose since then.

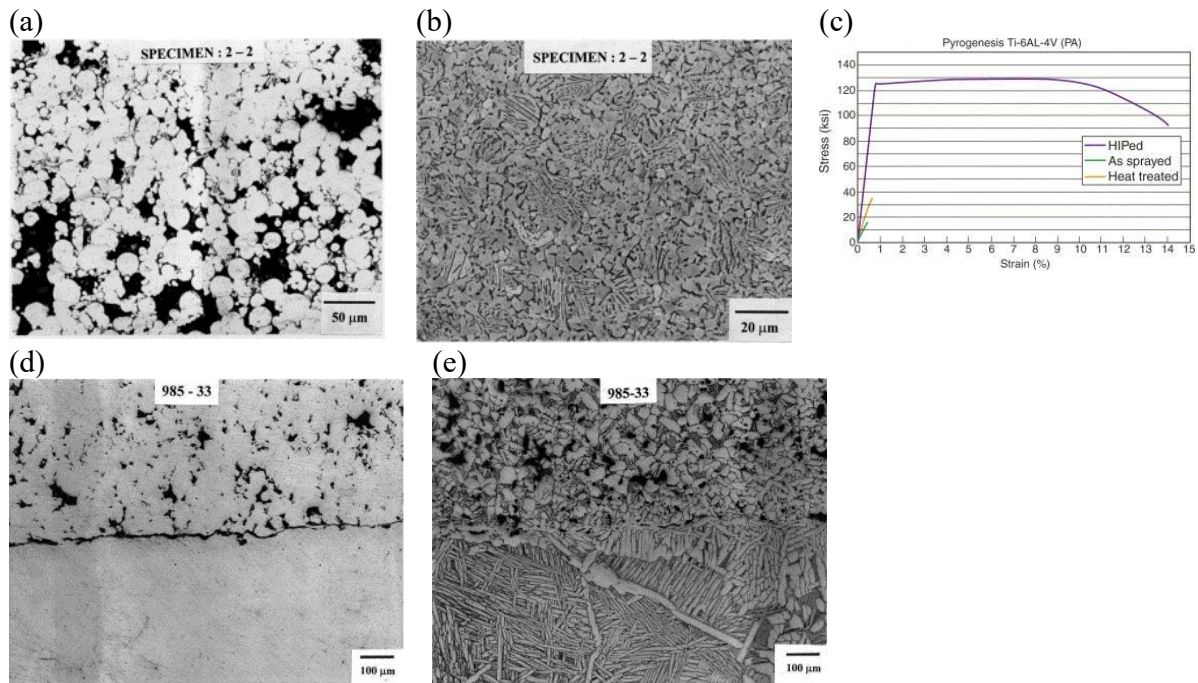


Fig. 2.39. Cold-sprayed Ti6Al4V with helium at 530°C in (a) as-sprayed condition, and (b) after HIP. (c) Stress-strain plot comparing the as sprayed, heat-treated and HIPed properties for Ti6Al4V specimens. (d) Cold sprayed Ti6Al4V with 450 psi helium, gas and powder coil temperatures at 500°C, and (e) the diffusion of the GB between the coating and substrate after heat treating at 1750°F for eight hours [197].

Kondas et al. [201] claimed that their cold-sprayed Ti6Al4V with plasma atomized spherical powder achieved a UTS of 950 MPa at an elongation of 21% (**Fig. 2.40c**) after their confidential self-developed procedures consisting of HIP and heat treatment cycles. The as-sprayed and heat-treated microstructures are displayed in **Figs. 2.40a** and **b**, respectively. It was alerted that Armstrong processed coral-like powder could achieve slightly lower porosity (0.66-1.06%) than the spherical powder (0.78-1.90%), but the coating with coral-like powder could not become ductile after the same heat treatment possibly due to higher nitrogen and oxygen contents, as shown in **Fig. 2.40d**. Morks et al. [202] compared the cold-sprayed CP-Ti coatings with spherical and irregular powders in 15-50 µm. Besides confirming the impact of higher oxygen and nitrogen

contents in irregular powder, the higher strength in coatings made of spherical powder were attributed to half porosity and double grain size after heat treatment at 1100°C. Wong et al. [203] once demonstrated the hydride-dehydride irregular CP-Ti powder could deposit much denser coatings on mild steel substrates than the spherical powders, where the irregular powder had a smaller average particle size. However, the mechanical strengths and effects of heat treatment were not studied for a fair comparison. The cost and time of milling and sieving for irregular powder under 10 µm are also questionable. Furthermore, their AA6061 substrates in the study by Kondas et al. [201] were removed prior to heat treatment, and thus the impact of this heat treatment on coating-substrate interfacial bonding could not be evaluated. More essentially, Al alloy substrates melt before reaching the recrystallization temperature of Ti alloys. The deposition of Ti alloy on Al substrates might be suitable for enhancing impact toughness, wearing and corrosion resistance, but the ductility should not be expected to be high. It was also noted that another attempt by Kondas et al. [204] heat-treated the Ti6Al4V samples at 900°C for 4 hours without HIP followed by aging at 538°C for another 4 hours (**Fig. 2.41a**), where the ductility varied from 4% to 8 % at UTS of 900 MPa (**Fig. 2.41b**). This indicated that the issue of local defects could not be resolved to ensure the quality of repair consistently.

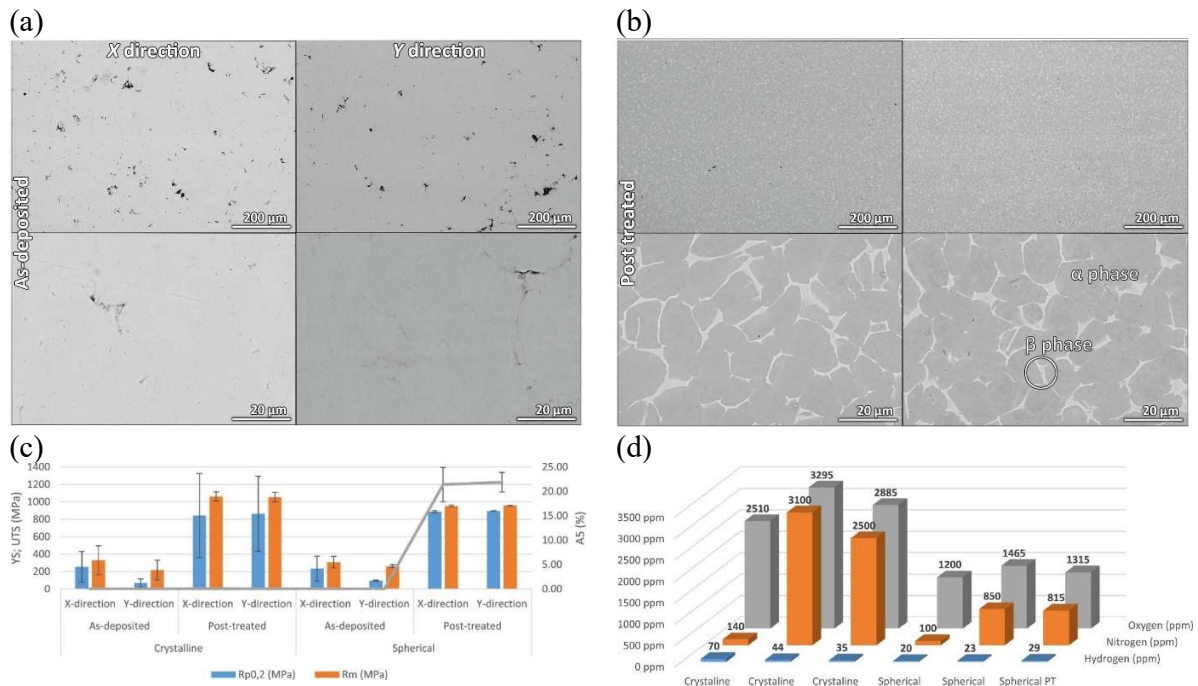


Fig. 2.40. Microstructure of the Ti6Al4V samples (a) as-deposited using the spherical feedstock powders and (b) changes after the performed post-treatment. (c) Mechanical properties of the as-deposited and post-treated CSAM Ti6Al4V samples. (d) Interstitial content analysis in crystalline and spherical powders and their deposits in as-deposited and post-treated state [201].

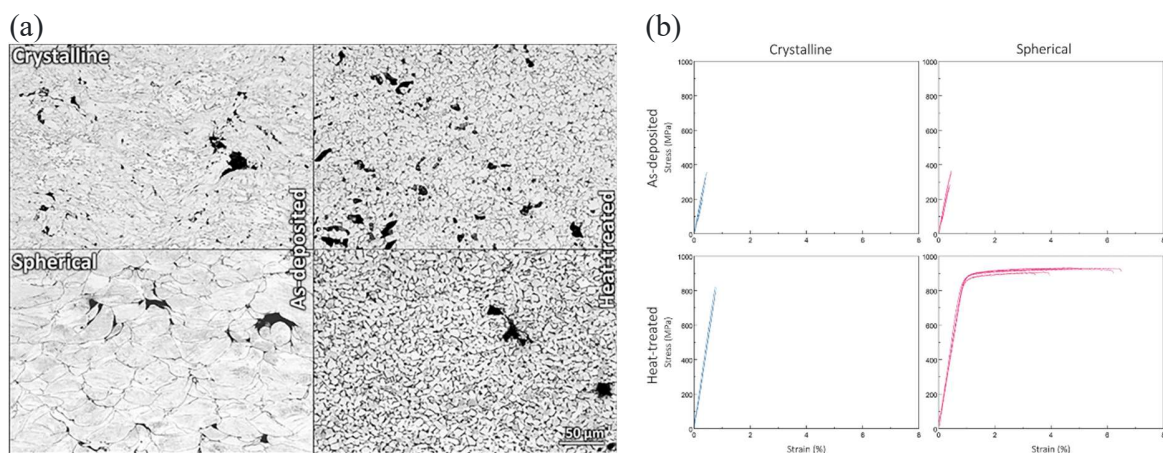


Fig. 2.41. (a) Etched microstructure of the final Ti6Al4V samples deposited from the two feedstock powders and changes after the performed heat treatment. (b) Stress-strain curves of the as-deposited and heat-treated CSAM Ti6Al4V specimens [204].

2.6.2 High temperature heat treatment

Lett et al. [205, 206] successfully recovered the ductility of cold-sprayed Ti6Al4V to the strain of 9.1% and 5% by annealing at 1050°C for 2 hours with a heating rate of 4°C/min, followed by air cooling and water quenching, respectively. The detailed microstructures, porosity, and strain curves are showcased in **Figs. 2.42** and **2.43**, respectively. The performance was contributed by the martensitic microstructure with bundle-like arrangement, prior β grain laths thickness of 0.76-0.27 μm , and coating porosity of 2%. Alternatively, annealing was conducted at 950°C for 2 hours, followed by furnace and air cooling. The equiaxed and bimodal microstructures further improved the strain to 10.8% and 4.5%, respectively. On the other hand, the stainless-steel substrates were also removed prior to heat treatment, and thus, the effectiveness of additive repair could not be assessed. Unless this concern is addressed, cold spray repair cannot be implemented in commercial aviation.

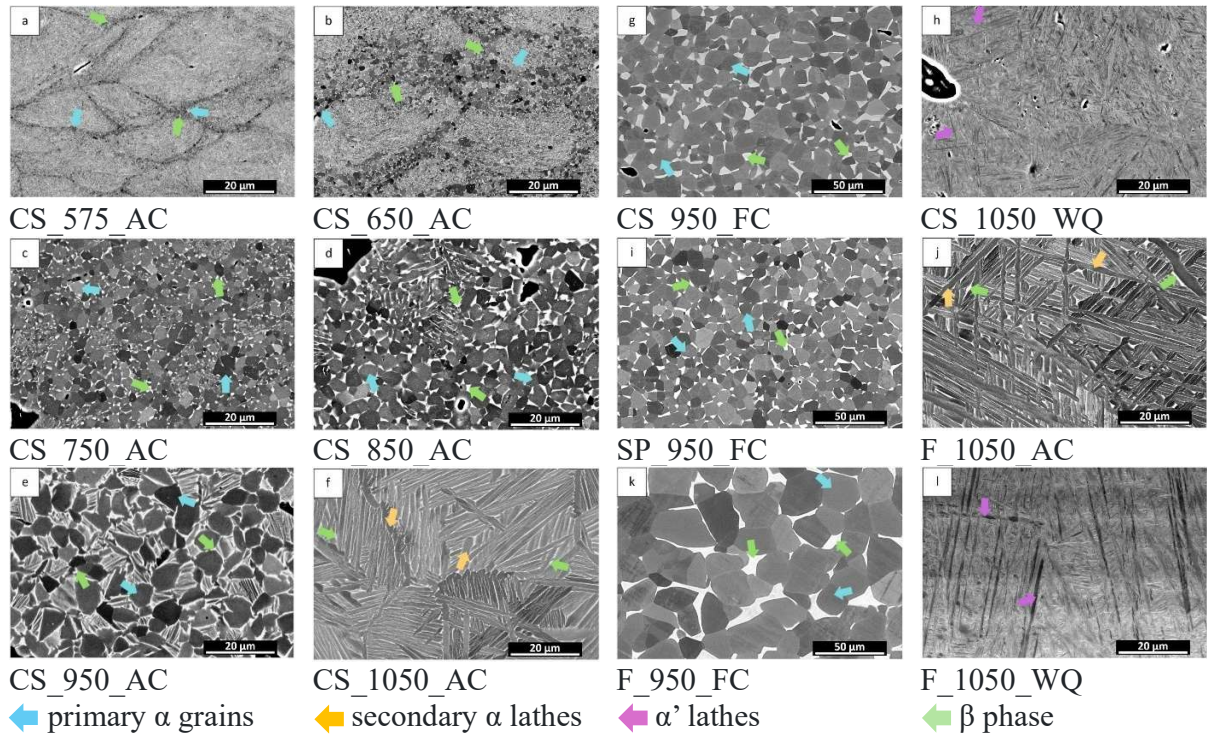


Fig. 2.42. SEM micrographs showing microstructures of cold-sprayed Ti6Al4V obtained after heat treatment [205].

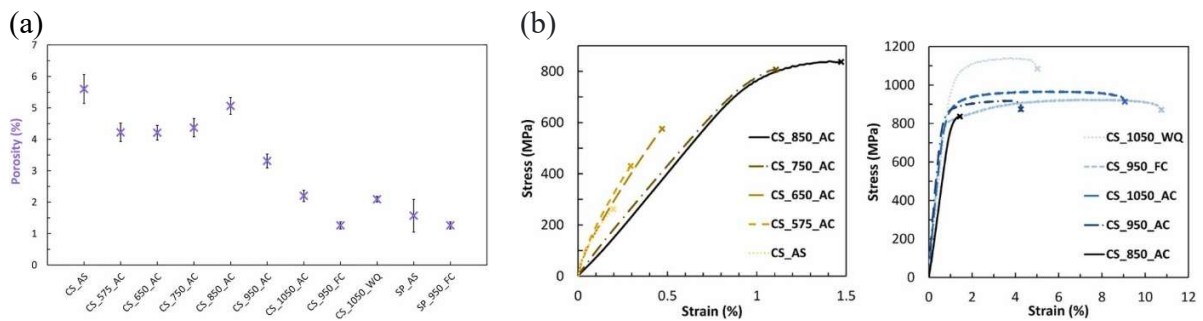


Fig. 2.43. (a) Porosity level in cold-sprayed samples evaluated using optical micrographs. (b)

Room temperature stress-strain curves of cold-sprayed samples showing the evolution of the tensile behavior following post-process heat treatments [205].

Heat treatment around 1000°C is not always effective in enhancing the ductility of cold-sprayed titanium and alloys. Huang et al. [13] suggested that annealing heat treatment of CP-Ti coatings at about 1000°C for 4 hours failed to eliminate the large pores, and thus, the tensile properties were

far lower than those of the wrought. Vo et al. [14] annealed N₂ and He sprayed Ti6Al4V tensile specimens at 1000°C for 4 hours and at 600°C for 2 hours, respectively. The N₂-sprayed microstructures are summarized in **Fig. 2.44**. Both the N₂ and He sprayed specimens fractured brittle with UTS and elongation of 462 MPa and 5.8%, 764 MPa and 6.3%, respectively, as shown in **Fig. 2.45**. The heat treatment at 600°C only softened the coating with static recovery. A slight ductility improvement was observed after heat treatment at 1000°C, which formed an interparticle diffusion bonding neck and resulted in the formation of coarse lamellar α grains through the decomposition of the β phase upon air cooling. These numbers were better than the as-sprayed ones but did not reach the wrought properties of annealed (900 MPa and 10%) and aged (1100 MPa and 8%) Ti6Al4V alloy [207].

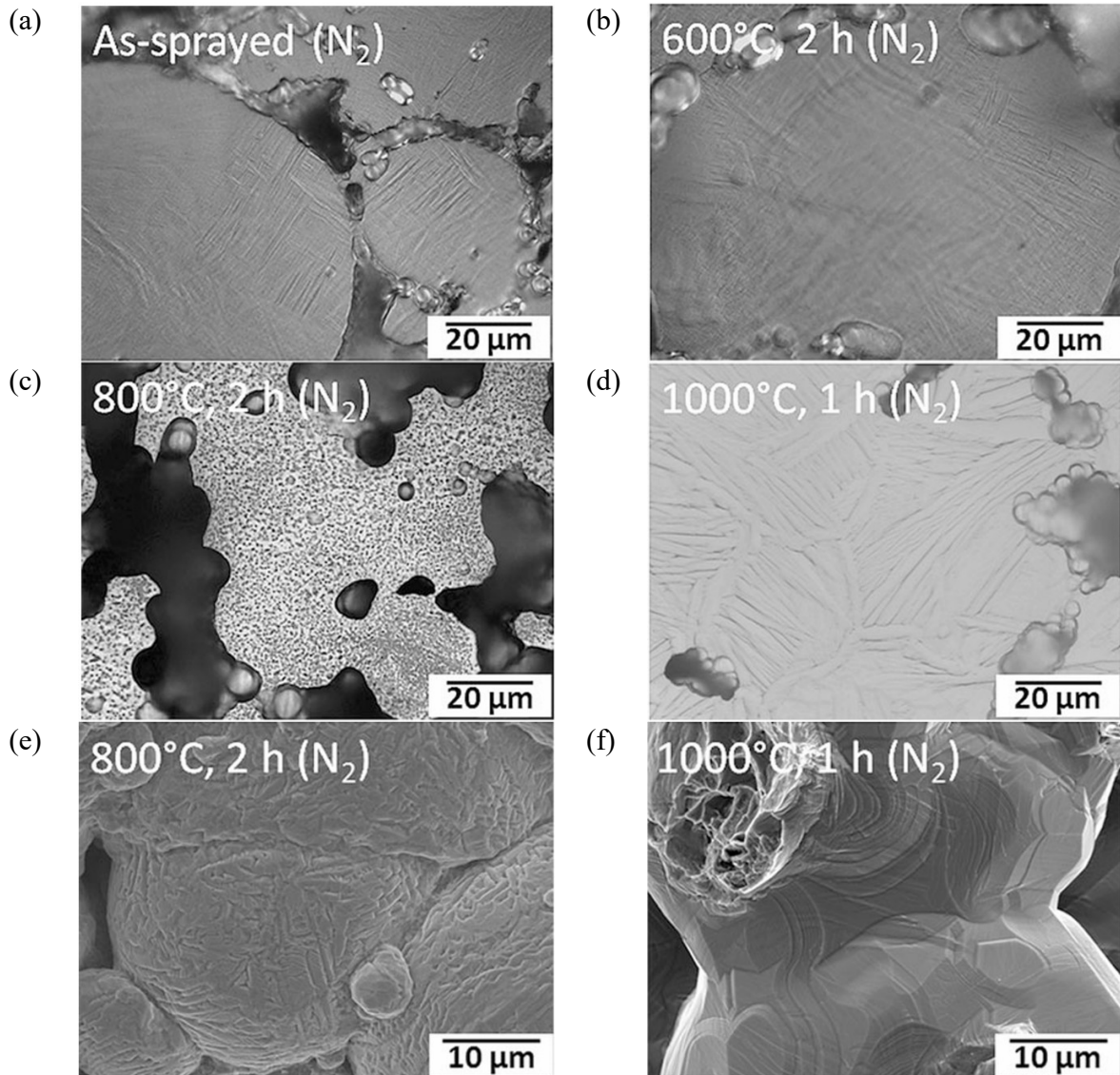


Fig. 2.44. Typical etched microstructures ($\times 1000$) of N_2 -sprayed Ti6Al4V coatings in (a) as-sprayed condition and (b) annealed at 600 °C for 2 h, (c) 800 °C for 2 h, and (d) 1000 °C for 1 h.

Typical fracture surfaces ($\times 5000$) at the pores of N_2 -sprayed Ti6Al4V tensile specimens annealed at (e) 800 °C for 2 h, and (f) 1000 °C for 1 h [14].

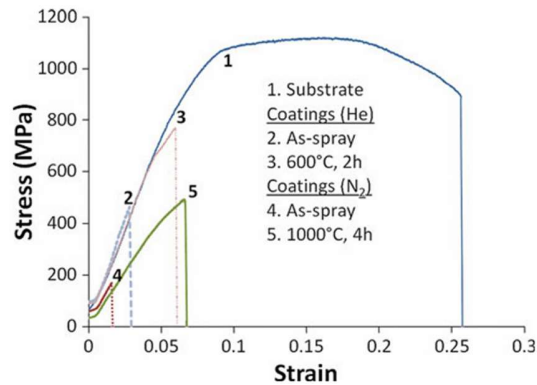


Fig. 2.45. Typical stress-strain curves for Ti6Al4V substrate, He-sprayed Ti6Al4V coatings (as-sprayed and annealed at 600 °C for 2 h), and N₂-sprayed Ti6Al4V coatings (as-sprayed and annealed at 1000 °C for 4 h) [14].

Molak et al. [208] compared annealing warm-sprayed Ti6Al4V with conditions of β transformation at 1025°C for 1 hour, and recrystallization at 940°C for 4 hours. The microstructures are compiled in **Fig. 2.46**. The coating sprayed at 4 MPa and 1.0 m³/min of N₂ performed the best strength and ductility among the sets, but β and recrystallization annealing could only achieve 820 MPa and 3.93%, 824 MPa and 2.84%, respectively, as shown in **Fig. 2.47**. The laths in the β annealed microstructure might not be thin enough to provide excess slip systems for ductility [205]. Furthermore, the planar slip bands between equiaxed α grains and intergranular β phase in recrystallized microstructure led to easy crack nucleation and fast crack propagation, hence resulting in lower ductility than the fully equiaxed α microstructure [209]. Moreover, Molak et al. [208] also revealed that the porosity and stack fault energy upon particle deformation by varying spraying parameters exhibited distinctive microstructures and mechanical performances due to different recrystallization kinetics. It is a problem in practical repair, as the material combinations and coating quality are determined on a case-by-case basis. Hence, the heat treatment for ductility enhancement must form a fully equiaxed α microstructure, while also considering the capabilities in terms of coating porosity and particle plasticity.

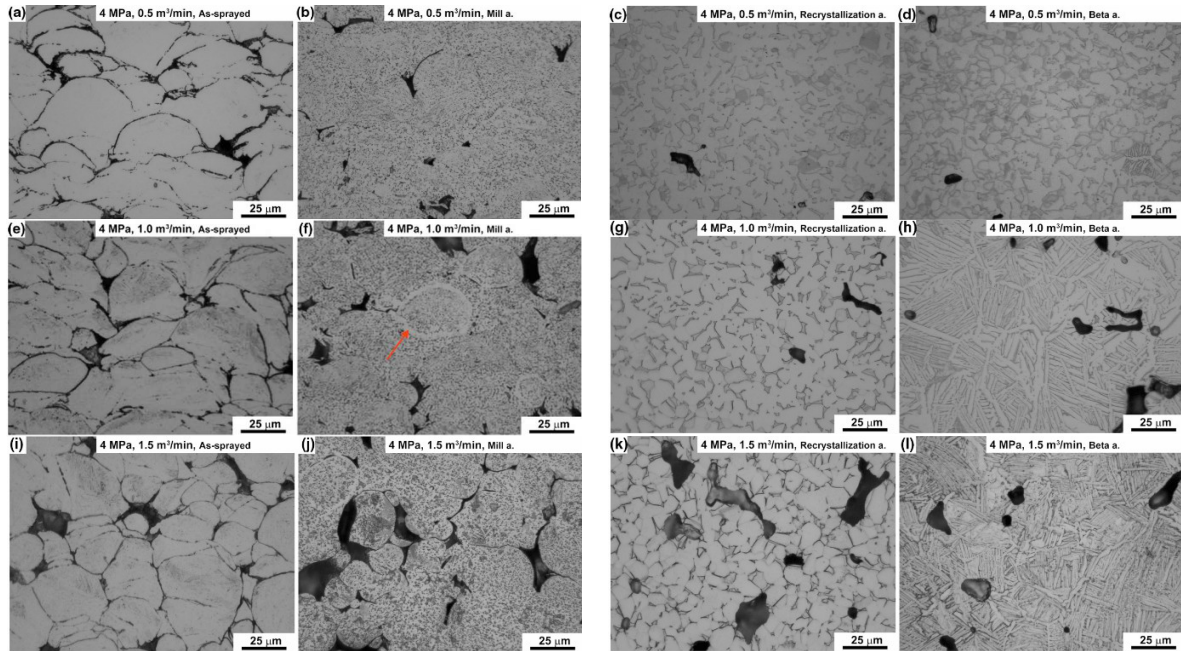


Fig. 2.46. Cross-sectional etched micrographs of as-sprayed and heat-treated Ti6Al4V coatings fabricated at three nitrogen flow rates of 0.5, 1 and 1.5 m³/min [208].

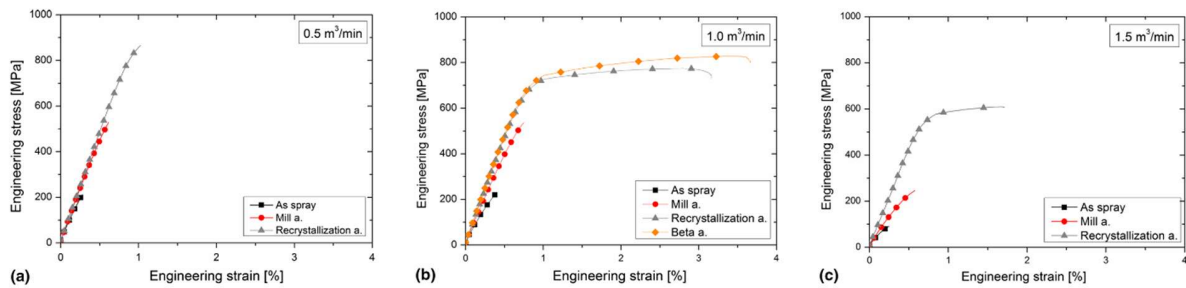


Fig. 2.47. Engineering stress-strain curves for as-sprayed and heat-treated Ti6Al4V coatings fabricated at three nitrogen flow rates of (a) 0.5, (b) 1.0, and (c) 1.5 m³/min [208].

2.6.3 Thermo-hydrogen processing

Paramore and his colleagues [210-212] utilized hydrogen sintering and phase transformation (HSPT) or thermo-hydrogen refinement of microstructure (THRM) to refine the microstructure of wrought titanium alloys, as well as improving the ductility of Ti6Al4V fabricated by powder metallurgy (PM) and LPBF better than the wrought. The general microstructural evolution along thermal profile is illustrated in **Fig. 2.48**. The principle involved using hydrogen and phase

transformation to facilitate an ultra-fine-grained microstructure with abundant GB energy, thereby prompting further globularization (**Fig. 2.49b** and **e**), as well as closing pores with enhanced diffusion kinetics. The bimodal microstructure in **Fig. 2.49c** and **f** can be fabricated by water quenching to achieve high tensile strength, while the globularized microstructure, obtained through furnace cooling, can exhibit high ductility. **Fig. 2.49g** shows a coarse lamellar microstructure with voids resulting from conventional super-transus vacuum sintering without subsequent sub-transus heat treatment.

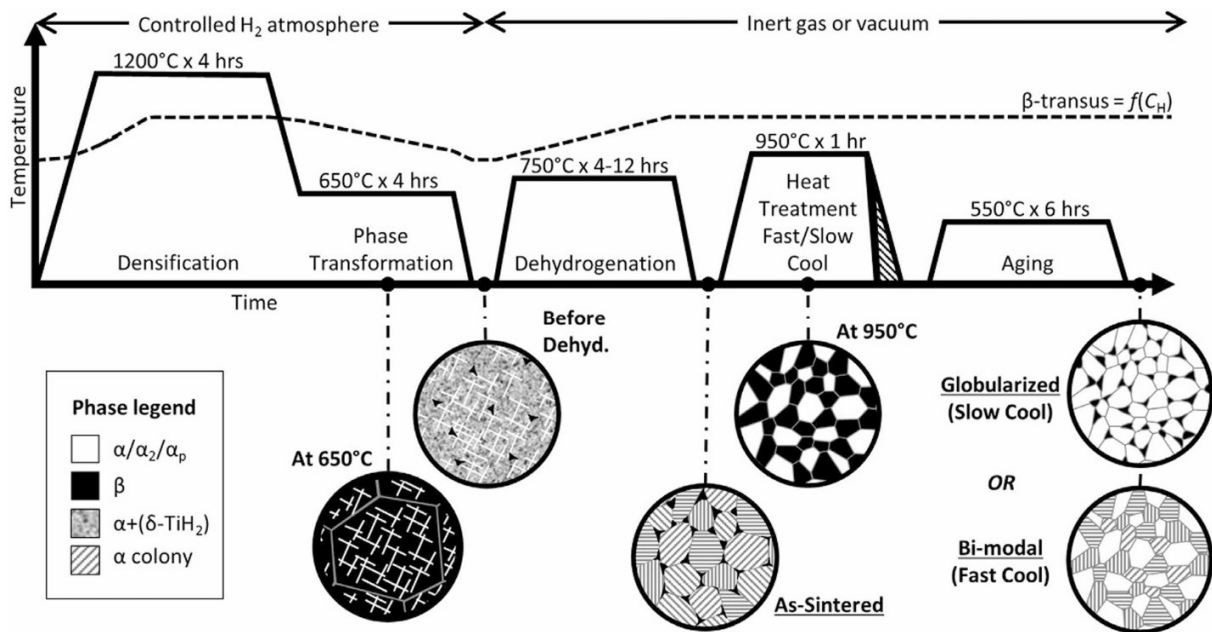


Fig. 2.48. Schematic of the thermal profile, microstructural evolution, and the β -transus (as a function of hydrogen content) during HSPT and subsequent heat treatments to produce Ti6Al4V with bi-modal and globularized microstructures [211].

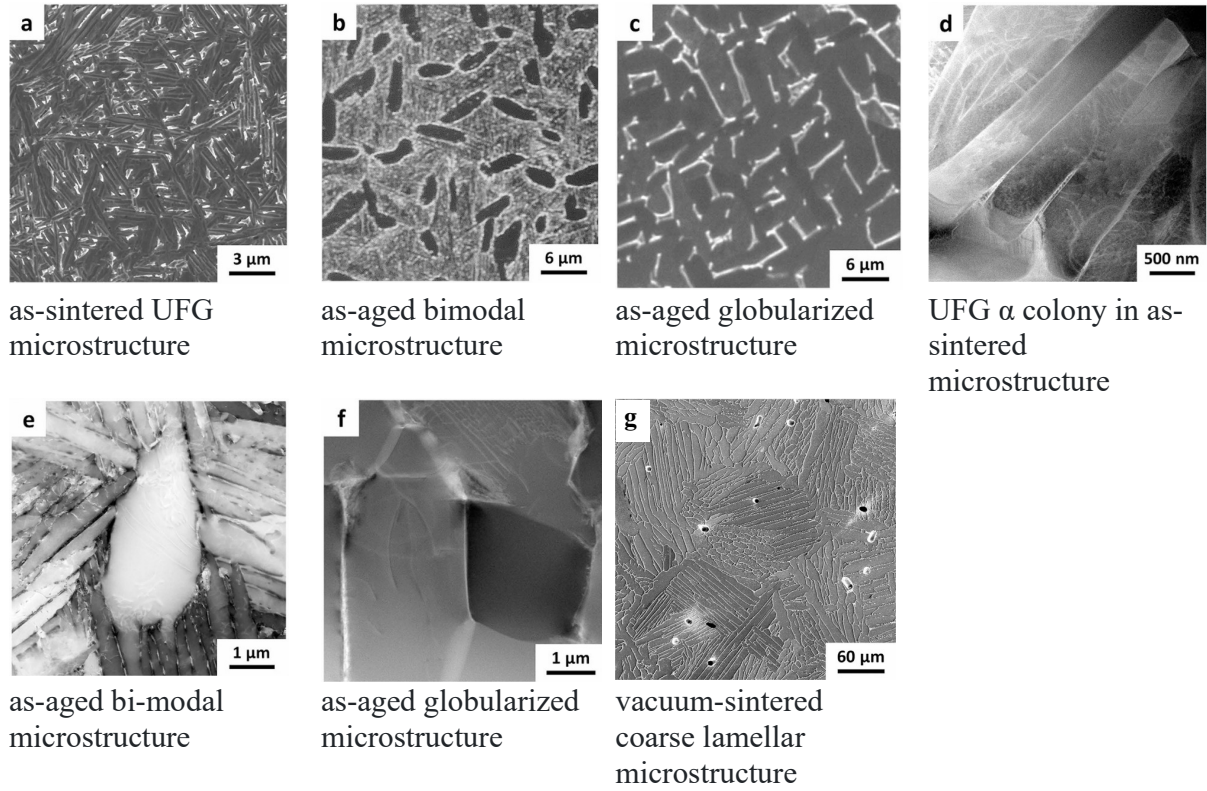


Fig. 2.49. SE/SEM (a-c, g) and STEM (d-f) of Ti6Al4V microstructures by HSPT [211].

The mechanical performance of Ti6Al4V after thermohydrogen processing relies heavily on the microstructure obtained through different fabrication methods. The PM Ti6Al4V with globularized microstructure after HSPT and gaseous isostatic forging (GIF) had improved both tensile ultimate strength and fracture strain compared to counterparts by vacuum-sintering with and without GIF afterwards [211], as shown in **Fig. 2.50a**. In contrast, the enhanced compressive strains of LPBF Ti6Al4V by THRM resulted in similar fracture strengths but sacrificed its yield strength by ~500 MPa, which applied to both loads along and perpendicular to the build direction [212], as shown in **Fig. 2.50b**. The remarkable feature was the tensile strain being tripled after THRM but both the yield and fracture strengths deteriorated by ~400 MPa. This tension-compression asymmetry is presumably attributed to the high propensity of cross-slip in tensile deformation, as well as the complex motion of screw dislocations, also known as non-Schmid

effects. It implies that the tension-compression asymmetry in cold-sprayed deposits would not be removed, although their root causes may differ.

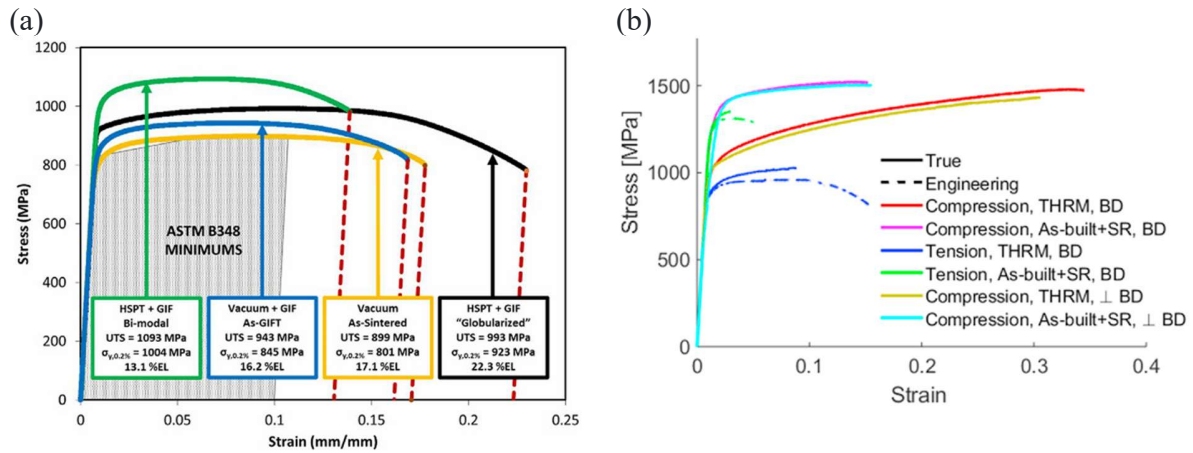


Fig. 2.50. Stress-strain curves for Ti6Al4V produced via (a) HSPT [211] and (b) LPBF as-built + SR and THRM [212].

Dunstan et al. [27] implemented the THRM process on the cold-sprayed Ti6Al4V samples and compared them with those that underwent HIP at 950°C and 200 MPa for 2 hours, as shown in **Fig. 2.51**. The tensile test results in **Table 2.3** suggest that the THRM coatings (587.3 MPa and 0.49%) outclass the HIP coatings (325.9 MPa and 0.27%). The disparity became broader in the bimetallic condition, where the UTS and strain of THRM and HIP were 963.3 MPa and 351.5 MPa, respectively, corresponding to 0.8% and 0.28%. The fractographies revealed that the HIP process was unable to eliminate porosity and unbonded regions. Nonetheless, all the samples were still far away from meeting the 9% elongation of wrought Ti6Al4V. The interstitial oxygen and nitrogen contaminations during the spraying process are considered to be the major cause. McGee et al. [213] utilized gas-nitriding Ti6Al4V powder to eliminate the nozzle clogging. The mechanism is reducing the polar cohesive forces by replacing about half of the surface oxide layer and hydroxyl groups with nitride. The samples nitridated at both 700°C and 800°C for 30 minutes did not show a noticeable difference in microhardness compared to the untreated powder. In other words, the

replacement of the oxide layer with a nitride layer has a limited influence on ductility. It can be seen that THRM can effectively improve the ductility of Ti6Al4V; however, the microstructure with deformed particles may hinder ductility improvement in cold-sprayed Ti6Al4V. The THRM bimodal microstructure of Dunstan et al. [27] had neither fully equiaxed grains nor laths with bundle-like arrangements for slip transfer like those by Lett et al. [205]. The inadequate phase transformation and globularization time of the severely deformed Ti6Al4V particles are likely the cause of the limited ductility.

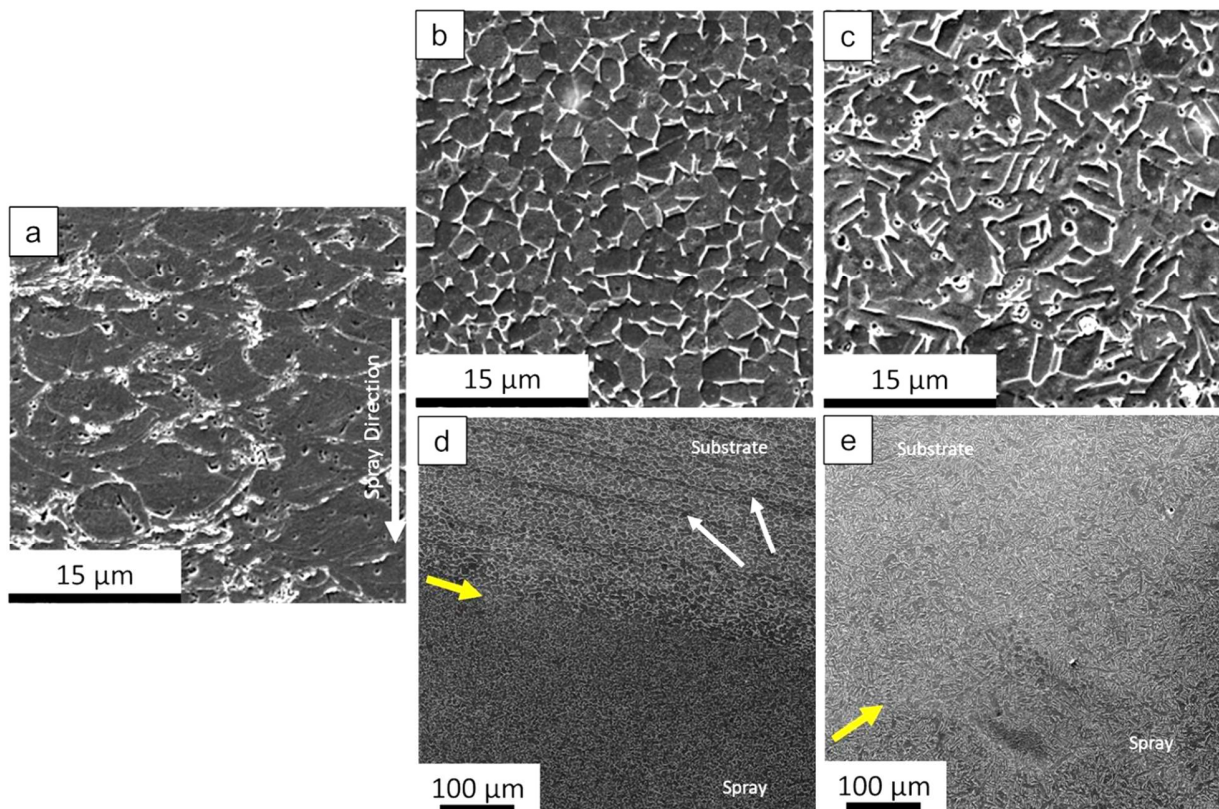


Fig. 2.51. SEM micrographs of the (a) as-sprayed, (b) spray only with HIP, (c) spray only with THRM, (d) bimetal with HIP, and (e) bimetal with THRM conditions. The α (hexagonally close packed) phase appears as dark while the β (body-centered cubic) phase appears as light [27].

Table 2.3. Tensile properties of cold-sprayed Ti6Al4V treated with HIP and THRM [27].

Material type	Heat treatment	UTS (MPa)	UTS increase (%)	EL (%)	EL increase (%)
Coating only	HIP	325.9 ± 26.1	-	0.27 ± 0.03	-
	THRM	587.3 ± 27.1	80.2	0.49 ± 0.03	84.4
Coating and substrate	HIP	351.5 ± 51.5	-	0.28 ± 0.04	-
	THRM	963.3 ± 82.5	174.0	0.8 ± 0.08	188.1
ASTM B988 (Grade 5 PM90)	-	806	-	9	-

2.6.4 Multi-step heat treatment (MSHT)

The MSHT process with extensive globularization time proposed by Li et al. [214] can achieve superior ductility in the selective laser melted (SLM) Ti6Al4V, as summarized in **Fig. 2.52**. The furnace is first heated to 950°C and held for 2 hours, then the furnace is cooled down for 100°C and held for another 2 hours. The step is repeated until the temperature holding at 650°C is completed, followed by furnace cooling to room temperature. The first step at 950°C facilitates the annihilation of dislocations, boundary splitting, and thermal grooving, resulting in a microstructure with thick and fine lamellar α grains. Cylinderization of lamellar grains is triggered at 850°C along with the formation of equiaxed grains. During the rest of the step-down temperature holding, termination migration and Ostwald ripening occur along with further grain growth and β -to- α transformation strain.

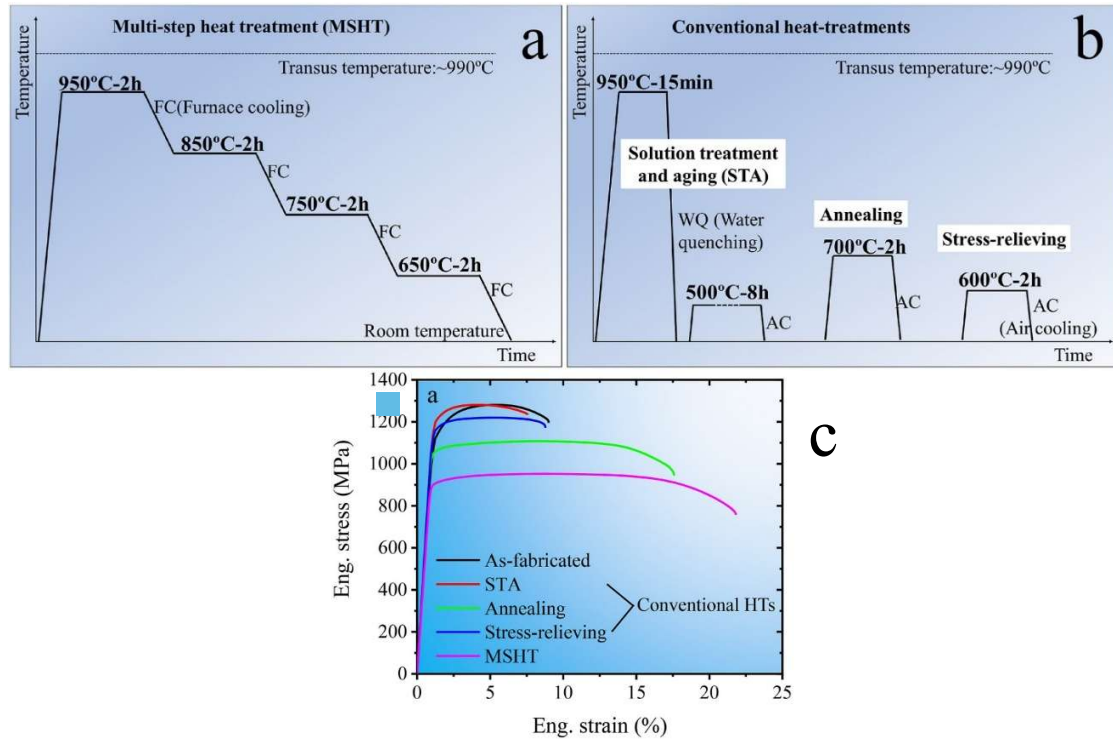


Fig. 2.52. Schematic map of (a) MSHT and (b) conventional heat-treatments. (c) Engineering tensile stress-strain curves of the SLM as-fabricated Ti6Al4V samples and those after post-heat treatments [214].

The equiaxed grains in the SLM Ti6Al4V after MSHT (**Fig. 2.53d** and **2.54d**) were about 10 μm with an aspect ratio of 0.42, which exhibited a yield strength (YS) of 900 MPa and a UTS of 953 MPa with an elongation of 21.8%. Nonetheless, it is not clear whether the MSHT process can overcome the high plastic strain and refined grains in cold-sprayed Ti6Al4V, which EBSD cannot index in the as-sprayed state [215]. Additionally, a heat treatment at 950°C for 8 hours in a vacuum was also suggested [197], which facilitated the removal of porosity and diffusion bonding across the coating-substrate boundary. The MSHT would save some electricity as it stops holding at 950°C after the first stage, but the product microstructure remains unclear. In addition, the influence of hydrogen charging on the MSHT has not been studied yet. Therefore, the MSHT

techniques in both vacuum and THRM variance deserve to be explored to determine if they can alter the brittle cold-sprayed Ti6Al4V into a ductile and well-adhered piece.

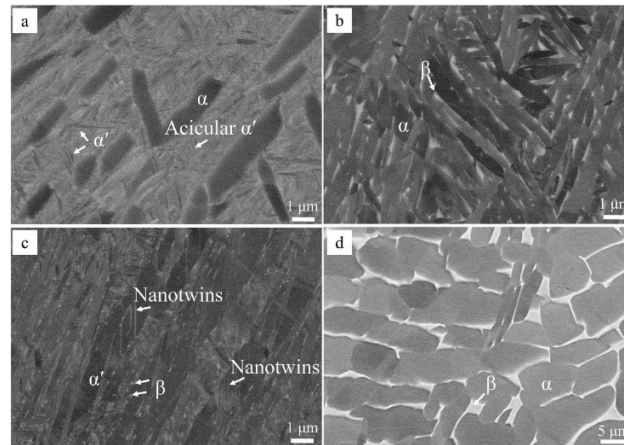


Fig. 2.53. Microstructures of the Ti6Al4V samples after post-heat treatments: (a) STA, (b) annealing, (c) stress-relieving, and (d) MSHT [214].

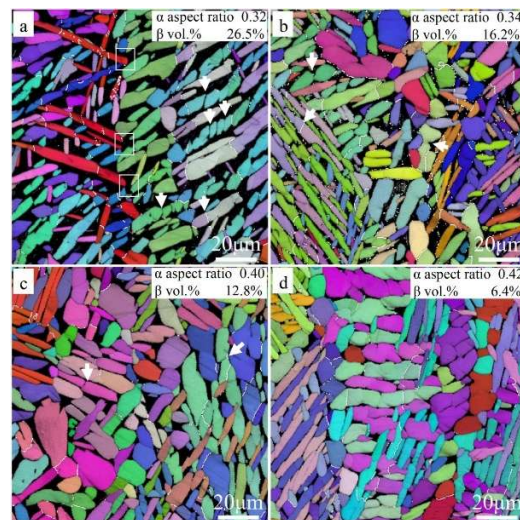


Fig. 2.54. Microstructural evolution of the Ti6Al4V sample during MSHT (a) 950 °C/2 h to 850 °C, (b) 850 °C/2 h to 750 °C, (c) 750 °C/2 h to 650 °C, and (d) 650 °C/2 h to room temperature. The white lines pertain to the LAGBs. The boxes and arrows indicate the cylinderization and boundary splitting, respectively [214].

2.7 Summaries

This chapter briefly reviews the principles of cold spray deposition, hydrogen embrittlement mechanisms, simulation methods for hydrogen diffusion, formation of porous cold-sprayed deposits and influence on fluid transport properties. Heat treatment strategies for enhancing ductility of cold-sprayed Ti6Al4V are also introduced, particularly holding at near-transus temperature, MSHT, and THRM. Four major research gaps are summarized as follows:

- (1) The hydrogen interaction with cold-sprayed Ti6Al4V microstructure has not been explored, i.e. high concentration for hydride formation or an ultra-high concentration for recombination on surface. This study uses cathodic charging method to reveal the hydrogen interactions in cold-sprayed Ti6Al4V at different heat treatment conditions.
- (2) There is a lack of methods to simulate hydrogen diffusion across the complex GB networks of cold-sprayed Ti6Al4V realistically. This study proposes an image-based method to convert the GB maps of cold-sprayed Ti6Al4V into models and perform hydrogen diffusion simulation.
- (3) The current understanding of statistical correlation between porosity induced by nozzle dynamics and subsequent fluid transport properties is limited. A cold-sprayed Ti6Al4V deposit with unique porous structure due to fluctuation of nozzle traverse speed is investigated in-depth by utilizing XCT reconstructed model and simulating permeation and diffusion of liquid hydrogen.
- (4) A reliable heat treatment strategy has not been available to guarantee ductility enhancement of cold-sprayed Ti6Al4V. This study compares the effectiveness of multi-step heat treatment in vacuum and hydrogen atmospheres to facilitate globularized microstructure for enhancing the ductility and adhesion of cold-sprayed Ti6Al4V on CP-Ti substrates.

Chapter 3: Hydrogen Damage on Cathodic Charged Cold-sprayed Ti6Al4V Coatings

3.1. Introduction

As reviewed in **Section 2.3**, the cold work offers hydrogen resistance to metals when the grains are refined to specific size with excess trapping sites. The microstructure of cold-sprayed Ti6Al4V meets the theoretical requirements of reduced hydrogen diffusivity; however, the actual interaction has not been tested yet. Furthermore, the heat treatment that aims to retrieve ductility may also lead to a loss of hydrogen resistance by an unknown amount. Understanding the electrochemical interaction of cold-sprayed Ti6Al4V can prevent damage during electrochemical processes such as cadmium plating.

This chapter investigates the relationship between the nano-mechanical properties and hydrogen interaction of cold-sprayed Ti6Al4V coatings to evaluate the feasibility of utilizing cold-spraying in hydrogen systems. The helium cold-sprayed Ti6Al4V coatings underwent low-temperature heat treatment and cathodic charging. Disparate post-charging surface morphologies were observed on samples with different heat treatment settings. In-depth investigations using a digital microscope, SEM, EDS, EBSD, XRD, and nanoindentation were conducted to understand the hydrogen embrittlement behaviors. The corresponding hydrogen damage mechanisms in coatings were elucidated based on the transition from a nanocrystalline structure to different heat treatment settings. The technical challenges in validating the proposed hypothesis were also discussed.

3.2. Methodology

3.2.1 Materials

Gas-atomized Ti6Al4V powder (Plasma Giken, JP) was used as the feedstock powder. Particle size distribution and morphology were analyzed with Morphologi 4 (Malvern Analytical, UK). A 7mm³ scope of powder was scanned individually with a diascope light source (bottom light) and a refractive index of 2.15 for pure Ti. An episcopic light source (top light) was used to observe powder with a shiny surface of iconic particles.

The substrates were 100 x 100 x 10 mm CP-Ti plates (Charmson Technology, HK). Two methods were used to smoothen the substrate surface for better adhesion. Two substrate plates were face-mill with Ecospeed F HT2 High-speed Machining Center (Starrag, CH) with a spin rate of 600 rpm. The other two substrate plates were laser-ablated with CL500 (CleanLaser, DE). Substrates were wiped with isopropyl alcohol and lens-cleaning tissue prior to spraying.

3.2.2 Sample Preparation

A cold spray nozzle (PCS100, Plasma Giken, JP) mounted on a robot arm (IRB 4600, ABB, CH) was used to deposit Ti6Al4V coatings. The spray nozzle had a glass divergent section with a 2 mm throat diameter, 8 mm exhaust diameter, and 300 mm length. Helium was heated up to 900 °C at 3 MPa. Particle velocity was measured by a cold spray diagnostic system (HiWatch CS2, Oseir, FI) prior to deposition. The particle speed was measured with a displacement of 25 mm away from the centre of the nozzle exhaust. Substrates were not preheated by the additional heater or warmup gas from the nozzle to reduce the uncertainty of heat distribution. Stand-off distance was maintained at 25 mm. The nozzle was traversing at a constant speed of 1 m/s. The toolpath was a

snake scan pattern from top to bottom with a vertical step of 1 mm, which was repeated for ten loops in each trial. The process flow of sample preparation is summarized in **Fig. 3.1**.

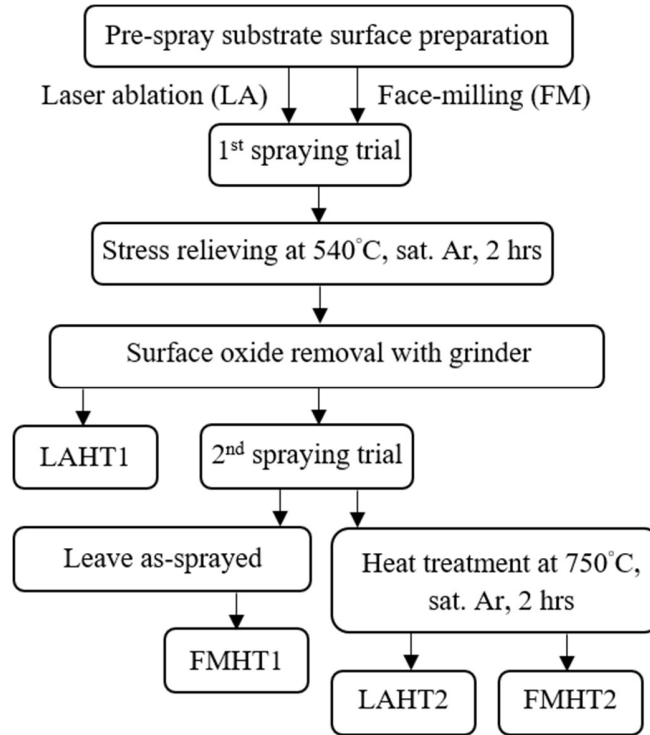


Fig. 3.1. Cold spray process flow chart.

The top surfaces of all the samples were then face-milled to obtain a uniformly flat finish. Specimens with dimensions of 15 mm x 15 mm x ~13 mm were wire cut from each sample plate using electrical discharge machining (EDM) (Agie Charmilles Robofil 240SL, GF Machining Solutions, CH). The cross-sections of samples with coating-substrate interface were then ground using a semi-automatic grinder polisher (EcoMet 30, Buehler, US) with progressively finer sand grit paper, starting from 120 grit down to 2000 grit. Samples were polished with a 0.05 μm alumina polishing suspension (MasterPrep, Buehler, US) to a mirror finish. The samples were then ultrasonically cleaned with 3-5% diluted degreaser for 20 mins at 50 °C. Ultrasonic cleaning was

repeated with acetone and deionized water, respectively. The samples were not etched to prevent interference with the interparticle bonding and percolation network of coatings.

3.2.3 Cathodic Charging

The specimens were winded with copper wire and connected in parallel. Cathodic charging was conducted with a current density of 0.207 V/cm^2 and 0.1 A/cm^2 for 4.5 hours at room temperature, as shown in **Fig. 3.2**. The measured voltage and current were 9.71 V and 4.695 A, respectively. Cold-sprayed specimens were cathodes, Pt-coated Ti mesh was used as the anode. H_2SO_4 with a concentration of 0.25 M was used as an electrolyte, and 0.1 M of thiourea was added as a hydrogen recombination inhibitor.

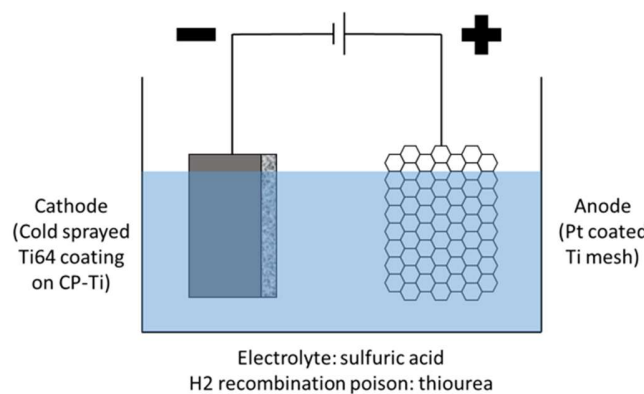


Fig. 3.2. Cathodic charging setup in schematic illustrations.

3.2.4 Microstructural and Mechanical Characterization

The following characterization methods on the samples were performed before and after cathodic charging. The cross-sectional microstructure of the samples was captured with a digital microscope (VHX-5000, Keyence, Japan). The optical micrographs captured (200x magnification) were stitched with the built-in function of the digital microscope (W:14 x H:2-3 images), open-source

software Hugin [216] and Autostitch [217, 218] respectively, depending on the quality of acquired images.

A scanning electron microscope (SEM VEGA3, Tescan, CZ) operated at 20 kV was used for high-resolution microstructural analysis on unetched samples. Elemental composition analysis was conducted using energy-dispersive spectroscopy (EDS, Oxford Instruments, UK) equipped on the SEM.

Electron backscattered diffraction (EBSD) was also performed. A semi-automatic grinder polisher (Abramin, Struers, DK) was used with SiC paper, starting from 220 down to 4000 progressively. Samples were then polished with MD-Chem/OP-S solution (260 ml OP-S: 40 ml H₂O₂: 1 ml HNO₃: 0.5 ml HF) from 50 N down to 12.5 N progressively. The samples underwent argon ion milling (IM4000II, Hitachi, Japan) to achieve a smoother surface, and then the grain structure was characterized using an EBSD camera (Velocity Super, EDAX, US) installed on an SEM (Apreo 2C, Thermo Fisher Scientific, US).

The sample phases were analyzed by an X-ray diffractometer (SmartLab 9kW, Rigaku, JP) with parallel beam focusing, CuK α radiation source ($\lambda = 1.54 \text{ \AA}$) and multidimensional detector. The radiation acceleration voltage and emission current were 45 kV and 200 mA, respectively. The scan was within the range of $2\theta = 10\text{--}110^\circ$. The dwell time was 5 s with an increment of 0.02° .

A nanoindentation system (TI900, Hysitron, US) was used to measure the reduced modulus and nano hardness of interested areas. The peak force was set to 1000 μN with a 3 x 3 matrix and minimum spacing of 10 μm .

3.3 Results & Discussion

3.3.1 Effect of feedstock powder on deposition

Particle size and morphology were decisive parameters for bonding dynamics and coating microstructure. Thus, the circle equivalent (CE) diameter and circularity of particles were measured by number distribution, as shown in **Table 3.1**. Most particles were spherical, with a diameter of $\sim 10\ \mu\text{m}$, as shown in **Fig. 3.3a**. Agglomeration and satellites of particles were observed, as shown in **Fig. 3.3(b and c)**, probably caused by contact of incompletely solidified particles during the cooling process in atomization [219]. It indicates that some of the interparticle bonding observed in the coating are metallurgical agglomeration instead of collision-induced bonding. However, oversized particles may act as a peening medium or enhance flowability with lower interparticle friction since these particles may not reach the critical velocity window [220-222]. Particle speed is the crucial parameter for the particle plastic deformation, consequently, casts the interparticle bond strength and nanocrystalline structure. The measured mean speed was 789 m/s, with a standard deviation of 530 m/s. It is considered the powder-gas jet being propelled normally to reach above Mach 1, which is within the critical velocity window.

Table 3.1. Morphologi 4 powder analysis on circle equivalent diameter and circularity.

Measurement	Min	Max	Mean	D [n, 0.1]	D [n, 0.5]	D [n, 0.9]	STDV	RSD (%)
CE Diameter (μm)	0.51	141.58	11.75	3.90	8.60	24.52	8.95	76.22
Circularity	0	1.0	0.968	0.915	0.991	0.996	0.087	8.95

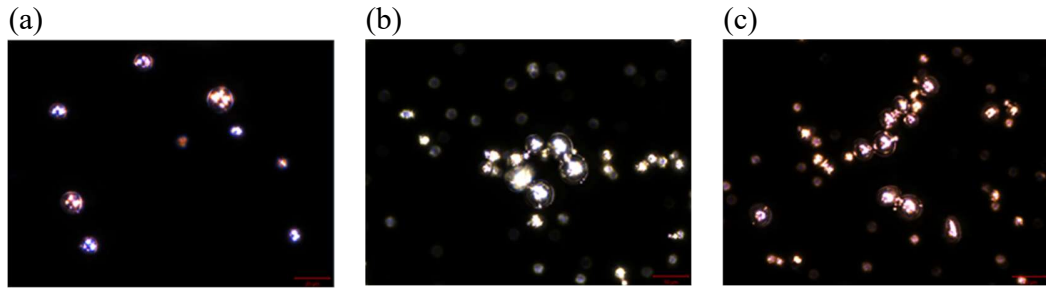


Fig. 3.3. Optical micrographs of Ti6Al4V particles with different morphologies and sizes. (a) Spherical particles were about 10 μm in diameter, captured at 50x magnification with a scale mark of 20 μm . (b) Agglomerated particles had a CE diameter of about 85.50 μm , captured at 20x magnification with a scale mark of 50 μm . (c) Agglomerated Ti6Al4V particles about 78.85 μm CE diameter at 20x magnification with a scale mark of 50 μm .

3.3.2 Effect of substrate surface preparation and heat treatments on microstructure and hydrogen damage

Optical micrographs were stitched into the cross-sectional profiles of coatings, as shown in **Fig. 3.4**. Vortex-like intermixing was not observed at the interface of all samples, indicating a lack of mechanical interlocking [60]. This observation aligned with **Figs. 2.12, 30, 33, 39, and 51** [27, 68, 180, 183, 197], where the interfacial bonding of cold-sprayed Ti alloys and metals were mostly contributed by the contact of fresh metal surfaces after breaking oxide films. Slight interface delamination and large pores were spotted on the right side of samples with laser-ablated substrate surface. These sites contained fragments along the coating-substrate boundaries, as shown in **Fig. 3.5(a)ii and b)ii**. Face-milled samples did not exhibit such a phenomenon, which had very intimate contact. A possible cause could be the hierarchical surface created by laser pulse [223], while face milling resulted in a smoother surface, allowing the particles of the first layer to be aligned more regularly and higher coating adhesion.

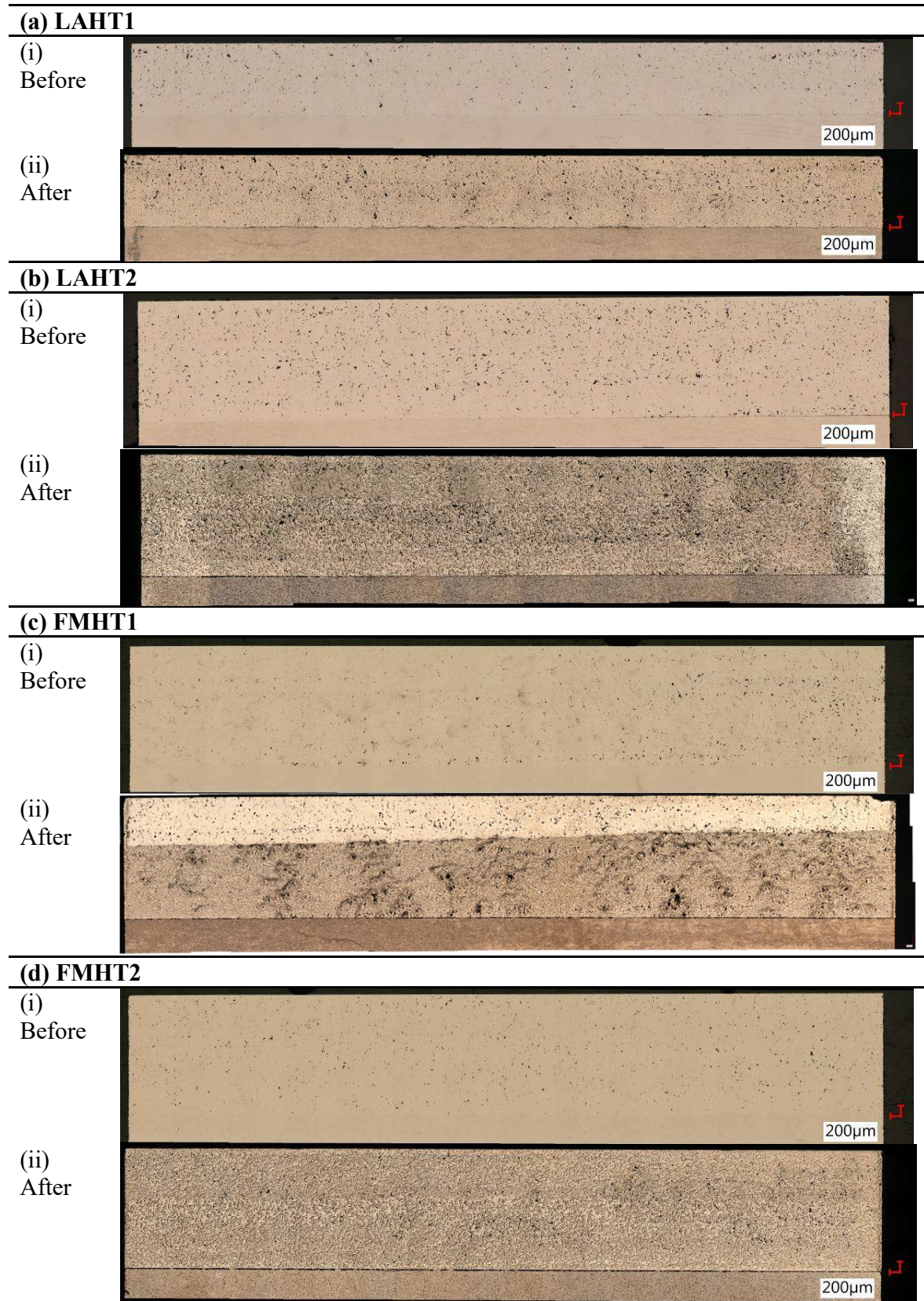


Fig. 3.4. Stitched optical micrographs (200x) showing the cross-sectional profile of coatings (a) LAHT1, (b) LAHT2, (c) FMHT1, and (d) FMHT2; (i) before and (ii) after cathodic charging. The coating thickness of samples LAHT1, LAHT2, FMHT1 and FMHT2 after top face-milling were measured to be about 1382, 2322, 2247, and 2274 μm , respectively.

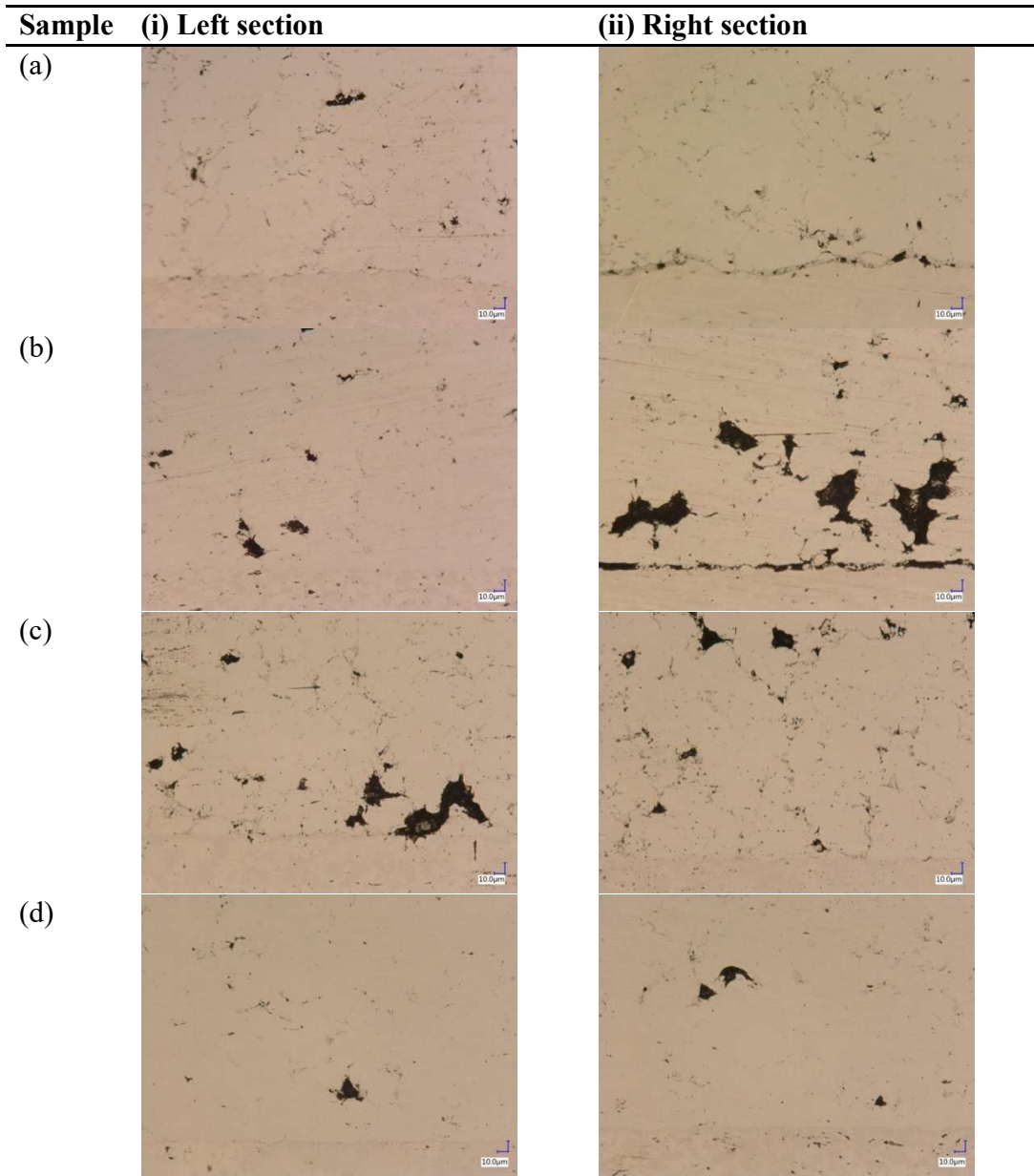


Fig. 3.5. Optical micrographs (1000x) showing microstructure at the coating/substrate interface on the left and right sections of samples (a) LAHT1, (b) LAHT2, (c) FMHT1, and (d) FMHT2.

The detailed particle deformation morphology and bonding after heat treatments were investigated by SEM. **Fig. 3.6** displays the splat morphologies in uncharged samples at different regions of coatings (top, middle, and coating-substrate interface). **Fig. 3.6(a and c) (i and ii)** show particles plastically deformed into hemispheres with about 1-2 μm thick jetting. A rebound region was observed at the south rim of the splat in **Fig. 3.6a_{ii}**, where a crystalline phase transition occurred at these sites due to dynamic recrystallization [224]. It is considered the particle velocity has reached near the optimal condition illustrated in **Fig. 2.5** [61]. However, tamped particles with detaching marks were observed in **Fig. 3.6(a and c) ii**, as some weakly bonded particles detached during grinding. This indicates that even the interparticle metallurgical bonding induced by impact at near optimal velocities, the coating would not be structural enough. This issue could not be solved by increasing the magnitude of particle deformation. Some splats underwent severe plastic deformation and were broken into small debris on the substrate ablated by laser pulse, as shown in **Fig. 3.6(a and b) iii**. This observation was similar to the overspeed particle shown in **Fig. 2.7c** [63], which became more brittle due to the accumulated peening effect along the buildup of layers and fractured eventually. It was also noted that the heat treatment at 750 °C for 2 hours failed to remove such defects related to extreme plasticity.

There were small grooves along the coating-substrate interface of face milled samples in **Fig. 3.6(c and d) iii**, where debris was not observed. The influence of heat treatments on uncharged samples was not significant, as indicated by the SEM micrographs. Despite Zhou et al. [70] suggesting the “bridging” effect being triggered at 750 °C heat treatment in nitrogen-sprayed Ti6Al4V coatings, the blurring of IPB was not observed at an unetched state. The influence of this nano-scale evolution became more observable in coming sections of cathodic charging, EBSD, and etching.

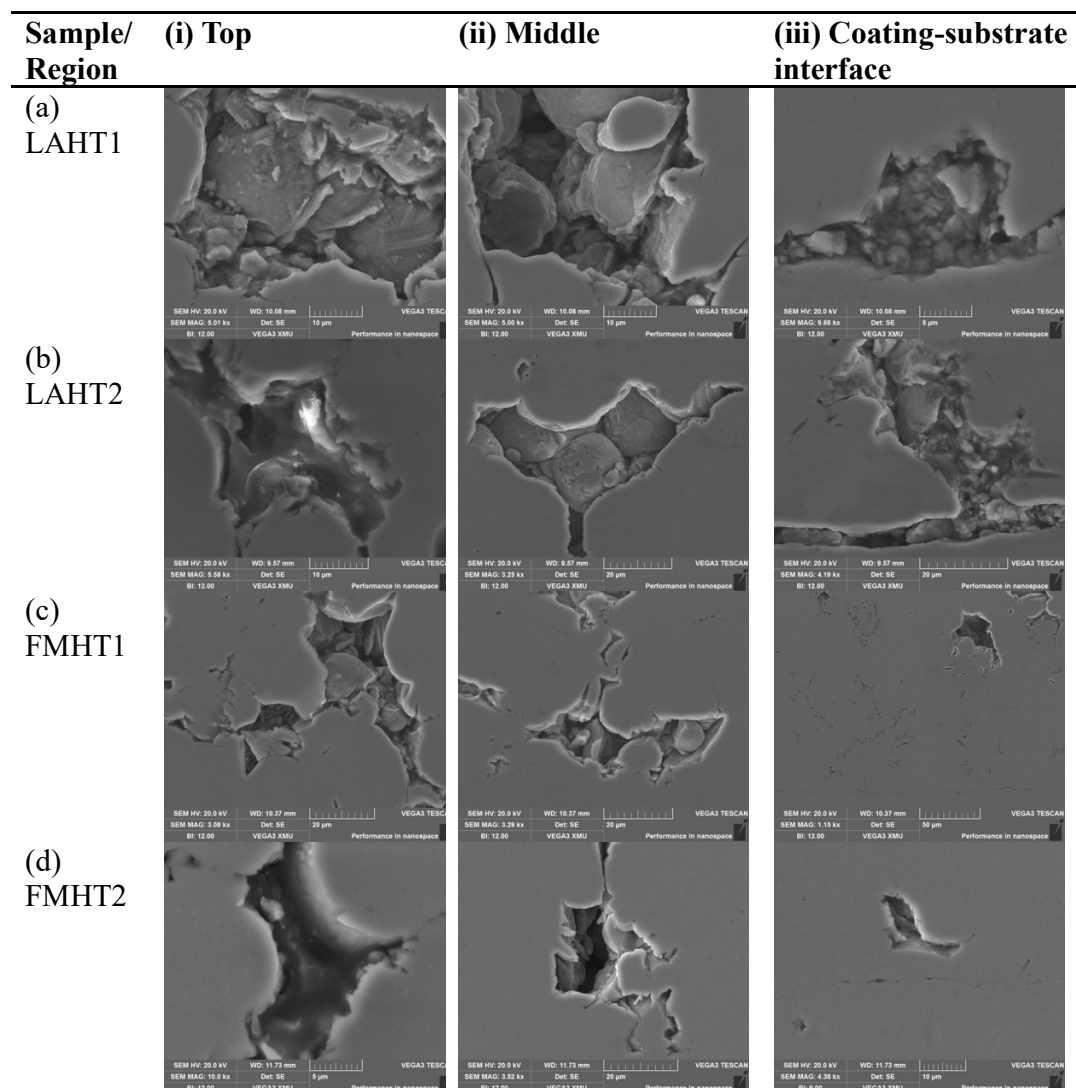


Fig. 3.6. SEM micrographs of internal microstructure of uncharged samples.

The forms of hydrogen damage or electrochemical corrosion were identified by microscopic examination. The optical micrographs after cathodic charging are shown in **Figs. 3.4ii** and **3.7**. Trenches were observed along the coating-substrate interface of all samples, where the damage marks were more likely to be located at CP-Ti substrates. In contrast, very narrow seams appeared along the coating-coating interface of samples heat-treated at 750 °C. This phenomenon is attributed to the diffusion bonding facilitated at some well-contacted locations across the

homogeneous Ti6Al4V layers. The “bridging” effect could not cover the entire interface due to inherent defects, but it still performed better than its counterparts.

Meanwhile, the coating-coating interface of sample FMHT1 (**Fig. 3.4cii**) was obviously recognized by the distinctive appearance of the as-sprayed layer and stress-relieved layer. Despite few small bubble nucleation marks being observed and severely deformed splat edges protruding on the as-sprayed layer, no apparent IPB was observed, as shown in **Fig. 3.7ci**. It implied that the as-sprayed Ti6Al4V coating was the most resistant to hydrogen damage. This could be attributed to the ultra-fine-grained structure or high dislocations density induced by supersonic impact [123, 163], which was analyzed with EBSD results in later sections.

Stress relieving led to pitting corrosion in the cold-sprayed Ti6Al4V coatings. IPB becomes observable on 540 °C stress relieved layers in **Figs. 3.7(a and c) (i and ii)**. Pits approximately 50 µm in diameter with splats debonding were also observed. **Figs. 3.4(a and c) ii** showed hydrogen pitting distributed in vertical tracks, which matched the bubble nucleation during cathodic charging. However, intergranular cracks had not yet been discovered. The coating treated at this temperature is at an intermediate point such that viscoplastic bonding is weakened while diffusion bonding has not been triggered yet. Since the grain structure of Ti6Al4V should not change at 540 °C, the reduced dislocations density is likely to be the reason for weakened hydrogen resistance along the interparticle boundaries.

The post-charged surface of the 750 °C heat-treated Ti6Al4V coatings exhibited a unique morphology with blisters, as shown in **Figs. 3.7(b and d)**. It was noted that there was severe pitting corrosion at the coating-substrate interface and the substrate side (**Figs. 3.7bii and dii**). The coating-coating interface did not exhibit pitting due to the enclosure by diffusion bonding (**Figs. 3.7bi and di**). The change in hydrogen damage mechanism is attributed to the recrystallized grains

settling in the range of grain size with higher hydrogen diffusion coefficient [163], while the bulk pores are shrunk after heat treatment and reduced the desorption paths for hydrogen. Hence, hydrogen ions recombine to gas molecules at subsurface of coating, then results in blistering when the gas pressure is accumulated to a certain level. The blisters on the heat-treated coatings did not burst or induce surface cracks as the pressure of hydrogen had not reached the level. Sub-surface cracks might occur [225], but further cross-sectional analysis of blisters was not conducted in this study. If future study aims to observe the evolution of burst blisters and surface cracks, it needs charging time longer than 4.5 hours or a higher current density. If the hydrogen remains deeper within the coating, the internal blisters and cracks connect with each other and further embrittle the coating. However, throughout blistering or total delamination of coating may take days. To avoid hydrogen damage without changing the main microstructure by heat treatment, appropriate surface roughening would enhance the hydrogen resistance [123].

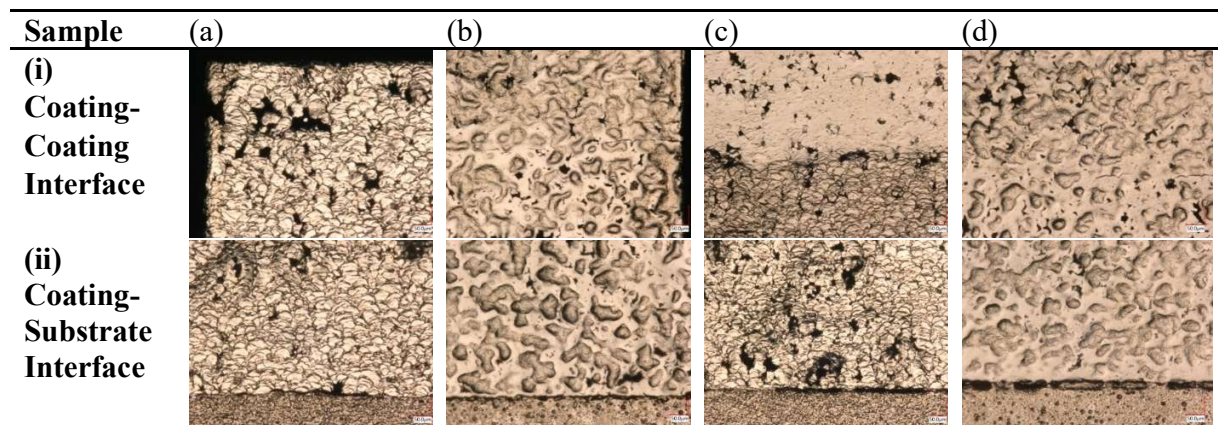


Fig. 3.7. Optical micrographs (500x, scale mark of 50 μm) showing microstructure after hydrogen charging at the interfaces between coating-coating and coating-substrate of samples (a) LAHT1 (top section instead of coating-coating interface), (b) LAHT2, (c) FMHT1, and (d) FMHT2.

3.3.3 Effect of hydrogen interactions on compositions, grain size and phases

The EDS analysis results are exhibited in **Table 3.2**. Before charging, the major elements (Ti, Al, V) and carbon contents were similar in all samples. Although feedstock powder should contain a thin outermost oxide film, no oxygen content was detected in the coatings before and after charging. There was ~2% carbon content in all Ti6Al4V coatings before hydrogen charging. The carbon weight percentage in the 750 °C heat-treated samples dropped to zero after hydrogen charging. This may indicate that carbon content reacts with some absorbed hydrogen atoms to form methane. The methane molecules are too large and cannot further diffuse into the coating. The formed methane and recombined hydrogen accumulate in the subsurface region, leading to blistering. However, the blisters are not easily observed as in optical micrographs possibly due to difficulty of focus in SEM. Decarburization was not observed in the as-sprayed and 540 °C stress relieved layers of LAHT1 and FMHT1. This reflects blistering by methane can be prevented if the cold-sprayed Ti6Al4V does not undergo heat treatment at recrystallization temperature, where the ultra-fine-grained microstructure and high dislocations density are necessary to be conserved.

Table 3.2. Elemental composition by weight percentage of coatings.

Sample	LAHT1		LAHT2		FMHT1			FMHT2	
Element	UC wt%	C wt% (SR)	UC wt%	C wt%	UC wt%	C wt% (AS)	C wt% (SR)	UC wt%	C wt%
C	1.98	3.12	2.04	-	2.24	3.04	4.41	2.31	-
Al	5.48	5.77	5.63	5.75	5.63	5.73	5.77	5.81	5.83
Ti	88.9	87.51	88.77	90.62	87.98	88.48	86.82	88.33	90.74
V	3.30	3.60	3.56	3.63	3.40	2.75	2.99	3.54	3.43
Si	0.28	-	-	-	0.45	-	-	-	-
Fe	-	-	-	-	0.30	-	-	-	-
Totals	100.00		100.00		100.00			100.00	

UC: uncharged; C: charged

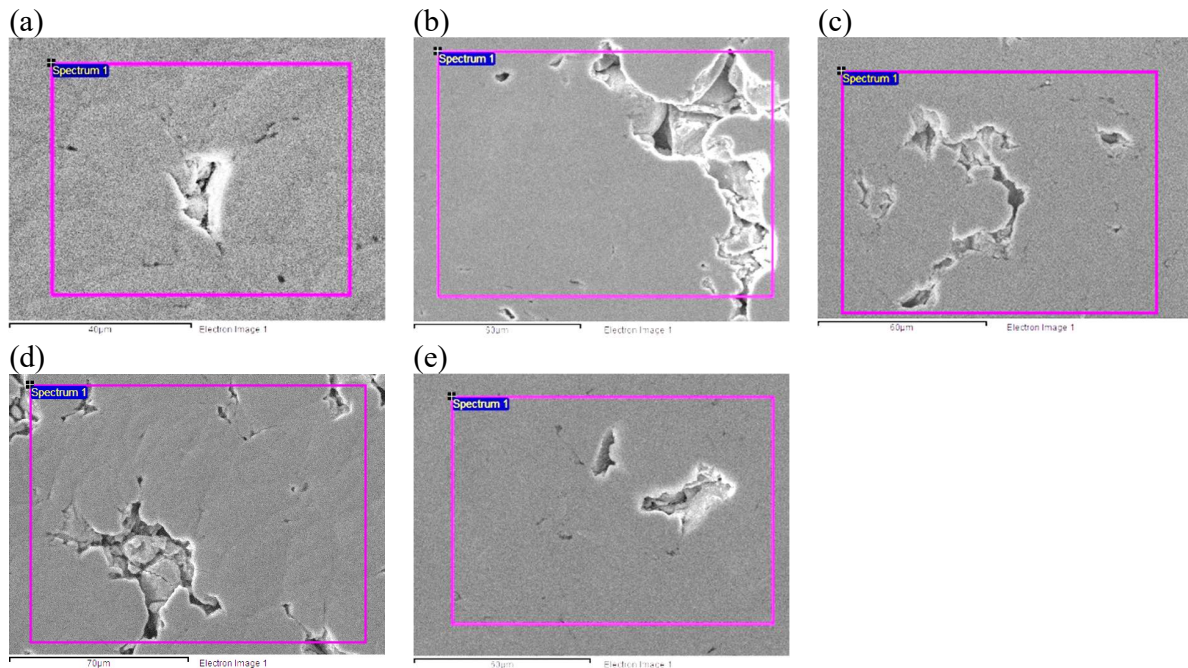


Fig. 3.8. SEM images of samples after charging (a) LAHT1, (b) LAHT2, (c) FMHT1_AS, (d) FMHT1_SR, and (e) FMHT2.

The nanocrystalline structure and internal porosity network in cold-sprayed coatings are the decisive factors for the hydrogen damage resistance. The as-sprayed layer (FMHT1_AS) failed to be indexed by EBSD (45%) even though the surface had been milled with argon ions (**Fig. 3.9a**). The non-indexed dark regions outlined the IPB where adiabatic shear initiated according to Goldbaum et al. [226]. The barely captured grains near the dark regions were in nanosized, where the largest grain found on the right was $\sim 1.5 \mu\text{m}$. The grain size of as-sprayed coating could be considered contributing to exceptionally low hydrogen diffusion coefficient [158, 227]. Exceptionally low diffusivity is attributed to near-zero misorientations according to Watanabe [168]. The near-zero misorientations in as-sprayed microstructure with refined grains may be the real contributor to both low diffusivity and low EBSD index rate. **Table 3.3** suggested the TiH formation was the least in the as-sprayed layer, but it was affected by the low index rate. HR-EBSD would be necessary to characterize the nanocrystalline and phase structure at IPB. The as-

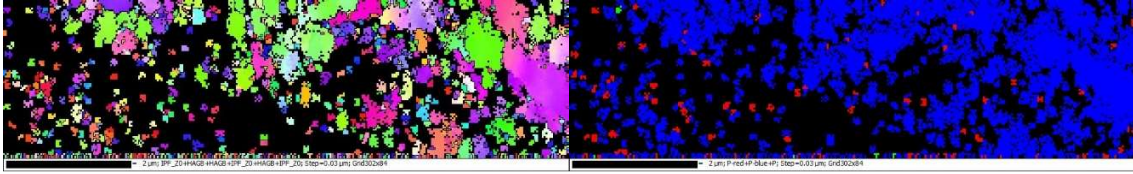
sprayed splats have high density of nanograins along IPB. The adsorbed hydrogen atoms would recombine into hydrogen molecules and escape into the environment. Most of the absorbed hydrogen atoms would be trapped in the surficial nanocrystalline layer induced by severe plastic deformation, then recombine and return to the environment. The hydrogen resistance may be further improved by addition of large peening particles to increase grain refinement at insufficiently deformed particles [228].

Nanograins in the stress relieved splats at 540 °C grew slightly where the dark non-indexed region in EBSD was reduced remarkably. It could be indexed (80.5%) when step size was 0.03 μm and scale mark of 5 μm . IPF of stress-relieved coating in **Fig. 3.9b** shows the bulk grain indicating the middle of jetting region, which was surrounded by fine nanograins in different orientations due to impact. Although the bulk grain was about 5 μm , most surrounding grains were still in nano-scaled with very low diffusion coefficient. According to the previous damage morphology, hydrogen attacked along the IPB of stress-relieved coating. This indicates that ultra-fine-grained microstructure alone is not capable of mitigating hydrogen attack. Aid from other factors such as dislocations density and residual stress may be necessary.

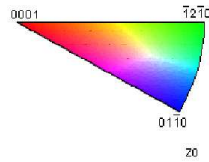
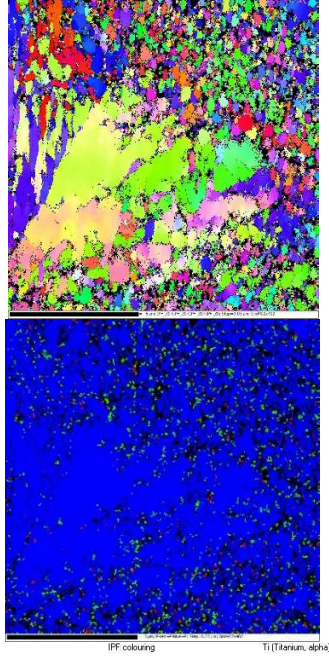
Both the top and bottom layer in the 750 °C heat-treated sample (FMHT2_T&B) were indexed with step size of 0.1 μm , scale mark of 10 μm , and index rate of 90.7%. Grains in FMHT2_T&B (**Fig. 3.9c** and **d**) had recrystallized with some grain growth into random orientations after heat treatment at 750 °C, where their interphase boundaries were intimate without apparent non-indexed area. Most grains had grown from nano-scaled to 1-5 μm at this stage, whereas the hydrogen diffusion coefficient should not rise significantly. In contrast, the optimum grain size with maximum hydrogen diffusion coefficient for X70 steel was about 46 μm [158]. In this case, the heat-treated microstructure fails to protect the coatings from blistering and formation of

hydrides. Heat treatment should enhance the mechanical strength and narrow the open paths for fluid. However, the enlargement of grains also leads to rise in hydrogen diffusion coefficient. Hydrogen recombination becomes more vigorous at subsurface, such that severe blisters are left on coating. On the other hand, the hydrides detected at the bottom of the heat-treated sample (**Fig. 3.9d**) were remarkably more than those at the top (**Fig. 3.9c**). It was alerted that hydrides were located near the non-indexed regions or distorted grains in IPF maps. The trustworthiness of detecting hydrides in cold-sprayed microstructure by EBSD needs to be investigated further.

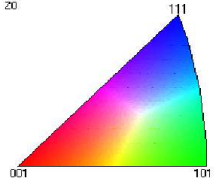
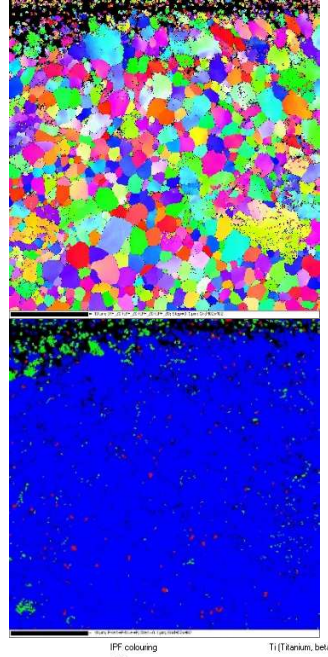
(a) FMHT1_AS (scale mark of 2 μm)



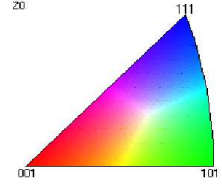
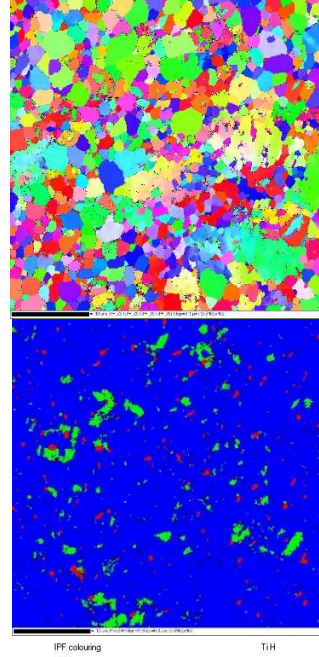
(b) FMHT1_SR
(scale mark of 5 μm)



(c) FMHT2_T
(scale mark of 10 μm)



(d) FMHT2_B
(scale mark of 10 μm)



■ α -Ti ■ β -Ti ■ δ -TiH

Fig. 3.9. EBSD phase maps of cold-sprayed Ti6Al4V coating layer (a) FMHT1_AS, (b)

FMHT1_SR, (c) FMHT2_T, (d) FMHT2_B, and their color keys.

Table 3.3. Phase compositions

Sample	α -Ti	β -Ti	δ -TiH
FMHT1_AS	43%	2.01%	0.0828%
FMHT1_SR	75.6%	0.881%	3.95%
FMHT2_T	87.8%	0.647%	2.27%
FMHT2_B	90.7%	1.9%	4.68%

The mappings of KAM of FMHT1_SR and FMHT2_B are generated from EBSD data and visualized in **Fig. 3.11a** and **b**. The area percentage of green regions with high GND density in FMHT1_SR was measured to be 37.8% according to the color extraction tool (TinEye, CA), much more than the 11.2% in FMHT2_B. The following equation is used to quantify the GND density ρ_{GND} [229, 230]:

$$\rho_{\text{GND}} = \frac{2\Delta\theta_i}{\mu b} \quad (3.1)$$

Where $\Delta\theta_i$ is the local misorientation angle acquired in KAM data, μ is the corresponding scanning step size known as unit length, and b is the magnitude of Burger's vector which is 0.3 nm for Ti6Al4V [231]. The normal distributions of GND density are plotted in **Fig. 3.11c**. The means of GND density in FMHT1_SR and FMHT2_B were $182.583\text{E}15/\text{m}^2$ and $34.939\text{E}15/\text{m}^2$, respectively. It could be considered that the 750 °C heat treatment reduced the GND density significantly and thus increased the hydrogen diffusivity according to Kim et al. [123]. The disparity in GND density somewhat explained the locally concentrated hydrogen damages on stress-relieved samples, while the damage marks on heat-treated samples were more evenly distributed. Nevertheless, the KAM data of as-sprayed coating could not be acquired to unravel the correlation between GND density and hydrogen damage comprehensively.

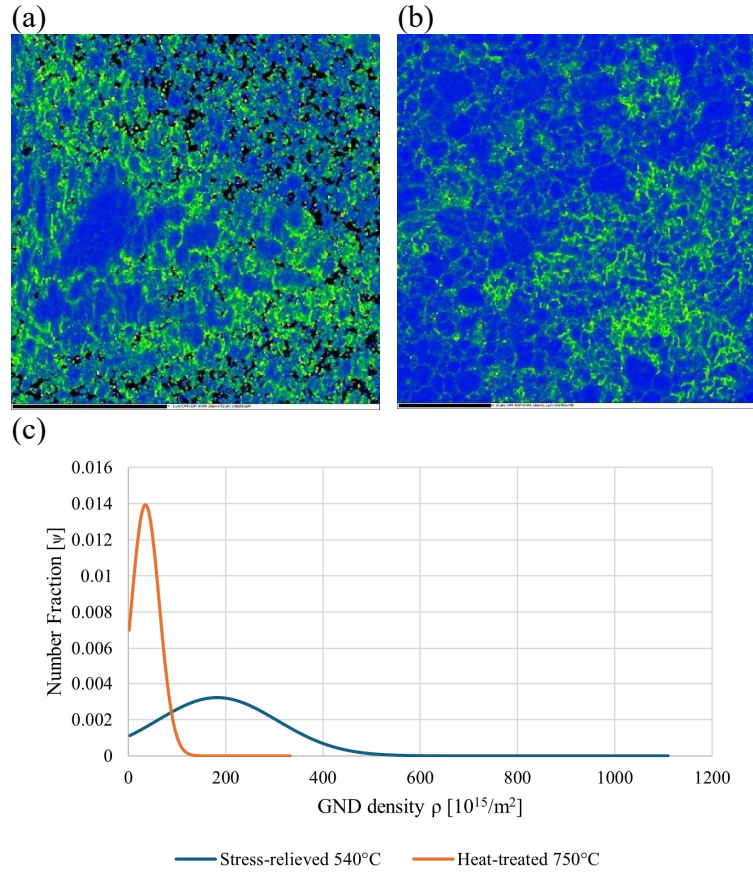


Fig. 3.10. KAM maps of (a) FMHT1_SR and (b) FMHT2_B, and their (c) normal distributions of GND density.

XRD results of all cold-sprayed Ti6Al4V coatings before and after hydrogen charging are shown in **Fig. 3.11**. Phases at notable peaks were recognized by comparing to the XRD results in other studies [29, 99, 232-234], then checked with Profex [235] and structure data of TiH₂ (tetragonal and cubic) from the Materials Project [236, 237]. According to the match results, it was noted that the peak intensity of $\alpha<002>$ in sample LAHT2 was exceptionally high, since the highest peak should be $\alpha<101>$ phase. Phases $\beta<110>$ and $\beta<200>$ should be detected at 39.5° and 57° if heat treatment induced recrystallization. However, the β phase signals were not detected on the 750 °C heat-treated samples, possibly due to a low phase transformation ratio. This indicated that heat

treatment at 750 °C was able to limit the formation of β grains and subsequent hydrides during cathodic charging.

After cathodic charging, new and weak peak signals were detected in all samples at approximately $2\theta = 36^\circ$, 37.5° , and 42° . According to Navi et al. [99], these peak intensities reflected the formation of δ hydride phases $\delta_a\langle 111 \rangle$, $\delta_b\langle 111 \rangle$, and $\delta_a\langle 200 \rangle$, respectively. On the other hand, the signal intensity of samples LAHT1 and FMHT1 decreased drastically after hydrogen charging, which may be attributed to the unique surface morphologies resulting from cathodic charging.

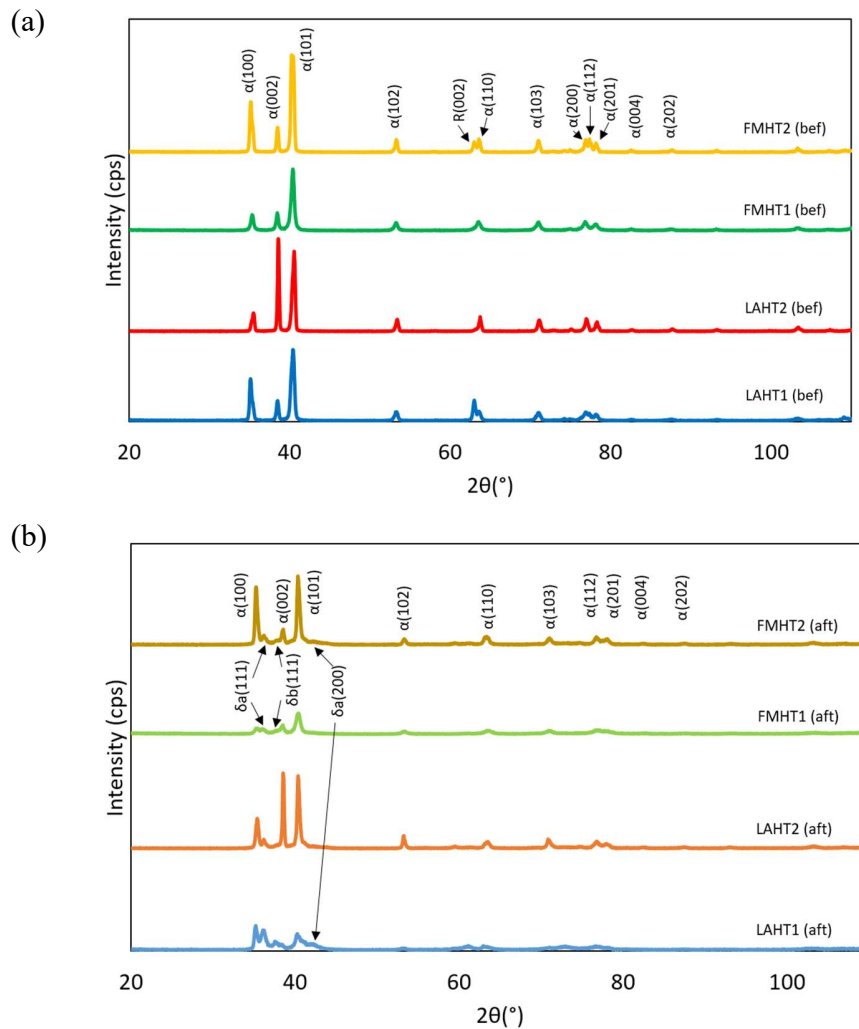


Fig. 3.11. XRD spectra of coating samples (a) before and (b) after cathodic charging.

3.3.4 Effect of hydrogen damage on nano-indentation properties

The effect of hydrogen damage on the mechanical properties of the coatings was investigated using nano-indentation, as shown in **Fig. 3.12**. Before hydrogen charging, the as-sprayed layer had a mean reduced modulus of 112.656 GPa (**Fig. 3.12a**) and the maximum nanohardness of 5.255 GPa (**Fig. 3.12b**). The nanohardness was within the range of Ti6Al4V coating sprayed with 73% He: 27% N₂ mixture (1.8 to 6.5 GPa) reported by Birt et al. [238]. The reduced modulus increased with the rise in heat treatment temperature; the mean reduced modulus of the heat-treated sample layers was approximately 140 GPa. This is sensible since heat treatment triggers diffusion bonding, which enhances the strength [14]. Meanwhile, the mean nanohardness remained approximately 5-6 GPa, but there were significant variations in the maximum and minimum values in some heat-treated samples. A possible explanation of this phenomenon would be local pore shrinkage and expansion due to heat treatment, resulting in variation of hardness at different locations [70]. Another potential reason might be the uneven tamping effect leading to a broad hardness range [239].

Cathodic charging resulted in degradation of the reduced moduli in all sample layers (**Fig. 3.12a**). Stress relieved layers dropped most significantly from about 130 GPa to 70 GPa. The reduced moduli of other samples dropped by about 20 GPa, including the as-sprayed layer where previous characterizations suggested it was the most hydrogen resistant. However, the nanohardness of the as-sprayed layer remained the same (**Fig. 3.12b**). Only the stress-relieved layers demonstrated an increase in hardness, possibly due to plasticity induced by hydrogen damage.

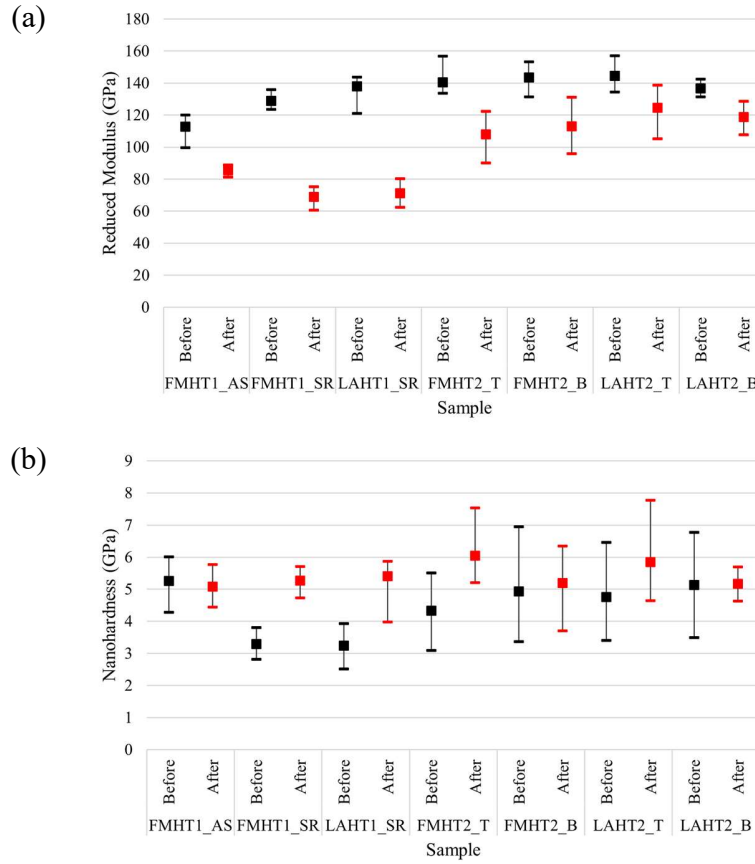


Fig. 3.12. Reduced modulus (a) and nanohardness (b) of samples before and after cathodic charging. AS: as-sprayed layer; SR: stress-relieved layer; T: top layer; B: bottom layer.

3.3.5 Challenges in SEM Analysis of etched CS Coatings

The samples were immersed in an etching bath of 0.5 M NaOH and 0.2 M H₂O₂ at 65 °C for 20 minutes to avoid the use of hazardous HF acid [240]. This SEM observation on etched samples had revealed the chemical attack behaviors by correlating the grain refinement and dislocation density. The as-sprayed layer mostly contained hexagonal Ti- α grains in **Fig. 3.13a**, where only two dots of Ti- β grains were found in the observed area, probably due to segregation of V to the edges of large laths [238]. The dominance of the martensite phase might be due to rapid solidification during atomization [65]. The lack of Ti- β phase and α - β interphase boundaries implies that the coating layer with lower hydrogen solubility and diffusivity would limit the

formation of hydrides [29]. The critical factor in recombining hydrogen atoms into molecules is the high dislocation density. The microstructural evolution of particles during impact resulted in predominantly smooth regions, which indicated a high dislocation density [238]. Despite SEM analysis on the etched as-sprayed layer, which could reveal the grain pattern that EBSD could not index, intersplat boundaries remained a challenging area to characterize. The hot, wet, alkaline peroxide etching method induced pitting holes along the intersplat boundaries, such that the dislocations within the area would be unable to be characterized. Conventional etching method with Kroll's reagent by immersion for about 10s would lead to protrusion of boundaries instead [65]. The suitable etching method would need to strike a balance between revealing microstructure and preserving intersplat boundaries. In addition, SEM with image processing could not achieve accurate dislocation density analysis, where SEM-ECCI coupled with appropriate contrast patterns and dislocation detection algorithms would be needed for further investigation [241, 242].

The etched appearance varied significantly depending on the different heat treatments. Stress-relieved layer in **Fig. 3.13b** exhibited predominantly texture regions with large martensitic laths, where needle-shaped Ti- β grains were not observed. This implies there is no sufficient phase change to increase the susceptibility of hydride formation. Even if hydrides form during hydrogen charging, they will react with alkaline peroxide to form water. In spite of the pitting holes along intersplat boundaries and at the interior of the splat, enlarged compared to the as-sprayed layer, they had not developed into microcracks. The dislocation density became more difficult to estimate due to the distortion of intersplat boundaries. The coarsening and damage by alkaline peroxide etching were more severe than those by electrochemical charging.

The etch resistance of the coatings weakened further as the heat treatment temperature rose. The 750 °C heat-treated layer (**Fig. 3.13c and d**) exhibited over-etching morphology with equiaxed

grains. The intact splats were difficult to recognize at this stage due to diffusion bonding between intersplat boundaries and necking of the boundary edges. The location of damages had shifted away from the intersplat boundaries to more refined sites. The etching artifacts were concentrated at the intersections of grains and the interior of bulk grains. However, the damage can be worsened if these pits accumulate or penetrate the coatings. A crack formed by the alignment of multiple pits along GB in **Fig. 3.13c**. Pitting was also observed on the equiaxed grains beneath the $5 \times 10 \mu\text{m}$ pore in **Fig. 3.13d**. A notable whole splat had dense and small pits on its textured region (north pole), while its smooth region (south pole) was less blemished with fine ($\sim 5 \mu\text{m}$) recrystallized and slightly grown grains. From the perspective of recrystallization kinetics, fine grains recrystallize faster than coarse grains due to higher stored energy and nucleation site density [243-245]. The grain refinement gradient across the splats is responsible for the gradient of recrystallization rate during heat treatment, as well as the corresponding hydrogen and etching resistance at different regions of splats. Shot-peening-assisted cold spraying has been considered a technique to improve coating density by tamping the north pole of splats [220, 221]. It might also contribute to an even recrystallization rate during heat treatment and homogeneous properties across the coating.

The etching of samples in this study had overridden the effect of electrochemical hydrogen charging. Notwithstanding, there are some takeaway points from scientific and practical perspectives. Firstly, the chemical attack location preference changes from intersplat boundaries to interphase boundaries along with the rise of heat treatment temperature, where the severity of damage also increases. The mechanism behind this is the stored energy of dislocations near splat boundaries being consumed for recrystallization and grain growth, thus losing the hydrogen or etching resistance. In real world engineering practice, the coatings should remain as-sprayed if the

primary function is hydrogen or chemical resistance. Moreover, heat treatment or alternative surface preparation methods like laser ablation would be needed if a well-etched surface is required, for example, components that need to be painted or coated with adhesive, and implants that need to form strong biomechanical bonding.

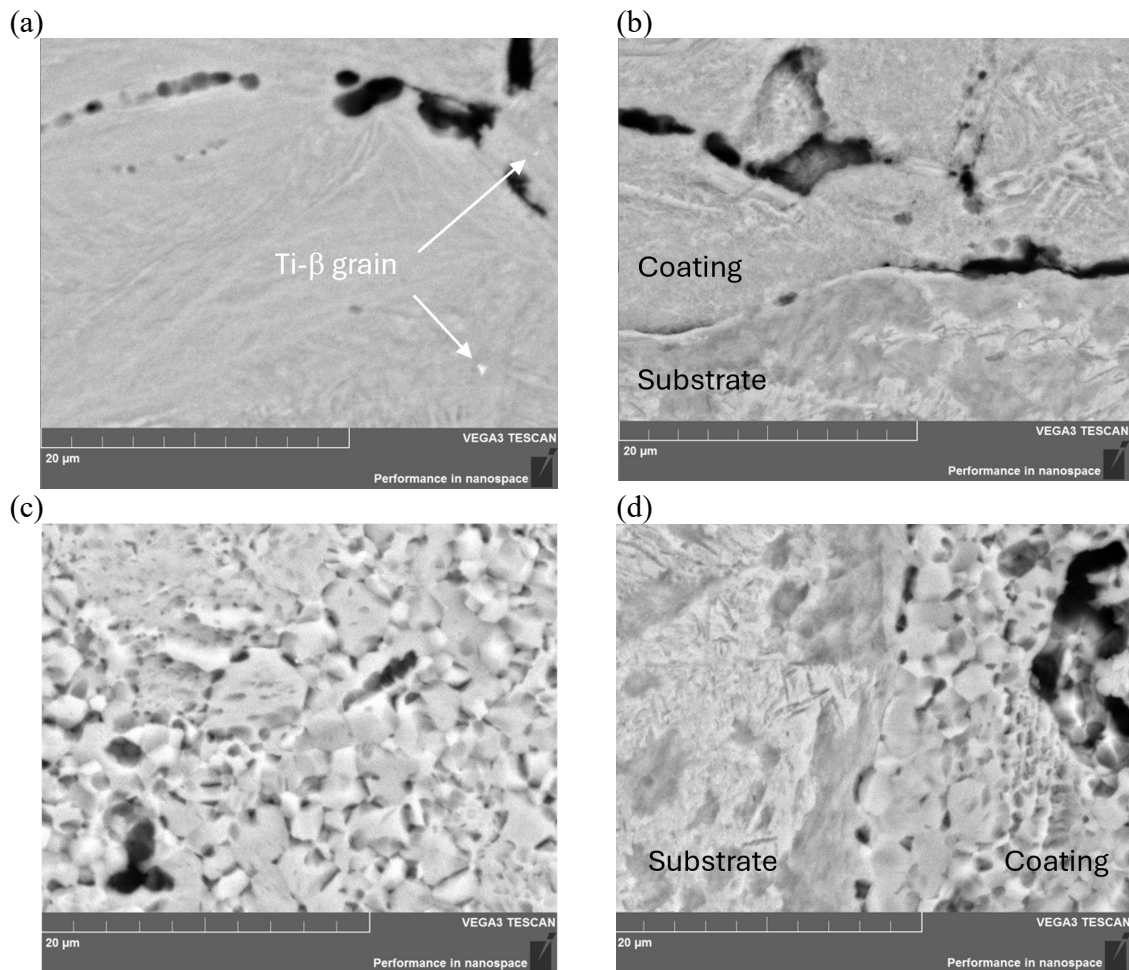


Fig. 3.13 SEM/BSE images of FMHT1 (a) as-sprayed layer and (b) stress relieved coating-substrate interface, and FMHT2 (c) coating and (d) coating-substrate interface after etching.

3.4 Summaries

This study used cathodic charging to investigate the hydrogen damage on cold-sprayed Ti6Al4V coating/CP-Ti substrate samples along with post-spray heat treatments. The post-treatment settings

included as-sprayed, stress-relieved at 540 °C, and heat-treated at 750 °C. Based on the experimental results, the main findings are as follows:

1. The refined nanocrystalline structure of super-plastic deformed particles in as-sprayed Ti6Al4V coatings exhibits excellent resistance to hydrogen damage.
2. Hydrogen damage on stress-relieved coating indicates ultra-fine grains with low diffusivity alone cannot facilitate hydrogen resistance, other criteria such as high dislocation density are also necessary.
3. Recrystallization heat treatment triggers the larger grains with higher hydrogen diffusivity and shrinkage of interparticle pores, which results in blistering on coatings.
4. The cold-sprayed Ti6Al4V coating should be maintained as-sprayed for the purpose of a hydrogen barrier. Heat treatment at 750 °C is recommended for moderate structural purposes, but not suitable for a hydrogen barrier, as it is susceptible to hydrogen damage. Stress relieving at 540 °C should be avoided, as the coating is susceptible to pitting and splat debonding due to its relatively low hydrogen resistance and interparticle bond strength.

Chapter 4: Macroscopic Simulation of Hydrogen Diffusion across the Grain-boundary Networks in Cold-sprayed Ti6Al4V

4.1. Introduction

As reviewed in **Section 2.4**, hydrogen diffusion across a metallic structure can be performed by the GB networks approach. However, the current virtual modeling methods cannot generate analogous cold-sprayed microstructures. Each method misses some crucial parameters that the other methods focus on, such as types of GB, grain morphology, and solubility. A general workflow is necessary to simulate a variety of cold-sprayed microstructures by different spraying parameters and post-spray treatments, which has not been well developed to date.

This study implemented the GB networks approach using realistic 2-D models to investigate hydrogen diffusion across cold-sprayed deposits at the stress-relieved phase and recrystallized phase after heat treatment. The GB network approach with image-based modelling simplifies the simulation of hydrogen diffusion across the irregular microstructure in cold-sprayed deposits. Firstly, the EBSD characterized GB maps were converted into realistic models, where the proportions of grains, random, and special boundaries were also quantified. Secondly, the diffusible hydrogen concentration maps revealed the hydrogen diffusion behavior in cold-sprayed deposits and the influence of varying the fraction of random and special boundaries. Thirdly, imaginary scenarios were compared with as-characterized GB networks and examined the mechanism to improve hydrogen resistance. Finally, the limitations in modelling, simulation and implementation in real-world engineering were also discussed. The simulation procedures and results in this work help create the synergy between hydrogen resistance and other properties of cold-sprayed deposits.

4.2. Methodology

4.2.1 Sample Preparation

Two realistic microstructural 2D models of cold-sprayed Ti6Al4V were constructed from two GB maps. The particle size of feedstock Ti6Al4V powder was about 45 μm (PG-AMP-1120, Plasma Giken, JP). The propellant gas was helium at 900 °C and 3 MPa. A glass-nozzle was used to prevent clogging and powder feeder instability. Stand-off distance was maintained at 25 mm from the CP-Ti substrates. The nozzle was traversing at a constant speed of 1 m/s. The toolpath was a snake scan pattern from top to bottom with a vertical step of 1 mm. The cold-sprayed Ti6Al4V coatings underwent 2 h of 540 °C post-spray stress relieving (SR-GB) and 2 h of 750°C post-spray heat treatment (HT-GB), respectively. As-sprayed deposits with helium carrier gas could not be indexed by EBSD due to the presence of ultra-fine grains [246], and thus omitted in this study.

4.2.2 Characterization

A semi-automatic grinder polisher (Abramin, Struers, DK) was used, with SiC paper progressively decreasing from 220 to 4000 grit. Samples were then polished with MD-Chem/OP-S solution (260 ml OP-S: 40 ml H₂O₂: 1 ml HNO₃: 0.5 ml HF) from 50 N down to 12.5 N progressively. The samples underwent argon ion milling (IM4000II, Hitachi, JP) for a smoother surface. Their GB maps were characterized by an EBSD camera (Velocity Super, EDAX, US) installed on SEM (Apreo 2C, Thermo Fisher Scientific, US). The scanning step sizes were 30 nm and 100 nm for SR-GB and HT-GB, respectively. The GB was categorized by defining LAGB as special boundaries if misorientation <15° and HAGB as random boundaries if misorientation >15°.

When the misorientation exceeds the threshold angle of 10-15°, the grain-boundary energy would become independent of misorientation due to tight dislocation spacing and overlapping of

dislocation cores [247]. Although the CSL index could be used to further distinguish between random and special HAGB [24], the $\Sigma 1$ LAGB would have a sufficiently high fraction to show the location of special boundaries. Furthermore, there would be more hydrogen properties of the GB with various CSL indices to be assigned without an experimental database. Thus, this simulation only categorized the GB into special LAGB and random HAGB for brevity.

4.2.3 Modelling

The meshing workflow is illustrated in **Fig. 4.1**. The resolution of GB maps is 1200 x 1200 pixels. The images were converted to B&W scale by the Windows Photo app and then stacked to RGB by ImageJ [248]. The pre-processed images were meshed into triangular elements by the MATLAB add-on im2mesh developed by Ma [249]. The im2mesh input parameters are listed in **Table 4.1**. The close-up of the mesh in the centre of **Fig. 4.1** shows the elements of random boundaries being assigned at the junctions rather than categorizing them as individual phases. The input scales refer to the ratio of the side length (μm) in the GB maps to the number of pixels in the corresponding images, where the output mesh parameters are summarized in **Table 4.2**. The quantity ratio of special to random boundaries in SR-GB and HT-GB samples is 1.92 and 2.63, respectively. This matches the trend of increased random boundaries and reduced special boundaries due to annealing recrystallization [24, 250]. The multi-section mesh files were then imported into ABAQUS for simulating transient hydrogen diffusion with the following constitutive equation [251-253]:

$$\mathbf{J} = -s\mathbf{D} \cdot \left[\frac{\partial \phi}{\partial x} + \kappa_s \frac{\partial}{\partial x} (\ln(\theta - \theta^z)) + \kappa_p \frac{\partial p}{\partial x} \right] \quad (4.1)$$

The normalized concentration ϕ is defined as [253]:

$$\phi \stackrel{\text{def}}{=} \frac{c}{s} \quad (4.2)$$

Since the simulation only considered concentration, the temperature and pressure variables are removed. Thus Eq. (4.1) is reduced to Fick's first law in its most common form:

$$J = -sD \cdot \left(\frac{\partial \phi}{\partial x} \right) = -D \cdot \frac{\partial c}{\partial x} \quad (4.3)$$

The continuity equation represents the change of hydrogen concentration in 2D with respect to diffusion time [254]:

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} \quad (4.4)$$

Substituting Eq. (4.3) into Eq. (4.4) obtains Fick's second law in 2D:

$$\frac{\partial c(x,y,t)}{\partial t} = D \cdot \left(\frac{\partial^2 c(x,y,t)}{\partial x^2} + \frac{\partial^2 c(x,y,t)}{\partial y^2} \right) \quad (4.5)$$

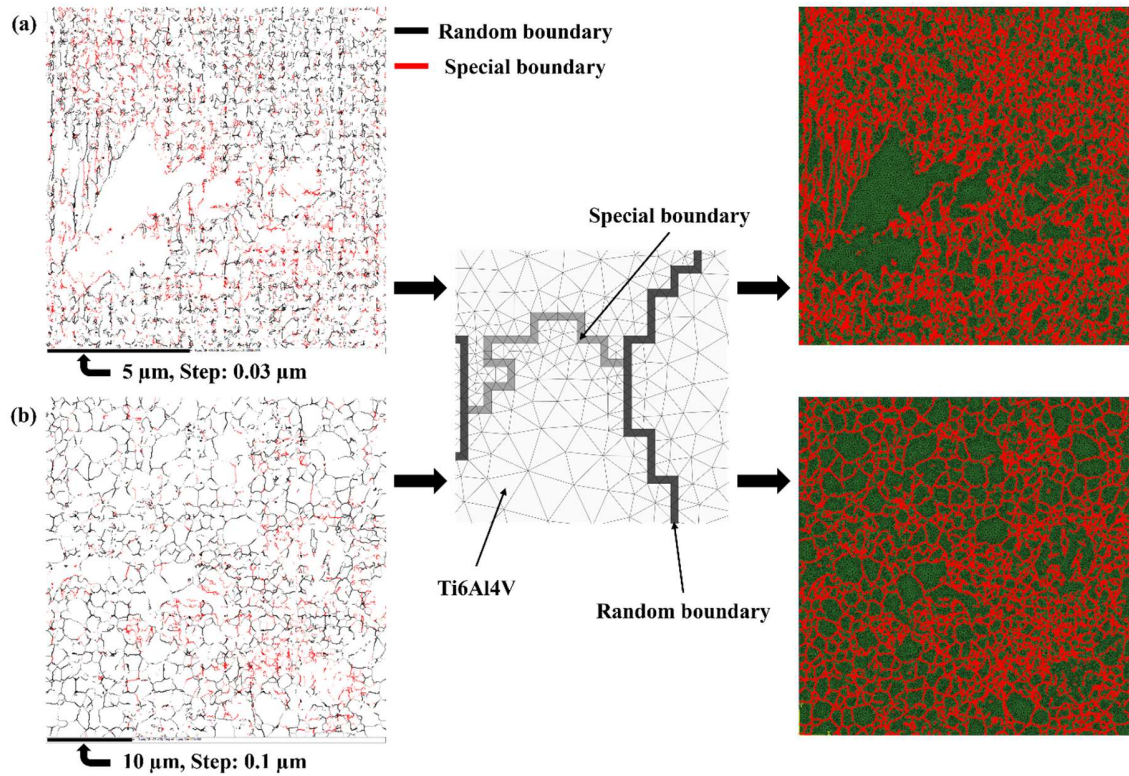


Fig. 4.1. Meshing from the GB maps of cold-sprayed Ti6Al4V deposits with (a) 540°C post-spray stress relieving and (b) 750°C post-spray heat treatment.

Table 4.1. Im2mesh input parameters.

Tolerance	Max mesh size $h_{\max}$	Mesh kind	Scalar gradient limit	Scale	Element order	Element type	Precision of node coordinates
Eps	10	Delaunay	+2	(a) 0.01 (b) 1/30	1	CPS3	8

Table 4.2. Output mesh parameters.

Output Mesh Parameters	(a) SR-GB	(b) HT-GB
Total number of nodes	360209	275614
Total number of elements	718368	549583
Number of random GB elements	123101 (17.1%)	101390 (18.4%)
Number of special GB elements	63644 (8.9%)	38566 (7.0%)
Number of Ti6Al4V-grain elements	531623 (74.0%)	409627 (74.5%)

The quantitative analysis of grain size was performed with MATLAB Manual Grain Size Measurement Tool developed by Buchely [255] to overcome the difficulties of grains recognition with automatic programs, as presented in **Table 4.3** and **Fig. S4.1**. Oudriss et al. [165] showed the diffusivities of grains in 0.05-5 μm would be in the same order of magnitude, where Li et al. [24] stated that the grain size effect on corrosion resistance would be negligible if there were not many nanograins. Thus, the hydrogen properties of grains in all sizes are assumed to be identical for brevity. Since there is a lack of reference about the hydrogen properties of cold-sprayed Ti6Al4V and its GB at various temperatures, the analogous material parameters are retrieved from the relevant studies of Ti6Al4V and GB network measured by the electrochemical method at room temperature [33, 100, 256], as listed in **Table 4.4**. Fick's law is selected when the diffusion properties of materials are defined. The units are converted to the μm scale. The influence of the β phase is neglected since the processes of cold-spraying and heat treatment are below the phase change temperature of Ti6Al4V [257]. The solubility of GB is assumed to be 10% of that of the bulk [258]. Since the hydrogen solubilities are defined manually, Sievert's law is not applicable to

the relationship between concentration and partial pressure of hydrogen in this case. The element type is standard linear heat transfer triangle DC2D3. The absolute zero temperature is set as 0. The time increments are 0.01, 0.1, and 1 h depending on the duration of diffusion time. The boundary condition assigns a normalized mass concentration of 500 ppm along the left edge of the model. No boundary condition is defined on the right edge of the model since the boundary with zero concentration should be infinitely far.

Table 4.3. Grain Size Measurement.

Statistics	SR-GB	HT-GB
Number of grains measured	406	400
Max d_{CE} (μm)	5.5346	7.3410
Min d_{CE} (μm)	0.0391	0.4442
Mean d_{CE} (μm)	0.4236	1.7424
STD d_{CE} (μm)	0.3880	0.8933

Table 4.4. Material parameters in ABAQUS.

Materials	Diffusivity ($\mu\text{m}^2/\text{h}$)	Concentration (ppm)	Solubility (ppm*μm*$\text{N}^{-1/2}$)	References
Ti6Al4V	12.6	0	2.1	[100, 256]
Special GB	0.36	0	0.21	[33, 258]
Random GB	360,000	0	0.21	[33, 258]

The simulation is verified by comparing the numerical results of the monocrystal scenario (time increment of 0.1 h) with the 1D analytical results of Fick's second law [37]:

$$\frac{\partial c(x,t)}{\partial t} = D_g \frac{\partial^2 c(x,t)}{\partial x^2} \quad (4.6)$$

The model is considered a semi-infinite object with a constant concentration of hydrogen diffusion from one side to the other. The initial and boundary conditions are set as [259]:

$$\text{I.C.: At } t = 0, c = 0 \quad (4.7)$$

$$\text{B.C. 1: At } x = 0, c = c_0 \quad (4.8)$$

$$\text{B.C. 2: At } x = \infty, c = c_s = 0 \quad (4.9)$$

Where c_0 is defined as 1050 ppm in analytical calculation, which is equal to the solution of Eq. (4.2) by substituting $\phi = 500$ ppm and $s = 2.1$. The solution of Eq. (4.6) becomes [259]:

$$c(x, t) = c_0 \operatorname{erfc}\left(\frac{x}{2\sqrt{D_g t}}\right) \quad (4.10)$$

Where the complementary error function is:

$$\operatorname{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \quad (4.11)$$

It is noted that the real hydrogen diffusivity of a single Ti6Al4V crystal should be higher due to the absence of micro-defects as hydrogen trapping sites, according to the GB cross-effect [163], which would drastically reduce the actual saturation time. Therefore, the monocrystal scenario is used only as a reference to verify the confidence in model implementation and examine the effect of the GB network on diffusion.

There are 1000 evenly spaced points along the true distance of SR-GB (12 μm) and HT-GB (40 μm) models in the analytical solution. **Fig. 4.2a** and **b** show the concentration maps of the monocrystal scenario in SR-GB and HT-GB, respectively, by assigning grain properties to the GB elements. The simulation step time is 50 h with an increment of 0.1 h. Their analytical and numerical diffusion profiles are presented in **Fig. 4.2c** and **d**. The settings of a linearly spaced vector do not alter the analytical values. Both solution results had good curve fitting for time instances of 0.1 h, 0.5 h and 1 h. However, the numerical result concentrations at the end of model SR-GB (**Fig. 4.2c**) were approximately 300 ppm higher than those of the analytical results, starting from $t = 5$ h to 50 h. On the other hand, the analytical and numerical results in the model HT-GB

(**Fig. 4.2d**) still align with each other for $t = 5$ and 10 h, although a disparity of approximately 300 ppm appears for $t = 50$ h. It is not surprising that the analytical and numerical results differ for extensive step time with cumulative disparity [260]. However, the time instances of disagreement depends on the true distance scales as the element sizes of models [261]. An image of a German flag with dimensions of 1600×959 pixel was converted into $12 \mu\text{m}$ and $40 \mu\text{m}$ wide models with scales of $3/400$ and $1/40$, respectively. The number of elements in both models is 73335. The same diffusion simulation of the monocrystal scenario was performed using the two German flag models (**Fig. S4.2**), yielding the same diffusion profiles as those in **Fig. 4.2c** and **d**. These results have proved that the model with a longer true distance provides higher confidence in model implementation, where the morphology of the mesh structure did not significantly affect.

This is because of the effect of finite domain boundaries in ABAQUS becoming significant over a prolonged period and deviating from the idealized semi-infinite domain solution. Increasing the size of the finite domain in ABAQUS could better match the semi-infinite domain, which explains the finite model with a longer true distance, delaying the time of deviation from the semi-infinite one. However, the size of the finite domain could not be changed as it depended on the true distance in the SEM/EBSD image. Introducing infinite elements in ABAQUS may better align with the analytical semi-infinite solution, which would need further study to debug the errors and ensure the validity of boundary condition settings. Moreover, verifying with other numerical solvers may also help check whether the deviation issue is specific to ABAQUS or consistent across numerical solvers. It is noted that importing the im2mesh output INP files into other FEM software like ANSYS might result in wrong scales, which would need extra calibration.

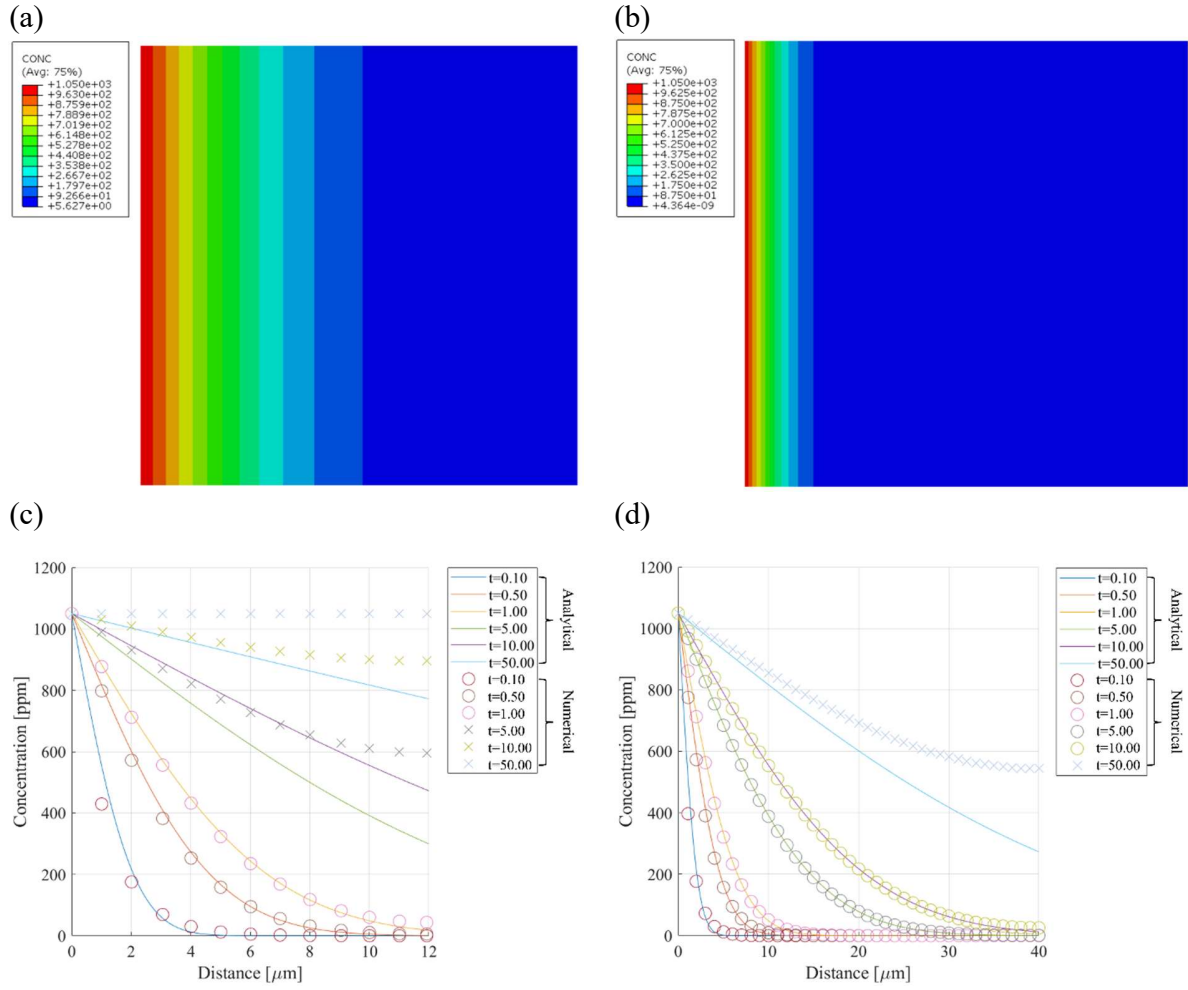


Fig. 4.2. Hydrogen concentration maps in numerical simulations of (a) SR-GB and (b) HT-GB monocrystal at $t = 0.5$ h. Comparison of analytical and numerical hydrogen diffusion profiles in the monocrystal scenario of (c) SR-GB and (d) HT-GB.

4.3 Results & Discussion

4.3.1 Diffusion across GB Networks after Heat Treatments

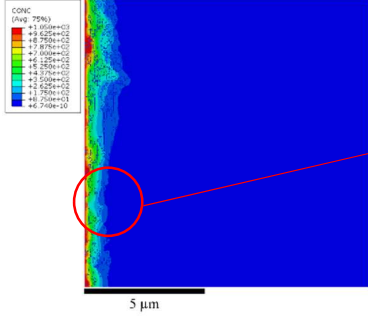
The simulation results with a time increment of 0.01 h are shown in **Fig. 4.3**. The hydrogen flux in both samples had already displaced 3-5 μm from the high concentration surface after 0.1 h of diffusion. The diffusion periods required to achieve a near-saturation state were approximately 7.72 h and 25.01 h for SR-GB and HT-GB, respectively. The videos of evolving concentration

maps are included in the supplementary files **Vids. S4.1** and **4.2**. Bulk (lattice) diffusion was dominant in both samples, which was reasonable since the grain elements accounted for about 74% of the total number of elements. A more tortuous diffusion was observed in HT-GB. Its range of grain size mainly was 1-5 μm , where the true overall width of the micrograph was 40 μm . In contrast, the SR-GB contained mostly 0.1 μm grains and a 6 μm bulk grain across the true overall width of 12 μm , where the evolution of the diffusion contour was relatively parallel. In other words, there is an optimum ratio of grain size to micrograph width (1:40 to 1:8 in this study) to observe a tortuous diffusion. However, the tortuosity of the GB network did not show notable differences in terms of diffusion speed in macroscopic observations. The hydrogen diffusion was slower in the monocrystal Ti6Al4V than in both as-characterized GB networks when the same value of hydrogen diffusivity was assigned. The GB network with the majority of random GBs provides straight pathways for hydrogen diffusion [262]. The straight pathways are removed in the monocrystals, so, of course, the diffusion is mitigated.

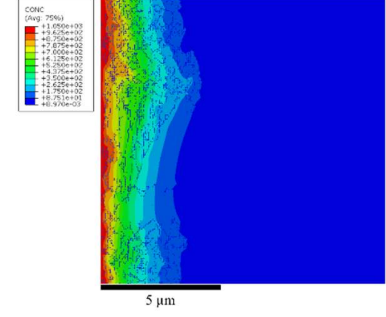
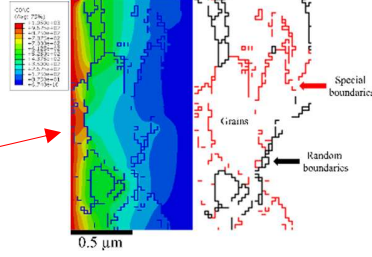
The close-up in **Fig. 4.3a** and **f** also shows the random boundaries breaking through the clusters of special boundaries and thus weakened its blockage effect [33]. The hydrogen diffusion was only blocked at a few locations, and then the special boundaries were soon circumvented by hydrogen that diffused through the grains and random boundaries. The details of diffusion between grain, random, and special boundaries are further illustrated with the German flag models in **Figs. 4.3** and **4.4**. The small proportion and discontinuity of special boundaries are the main reasons the GB network model in both samples fail to mitigate hydrogen diffusion, which agree with the observation by Adair and Johnson [170].

SR-GB

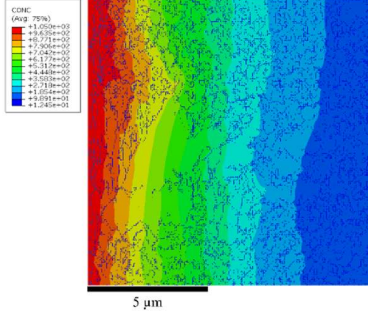
(a) 0.01 h



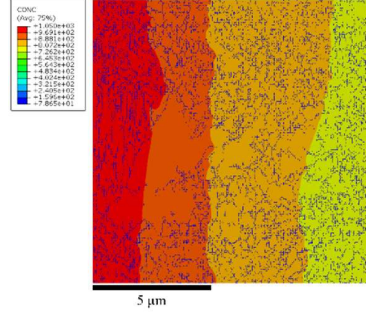
(b) 0.1 h



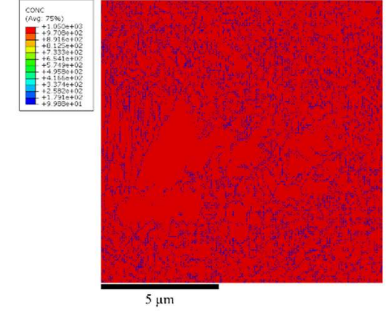
(c) 1 h



(d) 5 h

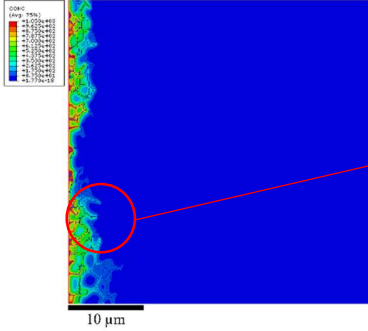


(e) 7.72 h

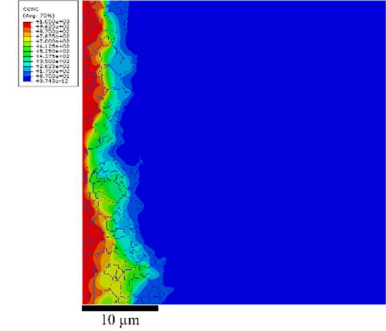
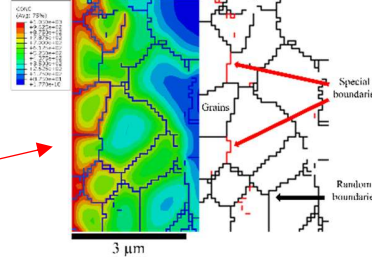


HT-GB

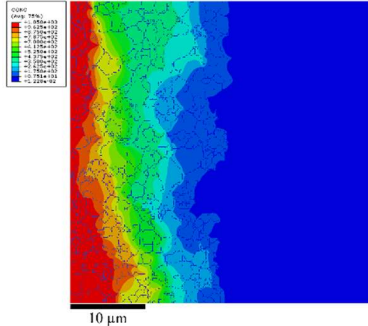
(f) 0.01 h



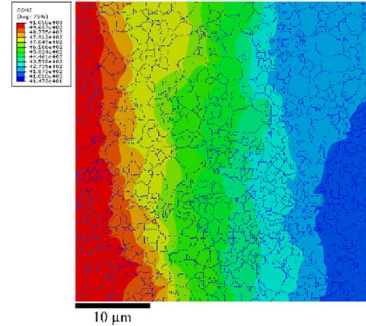
(g) 0.1 h



(h) 1 h



(i) 5 h



(j) 30 h

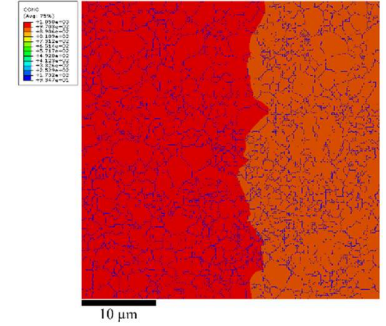
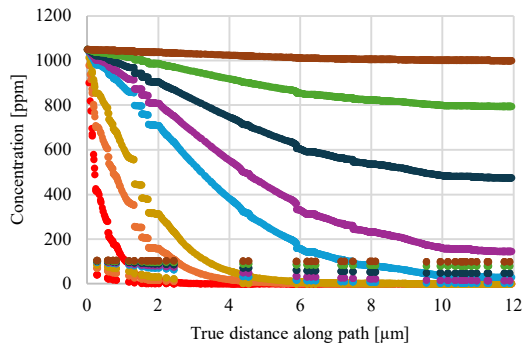


Fig. 4.3. Simulated hydrogen concentration maps across the as-characterized GB networks of cold-sprayed Ti6Al4V deposits with (a-e) 540°C stress relieving and (f-j) 750°C heat treatment

at the marked time instances. Close-ups of ROIs in (a and f) were matched with their corresponding GB maps.

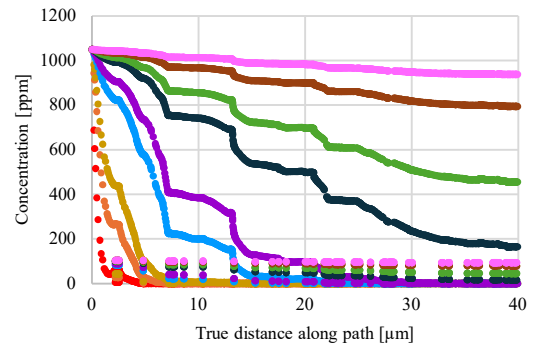
To further examine the impact of the GB network on the hydrogen diffusion, the hydrogen diffusion profiles along the displacement of the horizontal centerline in the models are plotted in **Fig. 4.4**. In general, the diffusion in SR-GB was smoother than that in HT-GB throughout different time periods. The GB contributed to an instantaneous low hydrogen concentration in a discrete pattern, but the hydrogen concentration rebounded to its previous level once the GB was circumvented. The sharp concentration drops in SR-GB (at 1.6-1.8 μm) and throughout HT-GB were due to hydrogen dissolving in bulk grains. In contrast, the hydrogen concentration descended steadily across the submicron grains. This is aligned with the aforementioned relationship between tortuous diffusion patterns and the ratio of grain size to micrograph width. However, the relationship between the tortuosity of the diffusion pathway and diffusion speed could not be compared fairly, as the models were meshed from source images with the same number of pixels but different true dimensions. Hence, the following section compares the diffusion of the same models with different ratios of grains to random and special boundaries.

(a) SR-GB



● 0.01 h ● 0.05 h ● 0.1 h ● 0.5 h ● 1 h ● 2.5 h ● 5 h ● 10 h

(b) HT-GB



● 0.01 h ● 0.05 h ● 0.1 h ● 0.5 h ● 1 h ● 5 h ● 10 h ● 20.15 h ● 30 h

Fig. 4.4. Simulated hydrogen diffusion profiles along the horizontal centerline in the models of cold-sprayed Ti6Al4V deposits with (a) 540°C stress relieving and (b) 750°C heat treatment at various time instances.

The previous simulation with analogous parameters yielded only bulk-dominant diffusion. Imaginary ratios of grains to random and special boundaries were set to estimate the conditions of other diffusion modes [158]. Properties of both special and random boundaries remained the same in the first two scenarios. The diffusivity and solubility of the Ti6Al4V grain were only changed in the last GB diffusion scenario.

4.3.2 Comparison with Diffusion in Whole-Random Boundaries

The first scenario involved replacing the special boundaries with random boundaries, as shown in **Figs. 4.5a** and **c**. The quantity ratio of random boundaries to grains in SR-GB changed from 8.31 to 2.85, and that in HT-GB changed from 10.57 to 2.9. HT-GB exhibited similar trends to its original counterpart. There were dense special boundaries at the lower half of HT-GB originally in **Fig. 4.1b**, blocking partial hydrogen diffusion through the region. The original high-concentration locations in the upper half were redirected to the lower half when the special boundaries became random boundaries, resulting in a diffusion displacement of 2-4 μm ahead at t

= 1 h. On the other hand, the previously discrete pattern in SR-GB (**Fig. 4.4a**) became continuous with about 200 ppm higher concentration (**Fig. 4.5a**), which was due to the increased connectivity of GB. Furthermore, this also reflects that the special boundaries had an extremely limited effect of mitigating the diffusion in the original scenario. In other words, the hydrogen traps are too few to overcome the short-circuit diffusion as the fraction of special boundaries is half of the random boundaries, which almost equals the short-circuit diffusion with random boundaries only.

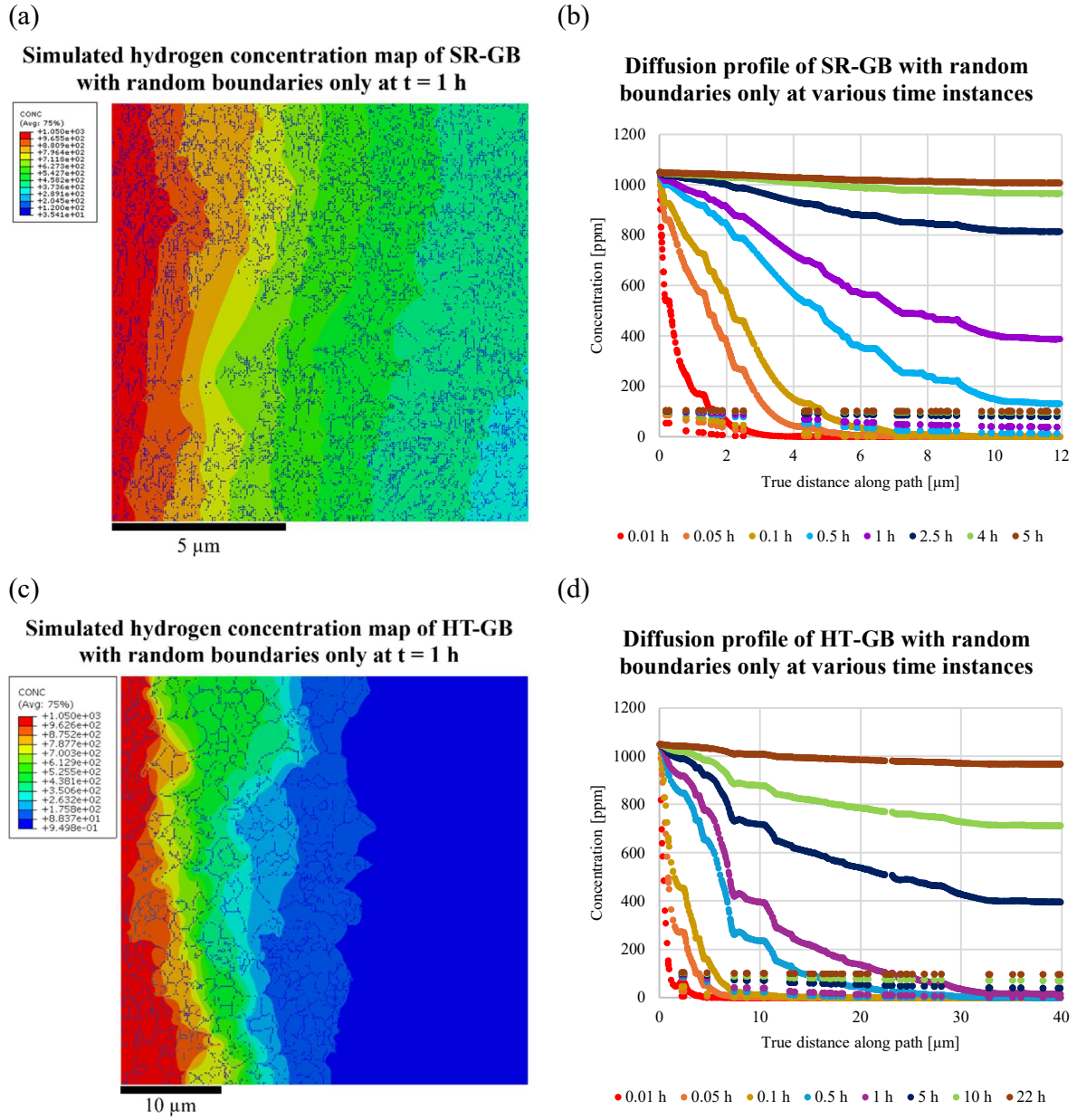


Fig. 4.5. Simulated hydrogen concentration maps and diffusion profiles of cold-sprayed Ti6Al4V deposits with (a and b) 540°C stress relieving and (c and d) 750°C heat treatment in imaginary conditions containing random boundaries only.

4.3.3 Comparison with Diffusion in Whole-Special Boundaries

The second scenario defines all GB as special boundaries, as shown in **Figs. 4.6a** and **c**. This remarkably increased the connectivity and blockage effect of special boundaries. The as-characterized SR-GB took 10 h to reach a saturation state (**Fig. 4.4a**), but it extended to 35 h with a complete special boundary network (**Fig. 4.6b**). The mitigation of hydrogen diffusion was more significant in HT-GB where the concentration at the right boundary reached only 320 ppm after 100 h (**Fig. 4.6d**). However, the diffusion scenarios are similar to surface diffusion, as illustrated by Yazdipour et al. [158], they are actually bulk diffusion. The low-diffusivity special boundaries segregate neighboring grains, and thus, hydrogen atoms need to circumvent longer distances. The diffusion tends to proceed to the next grain after a high concentration is reached across the previous grain. The original scenarios involve bulk diffusion across the “floodplain,” where the enhanced special boundaries network transforms the microstructure into “detention basins” to mitigate bulk diffusion. If the hydrogen diffusivity and solubility are substituted with those of the corrosive media in other metals, it may explain the localized corrosion resistance in cold-sprayed metals [24]. The two types of GB should form a connected network in the real world, but the GB clusters are discontinued in the GB maps due to the nature of cold-sprayed hard metal deposits with helium gas [246]. The as-sprayed Ti6Al4V microstructure should have excess special boundaries and achieve hydrogen mitigation without the influence of heat treatment. Hence, the hydrogen trapping behaviours of special boundaries need further study with improved EBSD characterization or processing on the GB maps.

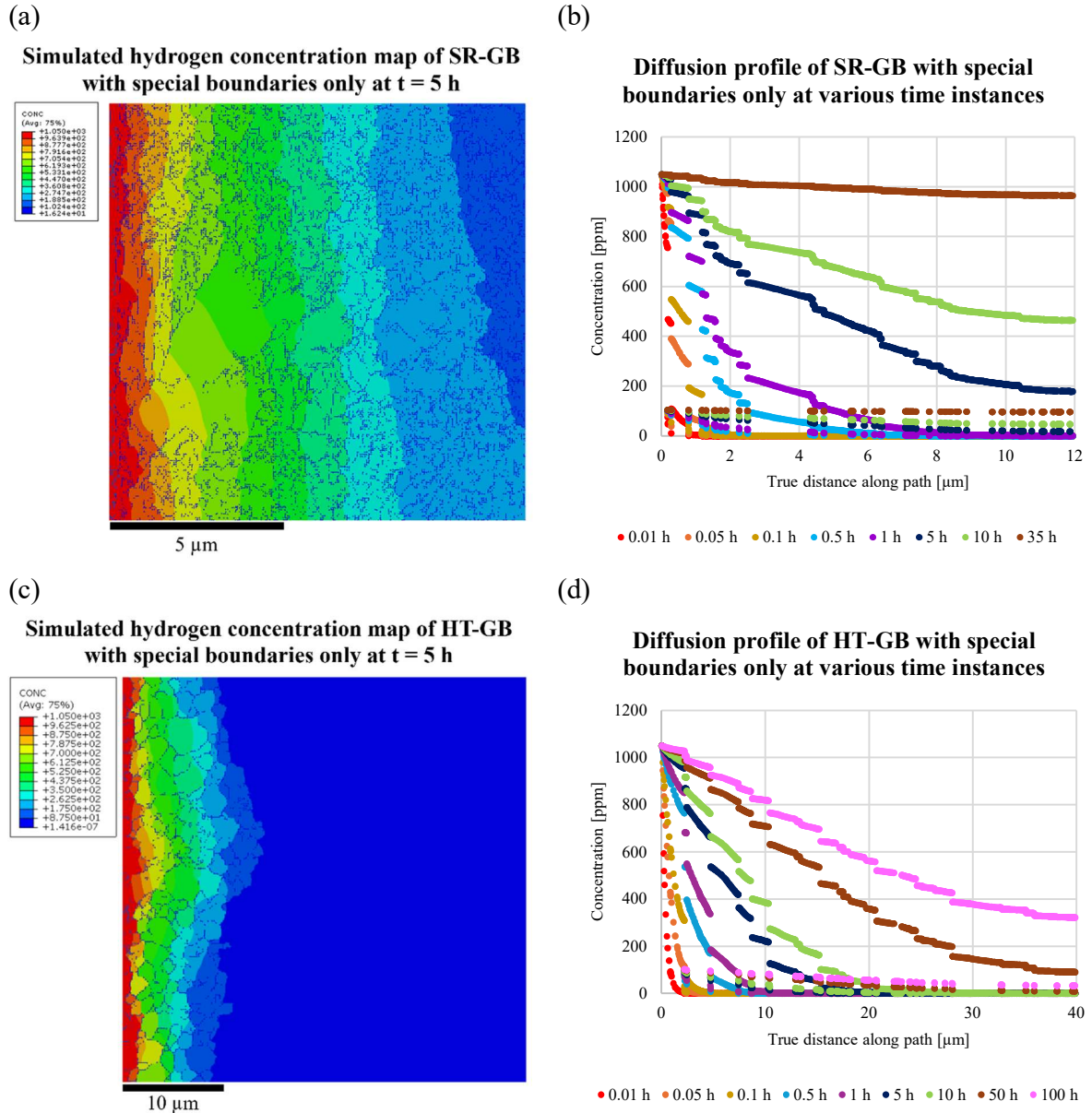


Fig. 4.6. Simulated hydrogen concentration maps and diffusion profiles of cold-sprayed Ti6Al4V deposits with (a and b) 540°C stress relieving and (c and d) 750°C heat treatment in imaginary conditions containing special boundaries only.

4.3.4 Effect of Hydrogen Properties of β Grains

The last scenario in **Fig. 4.7a** and **c** changes the diffusivity and solubility of Ti6Al4V grains to $1260 \mu\text{m}^2/\text{h}$ and $0.021 \text{ ppm} \cdot \mu\text{m} \cdot \text{N}^{-1/2}$, respectively. This mimics replacing the Ti6Al4V grains

with TiV in the BCC β phase, which featured higher diffusivity and lower solubility [143, 263]. The time increment changes to 0.001 h for a time range of 0-0.1 h due to the fast diffusion. The much lower solubility of grains than that of GB is the key parameter inducing GB diffusion to become the dominant mechanism. The highest concentration was reduced by a scale of magnitude as both random and special boundaries became more soluble than the grains. Jaseliunaite et al. [37] set the GB diffusivity to 10,000 times the grain diffusivity to obtain a GB diffusion across polycrystalline microstructure with solid grains. Still, solubility was not accounted for in that simulation. If the fraction of GB and their properties remained the same as the original scenario, SR-GB would reach a saturation state within 0.2 h (**Fig. 4.7b**), and HT-GB would be saturated within 1 h (**Fig. 4.7d**). Since hydrogen diffused across the GB network in the initial stage rather than dissolved in the surficial grains and proceeded bulk diffusion like in previous scenarios, the formation of hydrides along the GB network with deep displacement would occur.

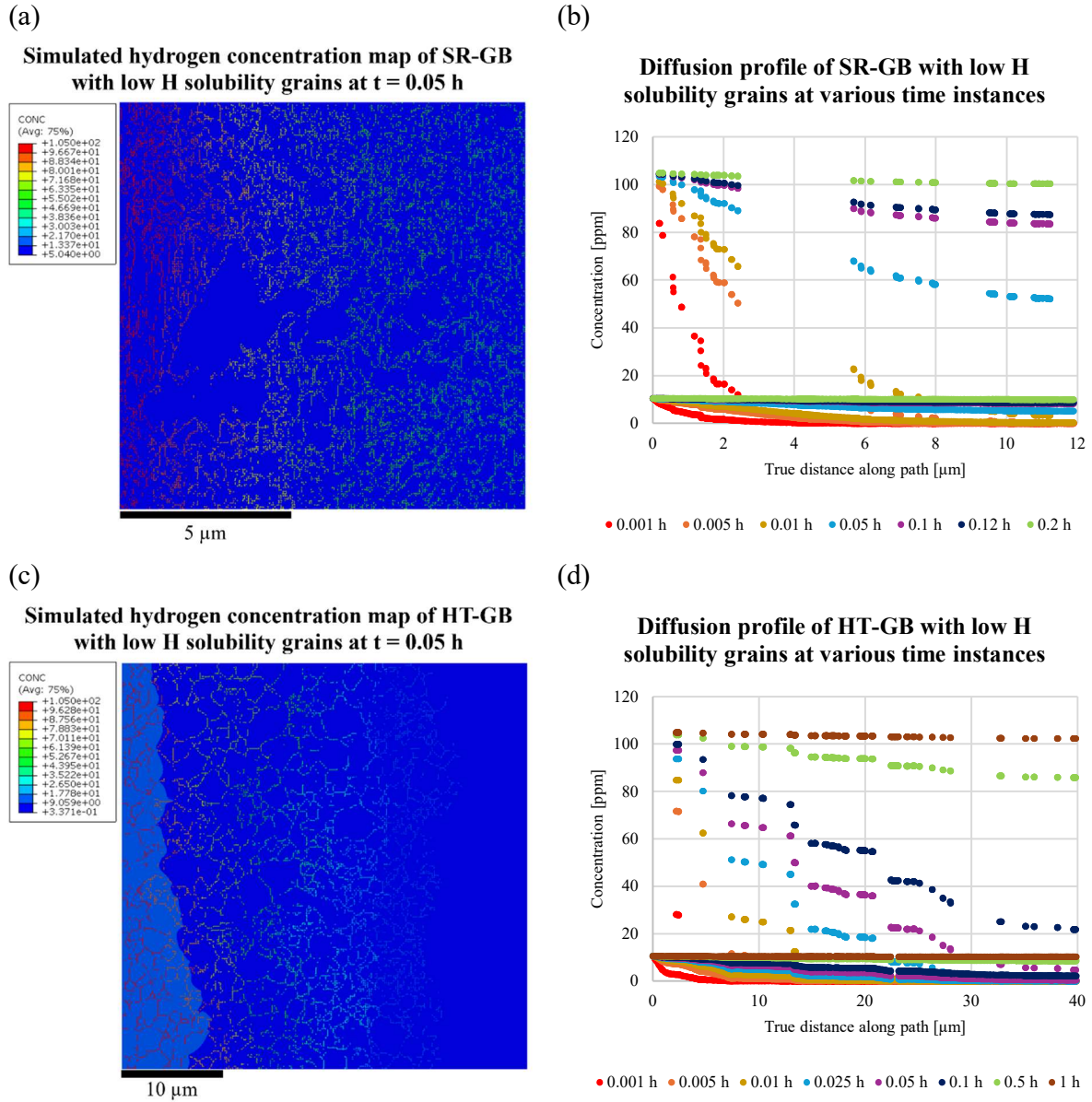


Fig. 4.7. Simulated hydrogen concentration maps and diffusion profiles of cold-sprayed Ti6Al4V deposits with (a and b) 540°C stress relieving and (c and d) 750°C heat treatment in imaginary conditions containing grains with low H solubility.

4.3.5 Limitations

The simulation of hydrogen diffusion with the GB network approach highly relies on the quality of EBSD characterization. The cold-sprayed deposits of soft feedstock metal powder, using

nitrogen or low-pressure helium carrier gas, would facilitate the acquisition of reliable EBSD data [4, 24, 264, 265]. The dark non-indexed regions in cold-sprayed and highly cold-worked hard metals like Ti6Al4V are inevitable [246, 266]. Wang et al. [267] used low-temperature (300°C) annealing to improve the index rate in severely shot peened Ti6Al4V, but its potential influence on submicron structure needs to be considered. In this study, the GB maps did not form a continuous GB network, even after heat treatment at temperatures above 300°C. Despite discontinuous GB structures serving as initiation sites for recrystallization [268], the discontinuous GB network in EBSD characterization of cold-sprayed deposits is more relevant to the step size and grain size.

The simulation procedures and parameters above were implemented in the well-indexed GB maps of cold-sprayed Al-2Cu and Al-5Cu coatings in the study by Liu et al. [264], where their fractions of LAGB were 55.5% and 62.8%, respectively. The true widths of both GB maps are 48 μm wide. The `rgb2ind` function in MATLAB was used to limit the number of colours to three. Material parameters remain the same as in **Table 4.4**. The simulated diffusion rate across the as-characterized Al-Cu GB maps in **Fig. 4.8a-f** was similar to that in Ti6Al4V due to excess random boundaries. Still, the diffusion became more tortuous with enhanced connectivity of the GB network. Al-5Cu coating had a slightly slower diffusion rate, likely because of the 7.3% LAGB, more than Al-2Cu. The diffusion mitigation became significant in the imaginary scenario with well-connected special boundaries only, as shown in **Fig. 4.8g-l**. This demonstrates that the connected GB network with a high fraction of special boundaries can mitigate hydrogen diffusion. Conversely, it also leads to a low EBSD index rate and certain brittleness in deposits due to such intense grain refinement. Heat treatment is necessary for structural repair, where the hydrogen barrier layer should stay as-sprayed or apply additional surface modification after heat treatment.

Anyhow, the cold-sprayed coatings with dense special boundaries make it difficult to obtain reliable GB maps and implement this realistic modelling method. The economic solution would be to integrate the discontinued GB through image processing, where assigning additional random and special boundaries is challenging. In addition, TJs also need to be recognized in image processing as their diffusivity can be triple that of GB and 70 times higher than that of interstitial sites in the case of nanocrystalline Ni [269]. The hybrid modelling methods are recommended to address the concerns above and enhance the accuracy of hydrogen diffusion simulations across cold-sprayed microstructures. If the CSL indices approach is used to categorize the GB with different misorientations, their corresponding GB energy and hydrogen properties would require extensive study before being implemented in the GB network model.

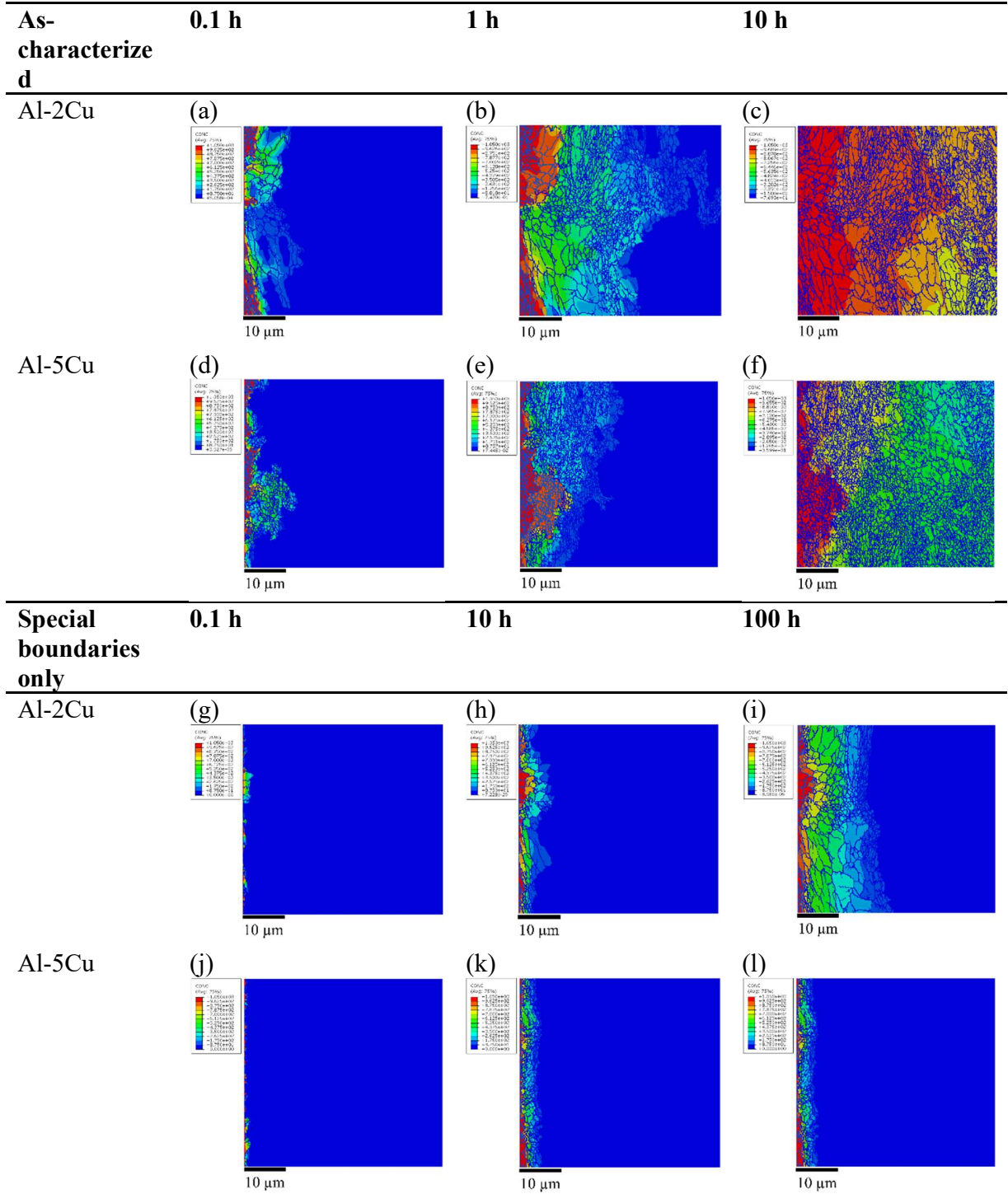


Fig. 4.8. Simulated hydrogen concentration maps of cold-sprayed (a-c, g-i) Al-2Cu and (d-f, j-l) Al-5Cu deposits in the study of Liu et al. [264] with (a-f) as-characterized GB fractions and (g-l) special boundaries only.

The hydrogen diffusivity and solubility of grains and GB are retrieved from literature. Still, they are not equivalent to the real hydrogen properties of cold-sprayed Ti6Al4V grains in various sizes and GB with various CSL indices. The im2mesh tool [249] could generate a multi-parts model with detailed classification of grains and GB, but the recognition and properties assignment would become extremely complicated in a polycrystalline microstructure like cold-sprayed deposit. Comprehensive simulation for interested metals will require an experimental database, such as [163, 258, 262], at various conditions, particularly for the hydrogen charging method, temperature, and pressure. It is noteworthy that fabricating standardized samples with cold-sprayed Ti6Al4V for hydrogen permeation tests or atomic probe tomography is challenging. The permeation foils and tomography needles bend severely due to the highly deformed microstructure plus the coating nature with biaxial stress. Wire-cutting can lead to surface grain recrystallization and loss of special boundaries by the elevated temperature of electrical current. A layer of brass oxide remains on the cut surface, which needs to be ground away. Furthermore, the contamination of epoxy resin infiltrated into micropores of cold-sprayed deposits leads to unreliable composition analysis, especially since the required accuracy of hydrogen content characterization is much higher than other bulky elements. Removing epoxy resin with multiple solvents also increases the uncertain influences of hydrogen content on the specimens [270]. Experimental validations remain a challenge unless the limitations above can be resolved.

4.3.6 Challenges in 3D Extension

Reconstructing the 3D GB network models from the 2D models is challenging for cold-sprayed deposits. Murgas et al. [271] attempted generating as-sprayed AA7050 with EBSD maps and the integrated SliceGAN-Dream3D platform. The detailed morphological and crystallographic information of ultrafine and coarse grains were successfully acquired with a step size of 166 nm.

SliceGAN is able to generate high-quality binary and three-phase microstructures but cannot recognize the GB well in polycrystalline microstructures. Although the SliceGAN-Dream3D is sufficient to simulate micromechanical performance, the GB recognition issue and sampling speed in diffusion models would require extensive study to overcome. For ideal synthetic models, Adair and Johnson [170] extended their diffusivity model to 3D by assigning the boundary conditions on the 2D line to the 3D plane. However, the 3D model was generated with Neper Polycrystal rather than converting the reference and GB engineered Ni models in their 2D analysis, where the GB conversion from 2D EBSD maps to realistic 3D models was not achieved. Implementing this method on cold-sprayed titanium alloys would be even more difficult due to the low EBSD index rate. Sayet et al. [169] compared the normalized effective diffusivity against the change of random boundaries fraction between synthetic 2D and 3D models with varying grain sizes. Both curves in 2D and 3D were exhibited as sigmoid functions with inflection points at 0.5 and 0.3, respectively. The normalized effective diffusivity of the 3D model was always higher than that in the 2D model with smaller nanograins in 20 and 50 nm. However, the disparity in normalized effective diffusivity reduced along with the increase of grain size, where the curve would be flattened if the grains enlarged to microscale. In other words, the difference in diffusivities between the 2D and 3D models are very limited for the cold-sprayed deposits with coarse grains by less deformation or recrystallization heat treatment. Cold-sprayed deposits with severely deformed particles contain grains from nano to microscale can use this relationship to predict 3D localized diffusivity but predicting 3D bulk diffusivity still requires further advance in 3D GB recognition and reduced computation time. Advanced EBSD with focus-ion-beam samples may be able to characterize and reconstruct the 3D model with detailed GB features.

4.4 Summaries

This study performed realistic modelling and hydrogen diffusion simulation on a macroscopic scale on the cold-sprayed Ti6Al4V samples after stress-relieving and heat treatment. The experience in this study may provide inspiration for researchers and on-site engineers to further investigate GB engineering in mitigating hydrogen diffusion, predict the hydrogen-affected zone in components, and establish safety standards for cold-sprayed deposits and other GB engineered materials in hydrogen applications. The findings are concluded as follows:

- (1) The fraction of special boundaries in cold-sprayed deposits needs to be high enough to trigger its hydrogen trapping ability and overcome the “short-circuit diffusion effect” by random boundaries. The as-characterized SR-GB and HT-GB samples with special to random boundaries ratio of 1.92 and 2.63, respectively, exhibit bulk diffusion across the “floodplain”. On the other hand, the complete special boundaries network in imaginary scenario acts as the “detention basins” to mitigate the bulk diffusion.
- (2) The hydrogen mitigation mechanism is elucidated as the low-diffusivity special boundaries segregating neighboring grains which hydrogen atoms need to circumvent for a longer distance with a high concentration across the whole grain before migrating to the next grain. Recrystallization during heat treatment reduces the fraction of special boundaries and thus deteriorates the hydrogen mitigation performance. Additional hydrogen mitigation methods are required if heat treatment on cold-sprayed deposit is compulsory.
- (3) The as-sprayed deposits with helium carrier gas cannot be indexed by EBSD due to the presence of ultra-fine grains, which may need prolonged low-temperature annealing to improve the index rate and proceed realistic modelling. Image processing is necessary to aid unrecognizable features like TJ in GB maps. Hydrogen properties of grains and

boundaries need to be measured and calculated on a case-by-case basis, whereas measuring hydrogen properties on cold-sprayed deposits is difficult due to problems like specimen bending and composition contamination.

Chapter 5: Unravelling the Statistical Correlation between Porosity, Permeability, and Diffusivity of Cold-sprayed Ti6Al4V

5.1. Introduction

As reviewed in **Section 2.5**, statistical correlation is a straightforward method to correlate porosity and properties of material. This benefits the quality control of cold spray in mass production and lowers the knowledge bar for technicians. Particularly, fluid tightness is sensitive to the porosity induced by speed fluctuations during cold spray process. The speed fluctuations occur more frequently by human operators than by robots. However, the required database with statistical references needs to be established on a case-by-case basis amid the instrumental deviations in fabrications and characterizations.

This is the first known cold spray study to comprehensively articulate the correlation between fluid transport properties and porosity in cold-sprayed deposits induced by instantaneous fluctuations of TCP speed. The Archimedes' principle-based densitometer, 2D optical micrographs and XCT were used to evaluate the porous structure of a small cold-sprayed Ti6Al4V “tsunami” deposit. The deposit is a side product at the deceleration/acceleration spot in cold spray toolpath from another study about repairing commercial aircraft components, but its unique internal porous structure provides an excellent opportunity for studying fluid transport in cold-sprayed microstructure. The reconstructed 3D model was utilized to study the relationships between the localized porosity, tortuosity, pressure-driven absolute permeability, and concentration-driven molecular diffusivity of the deposit. LH2 was chosen to be the working fluid in the simulation to explore the potential in quality control of cold-sprayed pressure vessels and functional deposits like transpiration cooling layer in future commercial hydrogen-powered aircraft. The deviation of

porosity results in different characterization methods, and the simulated fluid transport properties were discussed. The technical constraints of utilizing NDI methods for porosity and substantial properties assessment were also revealed.

5.2. Methodology

5.2.1 Materials & Sample Preparation

Cold spray nozzle (PCS100, Plasma Giken, JP) mounted on robot arm (IRB 4600, ABB, CH) was used to fabricate Ti6Al4V deposit. Gas atomized Ti6Al4V spherical powder (Plasma Giken, Japan) was used as feedstock powder, where the mean circular-equivalent diameter was measured as 11.75 μm by number distribution (Morphologi 4, Malvern Analytical, UK). Particle speed was measured by a cold spray diagnostic system (HiWatch CS2, Oseir, FI) prior to deposition. The spraying process parameters are summarized in **Table 5.1**. The plate mounted on the mild steel holder frame was for another study. Some small “tsunamis” (**Fig. 5.1**) formed on the mild steel holder frame where the U-turn sections of nozzle traverse path were not covered by the substrate plates. The tsunamis were peeled off with a sparkle knife and a hammer. The dimensions of the selected piece in this study were 31 x 22 x 26 mm measured from maximum distances.

Table 5.1. Cold spray process parameters.

Parameters	Descriptions
Gas	Helium
Nozzle	WC, 2 mm throat diameter, 8 mm exhaust diameter, 300 mm length (divergent section)
Temperature	900 °C
Pressure	3 MPa
Stand-off distance	30 mm
Traverse speed	0.8 m/s
Toolpath	Snake scan pattern, vertical step of 1 mm, ten loops Retracted 1 mm backward at the end of every loop
Particle speed	Mean: 740 m/s, SD: 336 m/s

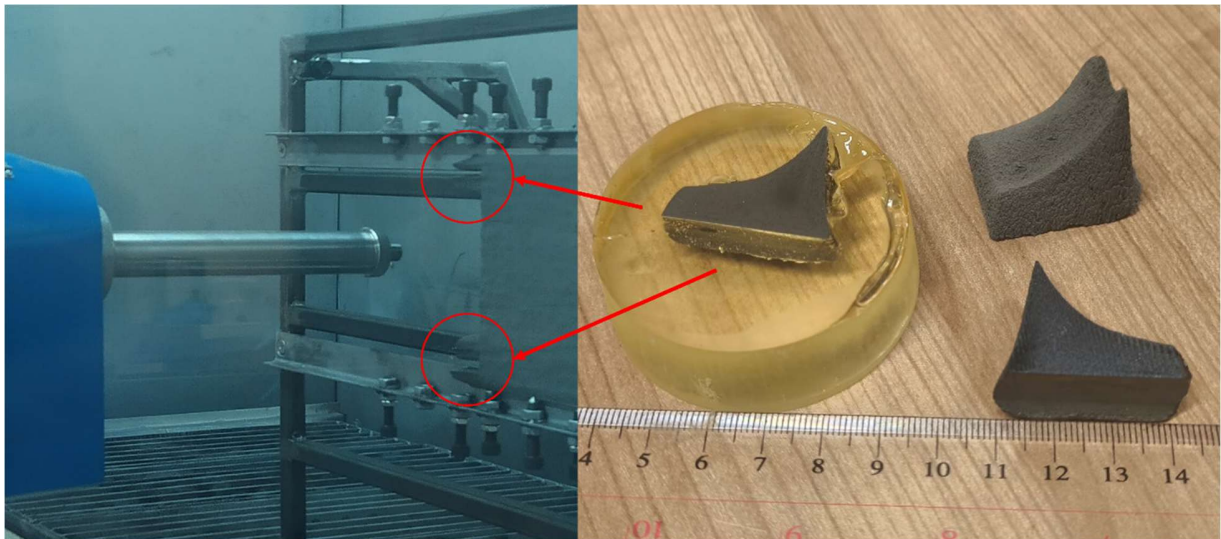


Fig. 5.1. Small Ti6Al4V tsunami deposits.

5.2.2 Characterization

The small Ti6Al4V tsunami was wire-cut (AS-540 TL WEDM, ACRO, TW) into half. One piece was mounted in epoxy resin, then grinded with semi-automatic grinder polisher (EcoMet 30, Buehler, US) with sand grit paper from 120 to 2000 and polished with 0.05 μm alumina polishing suspension (MasterPrep, Buehler, US) to mirror finish. The microstructure of polished cross-section was captured with digital microscope (VHX-5000, Keyence, JP) at magnification at 300X

then stitched together with its built-in stitching function. Four stitched micrographs were combined with the open-source software GIMP to display the whole cross-section of the deposit. The 2D porosities in three ROIs were measured with the built-in auto area measurement function of the digital microscope.

X-ray 3D CT (FF35 CT, COMET YXLON, DE) was used to obtain 2D radiographs of the internal microstructure of the other half without epoxy resin mount. The acquired data were reconstructed into a 3D model with a unit voxel size of 14 μm (YXLON Software Suite, COMET YXLON, DE). The analysis of internal structure was performed with CT analysis software (VGSTUDIO MAX, Volume Graphics GmbH, DE). The background, ISO value and materials peaks in surface determination were about 8640, 19980, and 25830, respectively. The rendering of display images was set with ISO value of ~ 20000 . ROIs were created as cubes with 1- or 0.5-mm edge length depending on the geometric boundary. The real density and volume of scanned piece were measured by Archimedes' principle-based densitometer (SKZ300D, SKZ Industrial, CN). The real porosity Φ_{real} is calculated using Eq. 1 and the theoretical Ti6Al4V density ρ_{Ti6Al4V} of 4.43 g/cm^3 .

$$\Phi_{\text{real}} = \left(1 - \frac{\rho_{\text{measured}}}{\rho_{\text{Ti6Al4V}}}\right) \times 100\% \quad (5.1)$$

5.2.3 Simulation

The virtual porosity was measured with the surface determination function in VGSTUDIO MAX. Capillary pressure simulation with mercury injection experiment was performed to preview the distribution of accessible and isolated porosity. The governing equations in the absolute permeability simulation were based on steady Stokes flow, which assumed complete flooding within porous material without turbulence, diffusion or gas [272]. Fick's first and second law were used in the molecular diffusion simulation [273]. Tensor mode was used to calculate the mean

absolute permeability and the mean effective diffusion coefficient of the entire deposit without substituting fluid transport properties. The edge length of the cubic mesh element was 0.5 mm. The tensor data acquired was analyzed with MATLAB and MS Excel. The fluid transport properties were compared with the absolute permeability and molecular diffusion simulation in experiment mode. The fluid transport direction was from the top to bottom boundary of ROIs. The fluid transport properties substituted in experiment mode are summarized in **Table 5.2**.

Table 5.2. Fluid properties in VGSTUDIO MAX permeability and diffusivity experiments.

Fluid properties	Values
Dynamic viscosity of LH2 ($\mu\text{Pa}\cdot\text{s}$)	7
Molar concentration difference (mol/m^3)	34727.33456
Molar mass of H (kg/mol)	2.01568E-03
Density of LH2 (kg/m^3)	70
Material molar diffusion coefficient of Ti6Al4V (m^2/s)	0
Pore space diffusion coefficient (m^2/s)	1.00E-06

5.3 Results & Discussion

5.3.1 Archimedes' Density

The density and volume of specimen measured by the Archimedes' principle-based densitometer are shown in **Table. 5.3**. The global porosity of the deposit was about 15%, which was close to the interlayer porosity of the cold-sprayed Ti by Vargas-Uscategui et al. [184]. It is noted that this porosity measured at atmospheric-hydrostatic pressure cannot represent all the accessible pores if their surface energy is much lower than that of water [274]. The precise porosity characterization for deposits with gas-tightness should be measured with the use of applied pressure and alternative fluid probe such as mercury and nitrogen. If ultrasound NDI with water or hydrogel is used to examine the porosity and fluid transport properties of cold-sprayed deposits on-site, the applications of deposits should be limited to the components in water environment like water pipes,

turbines of watercraft and hydropower plants. Moreover, it was discovered that ultrasound NDI could not be performed on this Ti6Al4V tsunami deposit. After taking the deposit out from the densitometer, water was desorbing out from pores slowly so that the portable ultrasound unit lost transmission medium to detect the defects. Immersing ultrasonic testing may be helpful if such a facility is accessible. However, the statistics of ultrasound inspection were not available in this study since the device was not water-proof.

Table 5.3. Archimedes' principle-based density and volume measurements.

Dry weight (g)	Weight in water (g)	Density (g/cm³)	Volume (cm³)	Real Porosity (%)
9.645	7.090	3.7637	2.5626	15.0406

5.3.2 Optical Microscopy

The stitched micrograph of the cross-sectional porosity distribution of the cold-sprayed Ti6Al4V tsunami deposit is presented in **Fig. 5.2a**. Most large pores in the deposit were filled with epoxy resin, where the air in the porous structure was pushed out and trapped in the resin. No cracking was found on the sample although the layer structure was barely recognized with porous shells. Most particles were not severely deformed except the first layer of particles at the bottom boundary of deposit. The IPB within the agglomerates were faintly noticed at the unetched state. The bonding mechanism should rely on the ASI with little intermixing of materials. The ROIs for 2D porosity analysis were near (1) the bottom centre and (2) the bottom edge, and (3) the top of the nozzle stroke at instantaneous zero-traverse speed. The 2D porosities measured were 35.5%, 54.0%, and 49.3%, respectively. These values were exceptionally high for the cold-sprayed deposits of any materials. Porosity measurement based on 2D images depends on magnification, ROIs selection, threshold and other settings. Hence, the later porosity measurements with the use of Archimedes'

principle-based densitometer and XCT 3D model offer considerable insights. The distribution histograms of pore maximum diameter in the ROIs are shown in **Fig. 5.2b-d**. There were about 5-14% of pores larger than 10 μm , and some of them were few hundred or a thousand microns. These large pores would function as open transport paths and reservoirs for liquid and gas, since their molecular diameters and free mean path are in pico-scaled and nano-scaled, respectively [275]. There were $\sim 30\%$ of pores marked as 0 μm , which were submicron pores captured as small dots by the microscope. These submicron pores require characterization with SEM, but it was not conducted in this study to conserve the global pattern of pores.

The asymmetric Gaussian shape indicates the nozzle deceleration where the peak aligns with the centerline of the nozzle at the instantaneous zero-traverse speed. It reflects the slower nozzle traverse speed increasing the coating thickness and sharpness. The first deposition layer at the complete stop is hump-shaped and is sharpened to triangle along the layer buildup. Kotoban et al. [276] explained this phenomenon was caused by the difference of particle velocity between the jet core and periphery. At the same powder feeding rate, there were more particles deposited on the substrate spot with slower traverse speed. Thus, the sharpening of deposit profile is faster with slower traverse speed. Spraying with faster traverse speed would result in similar profile with more passes to reach the total mass of particles deposited with slower traverse speed.

In addition, the outer porous regions exhibited quasi-columnar agglomeration, which became dominant beyond thickness of ~ 9 mm. It was difficult to recognize the head and tail of columns due to the cramming of particles. However, these top tips of quasi-columns were seen to be pointing a bit outward instead of aligning with the direction of jet dispersion. It indicates the particles slightly bouncing away from the sloped preceding layers before complete consolidation. The formation mechanism of this pattern would need additional investigations on particle bounce

under thermomechanical influence. Nonetheless, the study focused on how the transition of microstructural patterns affected the anisotropy and locality of fluid transport properties.

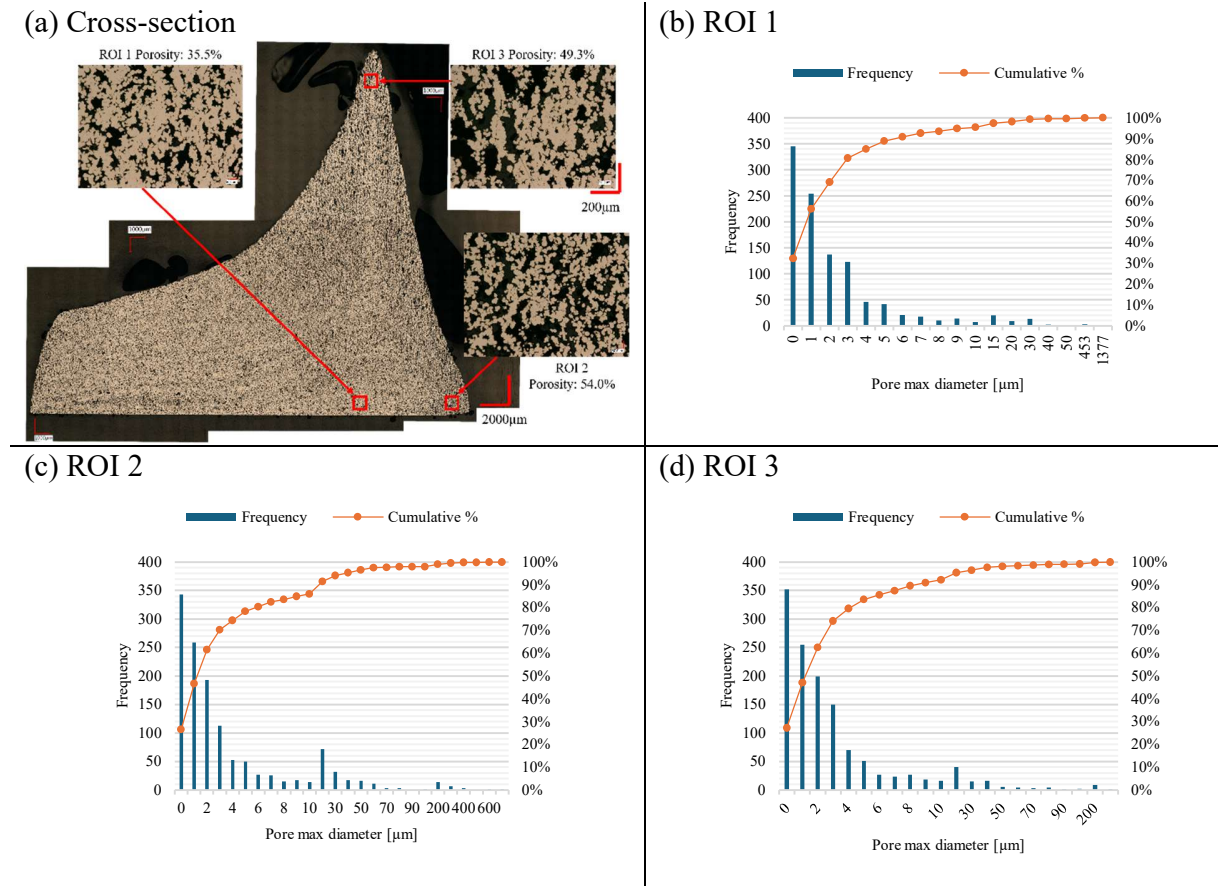


Fig. 5.2. (a) Stitched optical micrograph of the cross-section of the cold-sprayed Ti6Al4V tsunami, and the pore size distribution in (b) ROI 1, (c) ROI 2, and (d) ROI 3.

5.3.3 XCT Scanning and Analysis

5.3.3.1 Porosity Mapping

A 2 mm thick cross-sectional ROI on XZ-plane was used for the capillary pressure analysis in VGSTUDIO MAX. The simulated total porosity was 57.62%, where 1.20% was isolated porosity and the rest was accessible. However, these values might be misleading as some background spaces were included. The error is discussed in later sections. It is reasonable that the sub-milli

pores with approximate diameter of $22.2624\text{ }\mu\text{m}$ contribute to total volume of $6.27239\text{E}+10\text{ }\mu\text{m}^3$. These pores are categorized as macropores where the flow regime belonged to continuum flow [129]. Besides that, this analysis revealed the distribution of accessible and isolated pores in a global view. The pore mapping in **Fig. 5.3.** shows that most pores are isolated, where the accessible pores are concentrated in the porous shell with thickness of $\sim 2500\text{ }\mu\text{m}$ at the location of zero traverse speed. This indicates that the inter-connected microchannels are discontinued at such depth without further extension. Nonetheless, the XCT could not characterize the microstructure as clear as the previous optical microscope. It is expected that the actual fluid transport properties will be higher than the simulated values in this study.

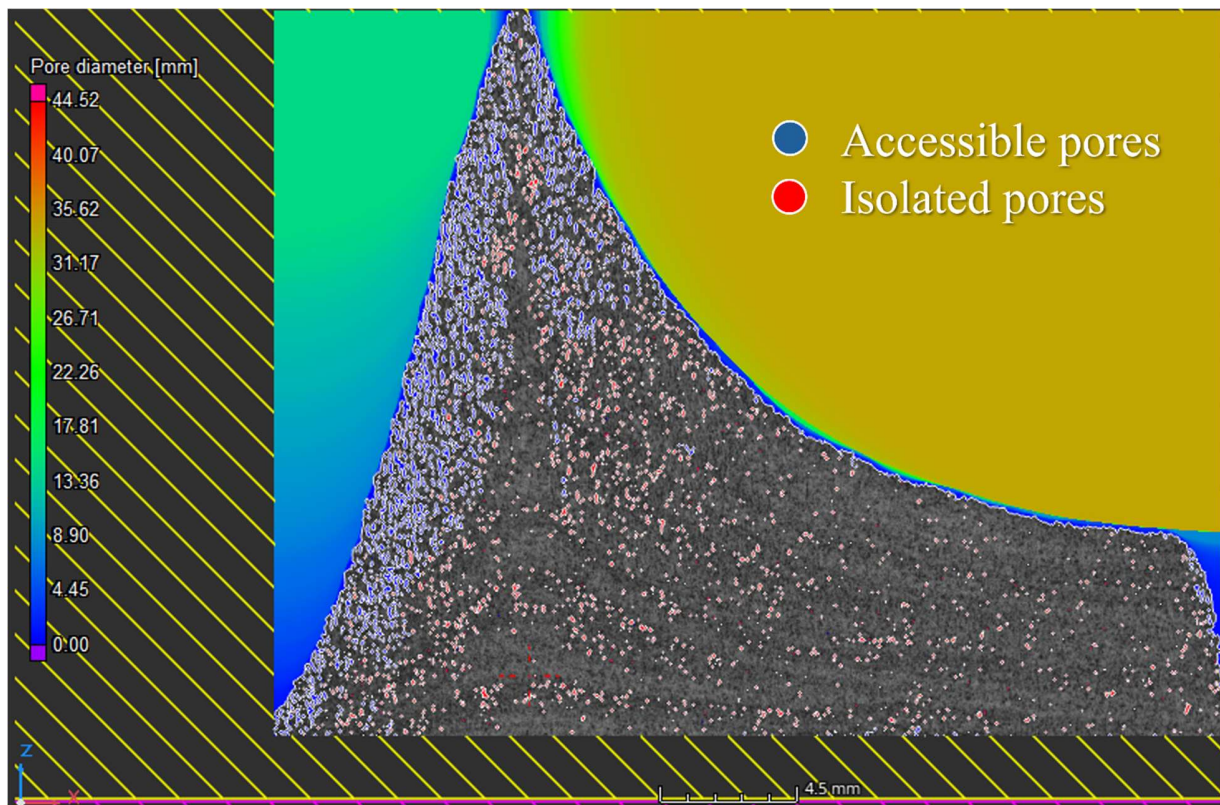


Fig. 5.3. Mapping of accessible pores and isolated pores in VGSTUDIO MAX capillary pressure analysis of 2 mm thick sliced ROI on XZ-plane.

5.3.3.2 Permeability Tensor Simulation

The local porosity was revealed further with permeability analysis in tensor mode, where the analyzed 3D model and cross-sections are shown in **Fig. 5.4**. The XZ- and YZ-planes were adjusted to the cross-section where the height of tsunami was maximum. The XY-plane was set near the bottom of tsunami. The porosity of the deposit was mostly about 10%. The porosity at inter-layer gaps and near-surface-regions were about 30-70%. Some boundaries between the surface of deposit and background might be indexed with porosity higher than 90%. The extremely porous boundaries mislead the previous capillary pressure analysis. The isolated porosity is unlikely affected since the pores near there are all accessible. These extremely porous boundaries would be excludable in industrial XCT inspection, but they are kept for statistical analyses.

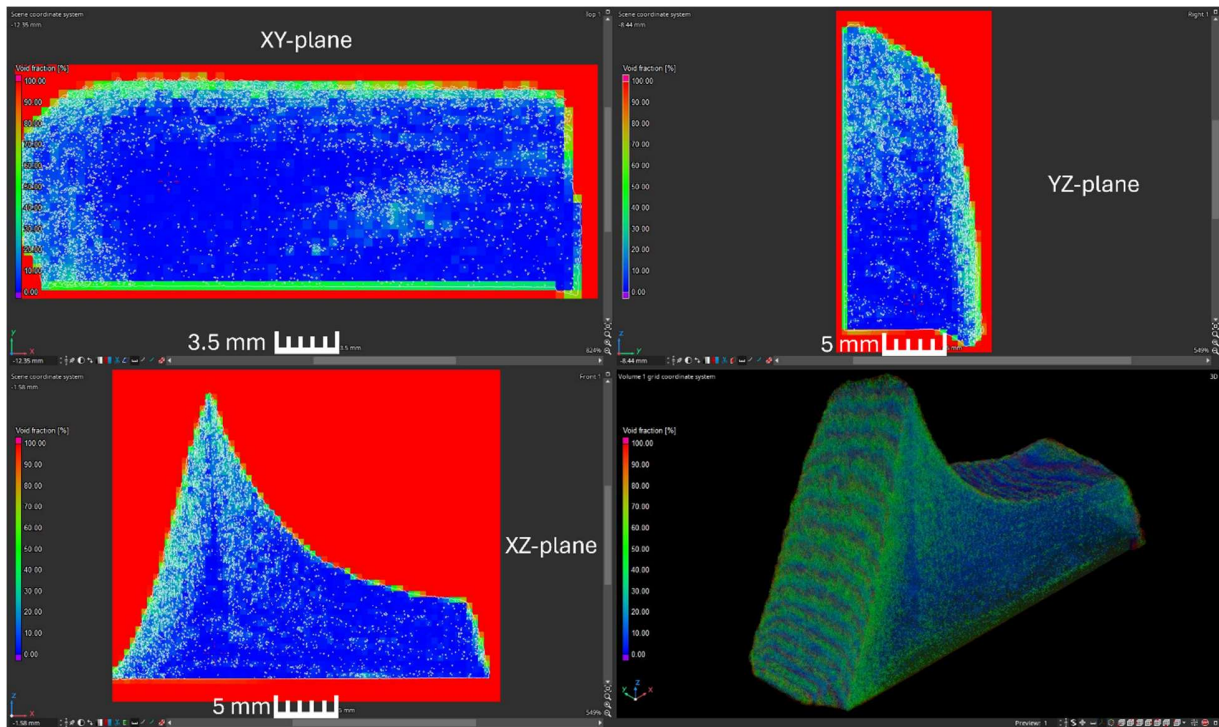
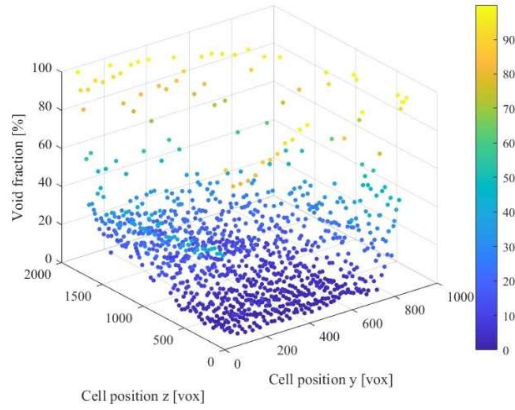


Fig. 5.4. The 3D model and cross-sections of deposits in the permeability tensor analysis.

The porosity distributions across position cells presented in **Fig. 5.5** provide more details. Despite the layer pattern being nonlinear, the horizontal porosity distribution on YZ-plane maintained

below 30% until reaching the porous shell (beyond $Y > 750$ vox), as shown in **Fig. 5.5a**. The curvature of layer pattern is influenced by the dimensions of substrate bar rather than the nozzle stepping direction after each stroke. Vertically, most mesh cubes had porosity below 10% at $Z = 50$ to 900 vox (0.7 to 12.6 mm), but the whole distribution steadily shifted up after $Z = 900$ vox. This indicates the max height that the dense regions could form along the nozzle centerline at instantaneous zero-traverse speed. The vertical porosity distribution on XZ-plane also shares similar pattern, as shown in **Fig. 5.5b**. Horizontally, the major porosity kept within 0 to 20% at the nozzle decelerate-accelerate band from $X = 2250$ to 1000 vox (31.5 to 14 mm). This reflects the correlation between the horizontal porosity distribution and the motion of the nozzle. When the nozzle centerline stopped at $X = 541$ vox, the spray stroke radius on the first layer was approximately 384 vox (~ 5.4 mm). However, it was observed that some near-zero porosity regions managed to form on the right half side, which was facing to the main traverse path. On the left side, the near-zero porosity zone discontinued beyond $X = 331$ vox (~ 4.6 mm). This implies that the ratio between dense and porous regions on the first layer is approximately 1:1; subsequently, the porous regions weigh more during the buildup. The XCT-simulated porosities at the ROIs in **Fig. 2a** were $\sim 20\%$ lower than those values measured with optical micrographs. Metallography is a destructive inspection method that is used to inspect every deposit in industrial practice. Hence, using statistical correlation between different porosity characterization methods would be a simpler approach than seeking a significant increase in the resolution and power rate of NDI instruments.

(a) At $X = 541$ vox, void fraction vs Y vs Z



(b) At $Y = 121$ vox, void fraction vs X vs Z

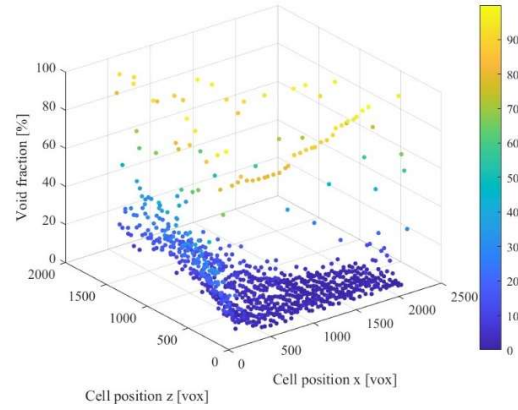
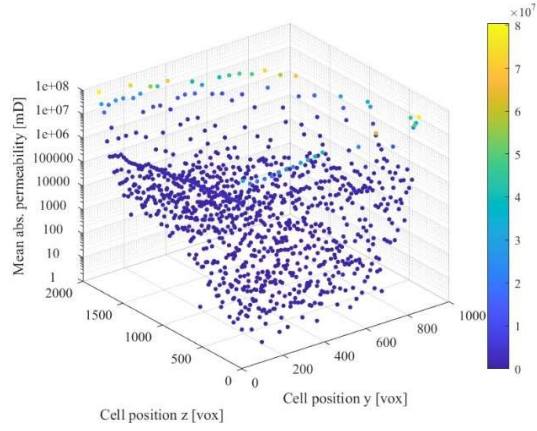


Fig. 5.5. (a) Void fraction of YZ-plane at $X = 541$ vox along cell position in Y and Z direction; and (b) void fraction of XZ-plane at $Y = 121$ vox along cell position in X and Z direction.

The permeability distribution across position cells presented in **Fig. 5.6** shares similar patterns with each corresponding plane and direction in **Fig. 5.5**. The permeability varied by 8 orders of magnitude at low porosity regions. In contrast, the permeability near the porous shell varied from about $1.0E+03$ to the default pore space permeability of $1.0E+08$ mD. However, the permeability above $1.0E+05$ mD might refer to the mesh cubes among the boundaries between the surface of the deposit and the background. Thereafter, the analysis was performed with split permeability ranges.

(a) At $X = 541$ vox, permeability vs Y vs Z



(b) At $Y = 121$ vox, permeability vs X vs Z

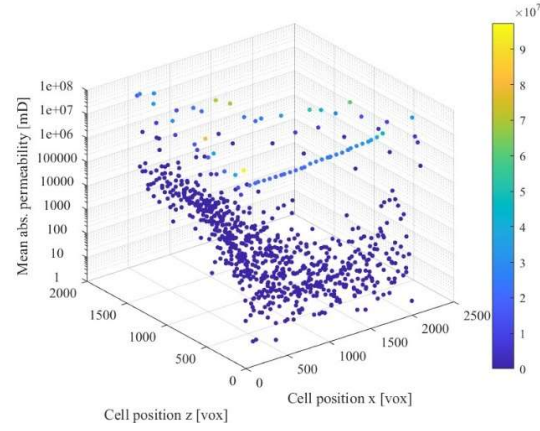
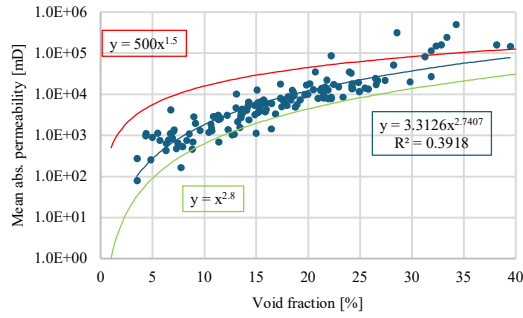


Fig. 5.6. (a) Mean absolute permeability of YZ-plane at $X = 541$ vox along cell position in Y and Z direction; and (b) mean absolute permeability of XZ-plane at $Y = 121$ vox along cell position in X and Z direction.

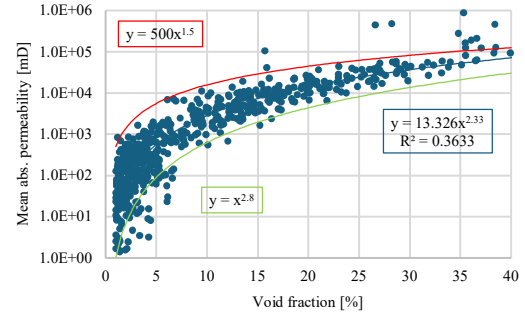
The permeability-void fraction distribution plots of YZ- and XZ-planes at porosity of 0-40% are displayed in **Fig. 5.7**. Some power functions had R^2 below 0.5. This might be caused by the broad permeability deviation at regions with porosity below 5%. A general equation could not inclusively correlate the permeability and porosity for all slices since the power of equations varied from 1.86 to 2.74. Niya and Selvadurai [277] suggested the permeability-porosity correlation for porosities below 70% would be unreliable and need to be estimated with 58% error. The nature of varying permeability at the same porosity is not alterable, but at least the permeability range can be predicted. Thus, the upper and lower bound power functions were established by graphical methods to include most of the data points in all plots. The prediction was valid for porosity values ranging from 0 to 30%, where the permeability spanned the range of $1.0E+4$ to $1.0E+5$ mD. The power regression on the permeability at porosities ranging from 30 to 100% was performed separately, as the initial upper bound power function underestimated the values.

In contrast, Furumoto et al. [179] used the selective laser sintering and metal powder blend (70% 42CrMo4, 20% C52100 and 10% Ni by weight) with a minimum energy density of 0.7 J/mm² to fabricate an injection mold, which resulted in a maximum porosity of 29% and horizontal permeability of 223 mD ($\sim 2.2\text{E-}13 \text{ m}^2$). The permeability of cold-sprayed Ti6Al4V was three orders of magnitude higher than that of the SLSed alloy blend, despite having comparable porosity. The cold-sprayed Al coatings fabricated by Weiller et al. [41] exhibited low 3D porosity varying from 1.1% to 7.8%, but the FFT-calculated permeabilities ($\sim 1.0\text{E-}18 \text{ m}^2 = 1.0\text{E-}3 \text{ mD}$) deviated from the experimentally measured one ($\sim 1.0\text{E-}20 \text{ m}^2 = 1.0\text{E-}5 \text{ mD}$) by 1-2 orders of magnitude for the samples with too low porosity (1.5-2.1%). The permeability prediction became aligned at $1.0\text{E-}15 \text{ m}^2$ ($\sim 1 \text{ mD}$) with the sample with porosity 7.8%, which was 3-4 orders of magnitude lower than the simulated permeabilities of the cold-sprayed tsunami at the same porosity level. Unacceptable helium leakage occurred on their $\sim 3\text{-}4 \text{ mm}$ thick Al coatings with porosity $>2\%$, but the coatings with porosity $<2\%$ demonstrated gas-tightness. It is considered that the helium atoms with a diameter of 280 pm are passing through the nanochannels in their cold-sprayed Al with a diameter of $\sim 10\text{-}40 \text{ nm}$. Thus, the most ideal cold-spray deposit for gas-tightness would have interparticle gaps smaller than the diameter of working gas atoms or molecules. The tsunami deposit could not achieve such gas-tightness, where even dense coatings would require intense heat treatments to seal all the interconnected pores.

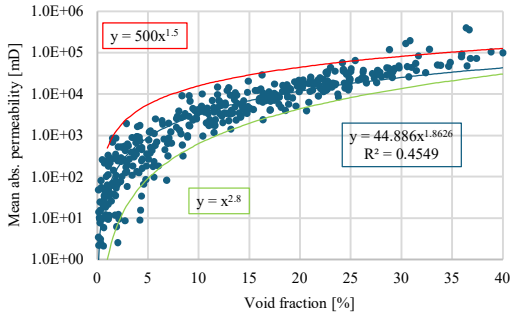
(a) X = 157 vox



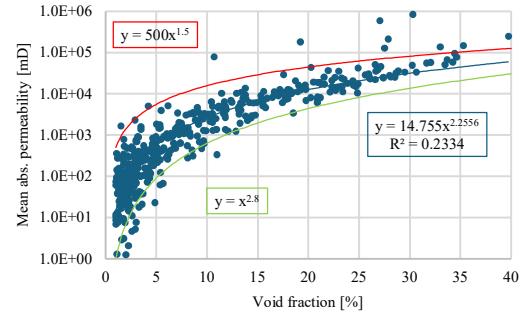
(d) Y = 121 vox



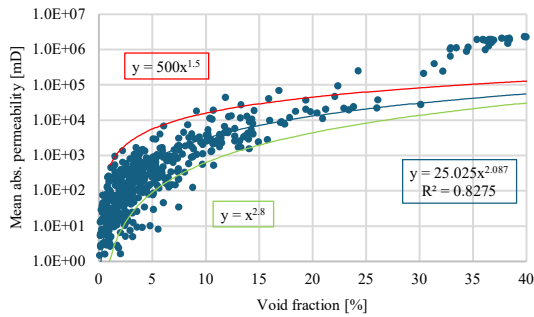
(b) X = 541 vox



(e) Y = 400 vox



(c) X = 1028 vox



(f) Y = 749 vox

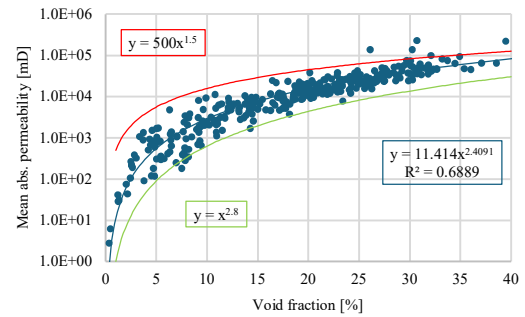
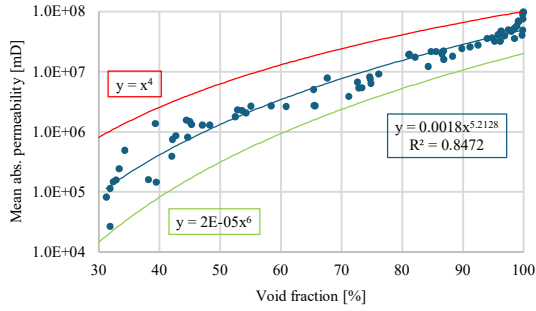


Fig. 5.7. Permeability-void fraction (0-40%) scatter plots of YZ-plane at (a) X = 157 vox, (b) X = 541 vox, (c) X = 1028 vox, and XZ-plane at (d) Y = 121 vox, (e) Y = 400 vox, and (f) Y = 749 vox.

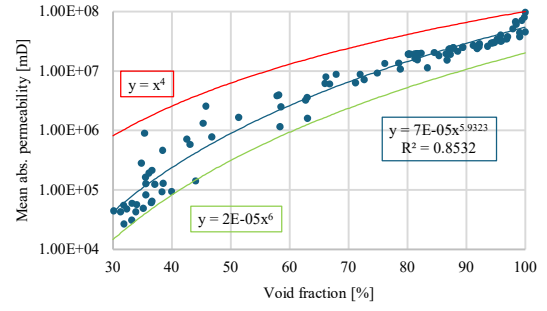
Fig. 5.8 shows the permeability power functions at porosities of 30-100%, with exponents ranging from about 3.60 to 5.93, coefficients varying from 7E-05 to 2.25, and R^2 values mostly exceeding 0.8. The diminished variation of permeability in high-porosity regions also matched the

numerically simulated trend by Niya and Selvadurai [277], which claimed that the admissibility of random 3D and 2D structures should reach a maximum beyond porosities of about 30% and 60%, respectively. The admissibility of reconstructed structure is expected to be improved by refining the voxel resolution and simulation mesh elements, as the percolating pore network may not appear at low resolution [41]. Notwithstanding, the permeability beyond porosity of 30% at the fifth or above orders could be considered as gravel in geology [278]. The diminishing variation of permeability along with increasing porosity is true statistically, but untrue realistically, as the cold-sprayed Ti6Al4V tsunami is a consolidated deposit without loose powder. Some mesh elements might be located exactly at the voids, which gives an illusion that the regions are exceptionally porous and permeable. Optimal mesh element dimensions should be considered to reveal the refined percolation network and prevent the over-estimation of transport properties. Furthermore, this statistical correlation between permeability and porosity tensors did not display the results of the interconnectivity and tortuosity. Thus, the permeability analysis in experiment mode was used to examine the permeation pathways.

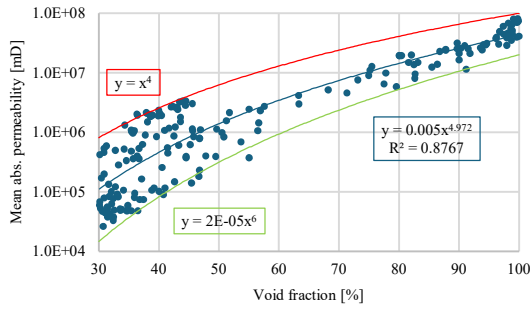
(a) X = 157 vox



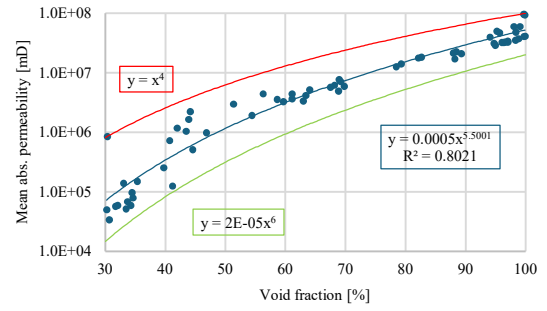
(d) Y = 121 vox



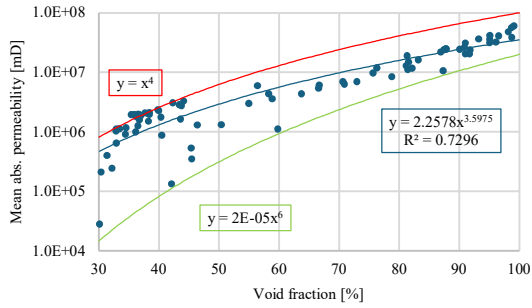
(b) X = 541 vox



(e) Y = 400 vox



(c) X = 1028 vox



(f) Y = 749 vox

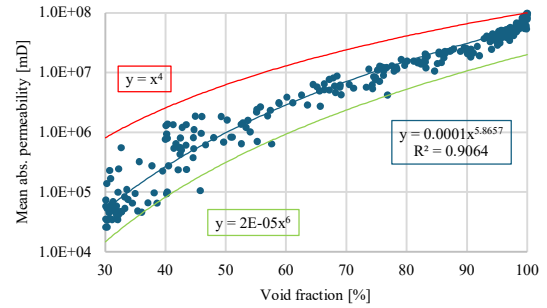


Fig. 5.8. Permeability-void fraction (30-100%) scatter plots of YZ-plane at (a) X = 157 vox, (b) X = 541 vox, (c) X = 1028 vox, and XZ-plane at (d) Y = 121 vox, (e) Y = 400 vox, and (f) Y = 749 vox.

5.3.3.3 Permeability Experiment Simulation

Fig. 5.9 shows the ROIs with the larger mesh element size in experiment mode. The model with velocity streamline indicates the high velocity due to expansion beyond the turns on a tortuous path. Notably, there were a few ROIs in the dense regions that failed to perform the simulation due

to no open pathway being found. This indicates the cold-sprayed deposit can hinder the fluid permeation if there are no interconnected channels. Contrariwise, the effective porosity range had been reduced to 2-34% in experiment mode, as shown in **Fig. 5.10a**, where the vertical absolute permeabilities simulated in experiment mode mostly sat within the prediction interval in tensor mode. The manually selected ROIs in larger dimensions did not encompass the interfacial boundary between the deposit and background, so that an extremely high porosity of over 90% was not observed. The value spots were closer to the lower bound at low porosity, then skewed towards the middle between the bound functions beyond 25%. Changing the input dynamic viscosity and pressure difference between top and bottom surfaces results in different values, but the geometrically decided absolute permeability is not influenced. Therefore, the experiment mode with selected ROIs can be used to analyze the anisotropic cold-sprayed deposit, thereby saving the long computing time associated with the permeability tensor. Nevertheless, the hydraulic tortuosity slowly declined from ~ 1.5 to 1 along the rise in porosity, as shown in **Fig. 10b**. This confirms that tortuosity is not significantly correlated with porosity or permeability.

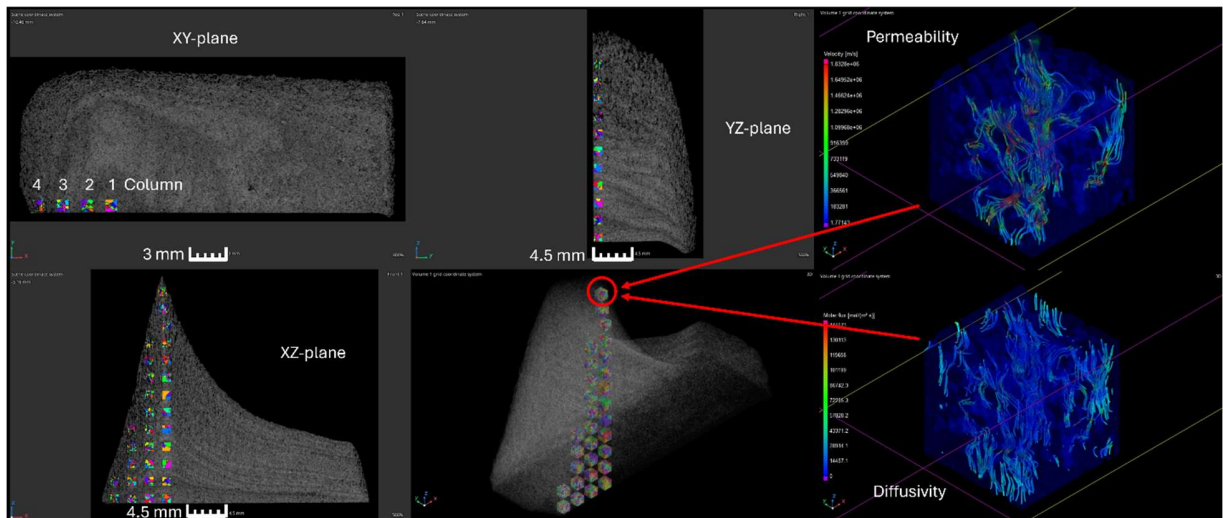
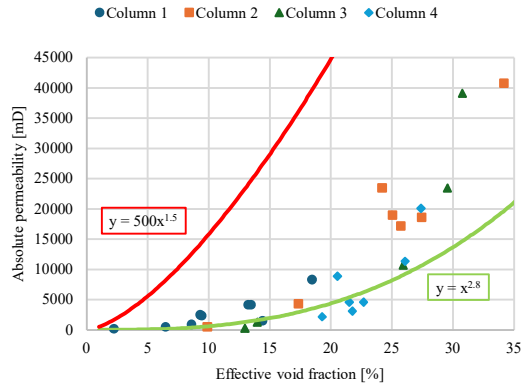


Fig. 5.9. ROIs on the XZ-plane of the cold-sprayed Ti6Al4V tsunami with permeability and diffusivity experiment analyses in VGSTUDIO MAX.

(a) Permeability-void fraction



(b) Tortuosity-void fraction

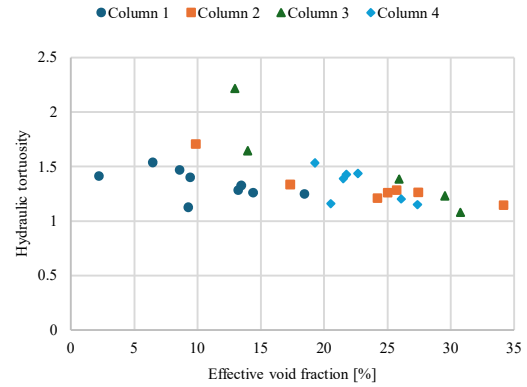
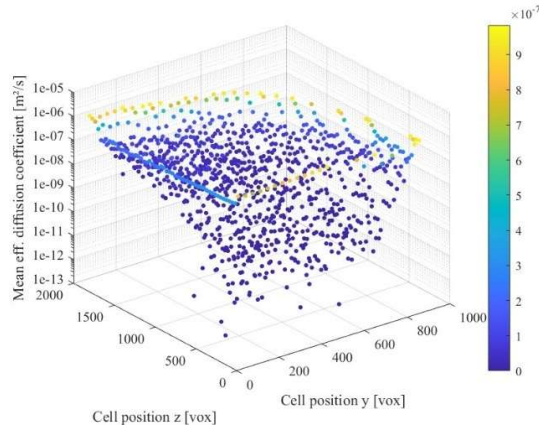


Fig. 5.10. (a) Absolute permeability-effective void fraction scatter plot, and (b) hydraulic tortuosity-effective void fraction scatter plot of ROIs in permeability analysis experiment mode.

5.3.3.4 Diffusivity Tensor Simulation

The mean effective diffusivity-geometry tensor plots shown in **Fig. 5.11** exhibit similar patterns to those in previous porosity- and permeability-geometry plots (**Figs. 5.5** and **5.6**), with diffusivity being proportional to permeability. The values also spanned by eight orders of magnitude, with the boundaries between deposit and background space reaching the default pore space diffusivity of $1\text{E-}06 \text{ m}^2/\text{s}$. However, it was noted that the distribution of data points shifted towards higher diffusivity. In other words, the variation at low diffusivity reduces despite both permeability and diffusivity being simulated with regard to the same geometry. Indeed, the diffusion in porous media should belong to anomalous diffusion, which is described by a power law with the mean squared displacement [279], and modified Fick's laws with the proportionality constant [280]. Hence, the following analysis revealed the compatibility of VGSTUDIO MAX, correlating the diffusivity and porosity.

(a) At $X = 541$ vox, diffusivity vs Y vs Z



(b) At $Y = 121$ vox, diffusivity vs X vs Z

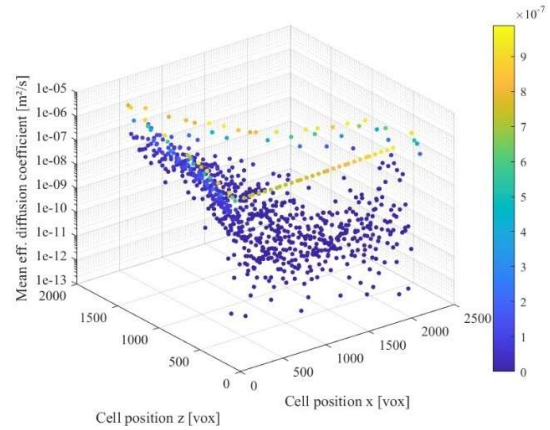
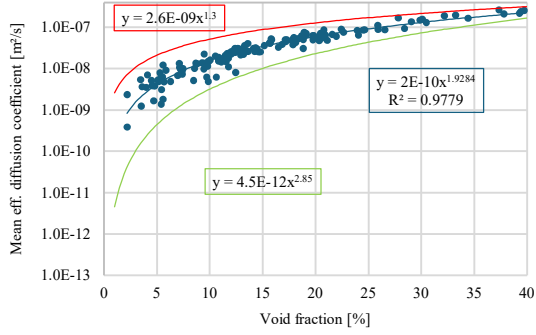


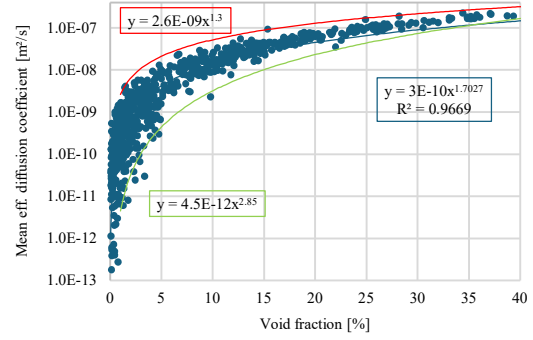
Fig. 5.11. (a) Mean effective diffusion coefficient of YZ -plane at $X = 541$ vox along cell position in Y and Z direction; and (b) mean effective diffusion coefficient of XZ -plane at $Y = 121$ vox along cell position in X and Z direction.

The diffusivity-void fraction distribution plots of YZ - and XZ -planes are displayed in **Fig. 5.12**. The power functions had R^2 above 0.95, whose deviation is much more restricted compared to that of permeability. The upper and lower bound functions were valid for covering porosity ranges of 0-40%. The coefficients of power functions were between $1.0E-10$ to $3.0E-10$ m^2/s . Meanwhile, the exponents ranged from approximately 1.7 to 2.1. The diffusivity increased above $1.0E-10$ m^2/s once the porosity exceeded 2.5%. In comparison, the organic lean mudrocks would reach this diffusivity level at a porosity of 30%. Mayoun et al. [100] reported that the hydrogen diffusivities of wrought and EBM Ti6Al4V in EHP experiments were about $3.1E-14$ and $3.5E-15$ m^2/s , respectively. The study correlated the hydride formation with the contents of α and β phases, whereas the as-built porosity was not apparent enough to be mentioned. Regardless of the deviation in the interested parameters, the diffusivity of the dense region in the cold-sprayed Ti6Al4V is barely comparable to that of mudrocks and unlikely to impede hydrogen diffusion. From this point of view, cold spraying hard metals without treatment aid is unsuitable for repairing any gas-tight components or fabricating a diffusion barrier.

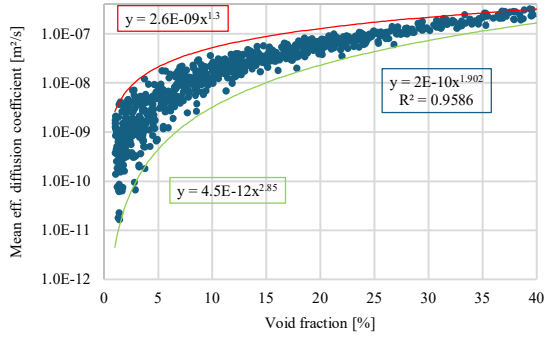
(a) X = 157 vox



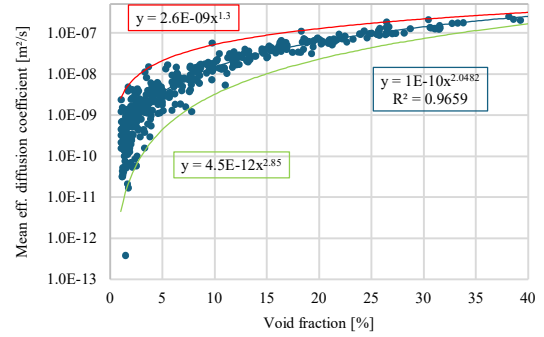
(d) Y = 121 vox



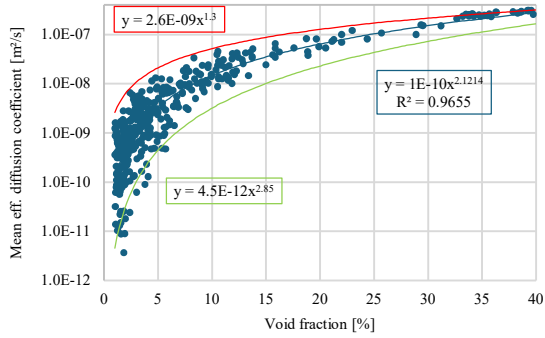
(b) X = 541 vox



(e) Y = 400 vox



(c) X = 1028 vox



(f) Y = 749 vox

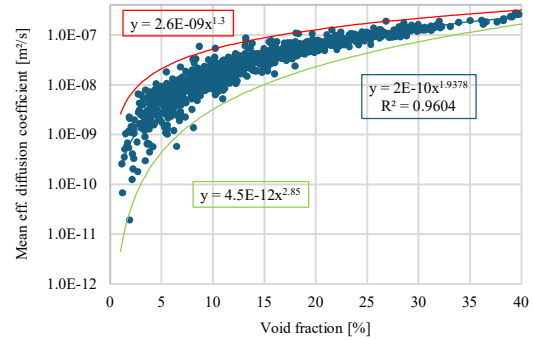
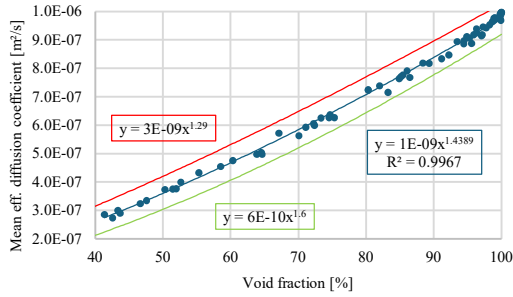


Fig. 5.12. Diffusivity-void fraction (0-40%) scatter plots of YZ-plane at (a) X = 157 vox, (b) X = 541 vox, (c) X = 1028 vox, and XZ-plane at (d) Y = 121 vox, (e) Y = 400 vox, and (f) Y = 749 vox.

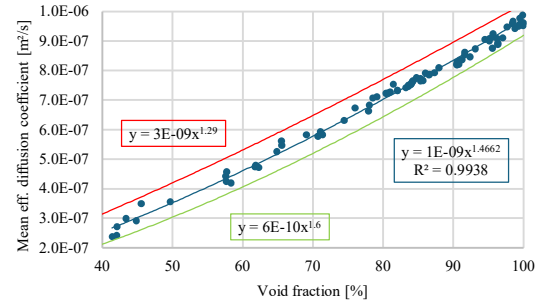
Fig. 5.13 shows the permeability power functions at porosities of 40-100%, with powers ranging from about 1.37 to 1.49, and their R^2 values are mostly 0.99. The coefficients of power functions

increased only one order of magnitude to $1.0\text{E-}9 \text{ m}^2/\text{s}$ along the rise of porosity, unlike those of permeability, which were reduced by a few orders of magnitude. This observation might be due to the different quantities of variables in the governing equations, which need the software developer to revise. In addition, the high porosity in this range is considered an illusion due to the deposit-background space boundaries or the sub-sized mesh elements located in the voids. Thus, the fitting issues between permeability and diffusivity at high porosity is not investigated further in this study.

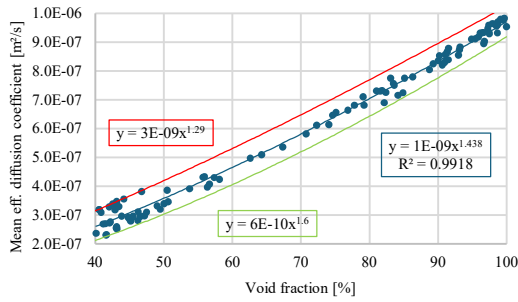
(a) X = 157 vox



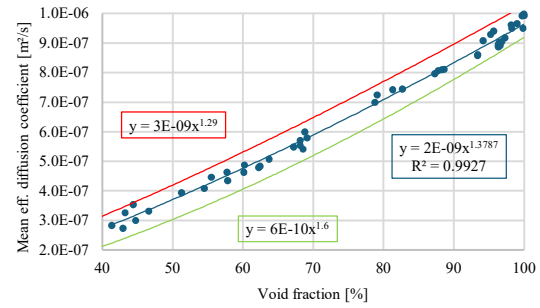
(d) Y = 121 vox



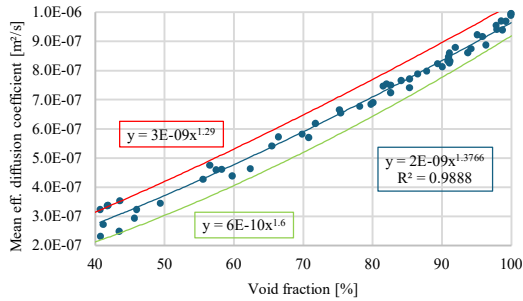
(b) X = 541 vox



(e) Y = 400 vox



(c) X = 1028 vox



(f) Y = 749 vox

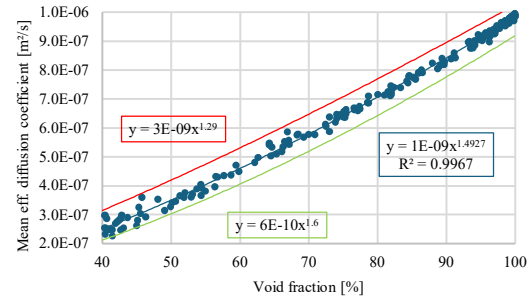


Fig. 5.13. Diffusivity-void fraction (30-100%) scatter plots of YZ-plane at (a) X = 157 vox, (b) X = 541 vox, (c) X = 1028 vox, and XZ-plane at (d) Y = 121 vox, (e) Y = 400 vox, and (f) Y = 749 vox.

The correlation between mean absolute permeability and mean effective diffusivity tensors is presented in **Fig. 5.14**. The permeability, which ranged from $\sim 1.0\text{E}+2$ to $5.0\text{E}+4$ mD, exhibited a positive linear relationship with the diffusivity, which ranged from $\sim 1.0\text{E}-9$ to $1.0\text{E}-7$ m²/s, reflecting that the transport properties could be predicted reliably at porosities ranging from ~ 2.5

to 30%. The results beyond porosity of 30% exhibited an exponential growth pattern, but the values would be elusive as mentioned previously. The pattern at porosity $<2.5\%$ was uncertain due to the unique geometrical characteristics of the deposit, the limited voxel resolution of XCT, and surface determination errors. It is necessary to demystify this variation by utilizing high voxel resolution scanning and the samples with ultra-low porosity in future studies.

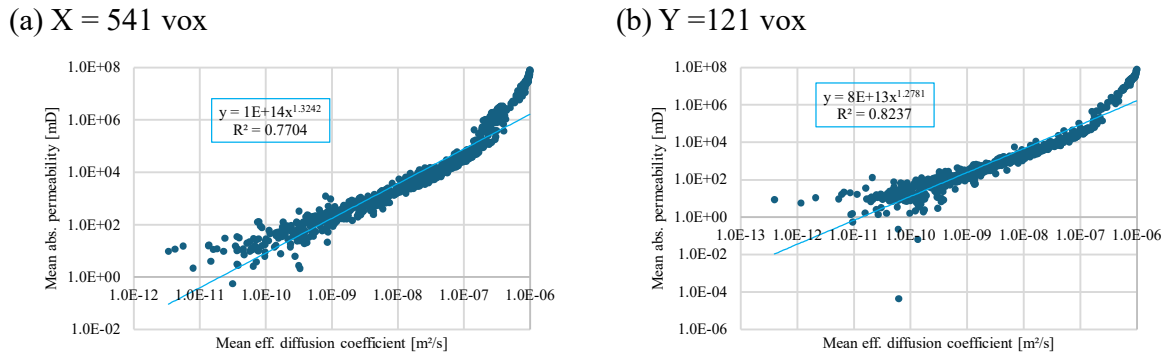


Fig. 5.14. Mean absolute permeability-mean effective diffusion coefficient scatter plot of (a) YZ-plane at $X = 541$ vox, and (b) XZ-plane at $Y = 121$ vox.

5.3.3.5 Diffusivity Experiment Simulation

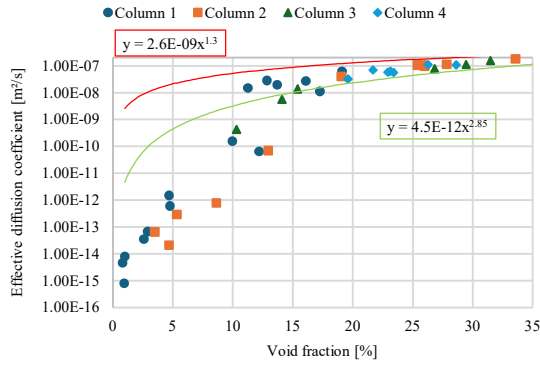
The max porosity reduced to 34% in the diffusion experiment. **Fig. 5.15a** shows the vertical effective diffusivities simulated in experiment mode, which mostly fall within the prediction interval in tensor mode at porosities of 15-35%. However, the diffusivities at porosities of ~ 1 -10% are lower than the previous prediction. It would be beneficial if the deposit is gas-tight. This observation is led by the change of formation factors at various porosity ranges. Formation factor is a parameter referring to the geometrical characteristics of a porous medium [280]. The relationship between the formation factor F_R and porosity Φ can be expressed as a power function with the pore-geometry factor a and the cementation factor m as exponent [281, 282]:

$$F_R = a\Phi^{-m} \quad (5.2)$$

The formation factor was extremely high, at $1.27\text{E}+9$, at a porosity of 0.95%, and then decreased exponentially to 35.5 at a porosity of 12.85%, as shown in **Fig. 5.15b**. There was a significant change in the coefficient and exponent in the power function at the porosity of 13%, which might reflect switching from consolidated to unconsolidated deposit in the VGSTUDIO MAX algorithms. The cementation factor indicates the reduction in the number and size of pore openings or dead-end channels [283]. The cementation factors of the deposit were about 4.86 and 3.25 at porosities ranging from 0 to 13% and 13 to 35%, respectively. This might mean the deposit being compact and well consolidated in geological perspective.

On the other hand, the pore-geometry factors $1.0\text{E}+9$ and 441038 were extremely high, as the common values would be around 1 or 2 in hydrogeology [284]. This observation is unlikely to have been triggered by tortuosity. The geometric diffusive tortuosity-void fraction scatter plot is omitted since it is remarkably similar to the one of hydraulic tortuosity-void fraction in **Fig. 5.10b**, with values of 1-1.5, except for the few ROIs at porosity $\sim 5\%$ indicated tortuosity as high as 76. This is also unlikely to be related to the limited voxel resolution of XCT and surface determination errors, since the same reconstructed model is shared with the tensor simulation. In lieu of that, such deviation should be attributed to variable consideration in the diffusion experiment algorithms, but it would be too complicated to extrapolate from the simulation output. Therefore, the diffusivity tensor is necessary to analyze the anisotropic cold-sprayed deposit despite using a longer time to compute than the experiment mode with the selected ROIs. Additionally, the experimental leak test and mechanical test would be necessary to investigate further the truthfulness of the formation factors and criteria to make such changes in the algorithm.

(a) Diffusion coefficient-void fraction



(b) Formation factor-void fraction

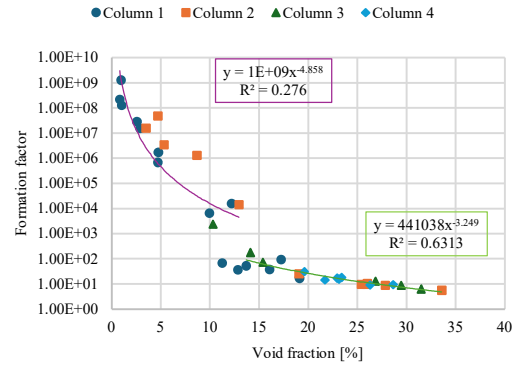


Fig. 5.15. (a) Effective diffusion coefficient-void fraction, and (b) formation factor-void fraction scatter plots of ROIs in diffusivity analysis experiment mode.

5.4. Summaries

This study investigated the fluid transport properties of a cold-sprayed Ti6Al4V deposit in a tsunami shape with a unique porosity distribution pattern due to the instantaneous zero-traverse speed of the spraying nozzle. The cold-sprayed deposit featured high porosity, irregularity and anisotropy. The reconstructed 3D porous structure was evaluated using optical micrographs-based 2D porosity analysis and measurements by an Archimedes' principle-based densitometer. Porosity, permeability, and diffusivity of the deposit were analyzed with industrial XCT and correlated statistically by power regression. The main findings based on the results are as follows:

1. The results of porosity measurement vary according to the characterization methods. The global porosity measured by the densitometer is 15%, whereas the measurements of porosity using the optical microscope and XCT experiments with selected ROIs are 35.5-54% and 1-34%, respectively. This reflects the necessity of using statistical correlation between results to examine the porosity and fluid transport properties of deposits comprehensively.

2. The transport properties can be predicted consistently by XCT tensor simulation at porosities ranging from ~2.5-30%. The permeability, which ranges from $\sim 1.0\text{E}+2$ to $5.0\text{E}+4$ mD, exhibits a positive-linear relationship with the diffusivity, which ranged from $\sim 1.0\text{E}-9$ to $1.0\text{E}-7$ m²/s.
3. The permeability (~ 1 to 10000 mD) and diffusivity ($\sim 1.0\text{E}-12$ to $1.0\text{E}-8$ m²/s) in tensor analysis deviate widely across a few orders of magnitude at porosity below 5%, where tortuosity does not show notable influence as it mostly maintained between 1-1.5 at porosity of 0-35%. It would be unrealistic to predict the exact transport property value with porosity. Still, two sets of power functions with upper and lower bounds could correlate the range of permeability and diffusivity with critical porosity at 30% and 40%, respectively.
4. The permeability analysis in experiment mode fits within the prediction range in tensor mode. However, the diffusivity analysis in experiment mode fails to align with the tensor prediction range at porosities below 13%. Due to the changing geometrical characteristics around the 13% porosity, the formation factor significantly drops from 10000 to 100. The drastic change of the formation factor at critical porosity in the algorithms would require further investigation with experimental leak and mechanical tests.

Chapter 6: Enhancing Ductile and Adhesive Performance of Cold-sprayed Ti6Al4V Coatings by Multi-Step Vacuum Heat Treatment

6.1. Introduction

As reviewed in **Section 2.6**, multiple heat treatment strategies have been proposed to enhance the ductility of Ti6Al4V, including prolonged high-temperature heat treatment, MSHT, and THRM. Notwithstanding, a reliable heat treatment strategy has not been available to guarantee ductility enhancement of cold-sprayed Ti6Al4V for aircraft repair.

This study investigated the feasibility of using MSHT in both vacuum and hydrogen atmospheres to enhance the ductility and adhesion of cold-sprayed Ti6Al4V. The spraying preparation used N₂ and He as separate carrier gases. A three-point bending test revealed that the cold-sprayed Ti6Al4V, using N₂ gas and a SiC nozzle, followed by MSHT in a vacuum, exhibited ductility that outperformed all cold-sprayed counterparts. The samples were characterized by OM, microhardness test, XRD, EDS line scan, SEM on fracture morphology, and etched microstructure. The spraying parameters were promising for ejecting a stable supersonic flow and depositing Ti6Al4V coatings with acceptable defects. Despite increasing the porosity, the MSHT in vacuum ensured the formation of a fine equiaxed microstructure as well as diffusion bonding at the IPB and the coating-substrate boundary. The limitations on He-sprayed coatings and the consequences of hydrogen charging were also discussed. The outcome of this study would advance cold spray repair and subsequent processing on an industrial scale for commercial aviation and other applications.

6.2. Methodology

6.2.1 Materials & Sample Preparation

The cold spray process was conducted using a high-pressure system (PCS-100, Plasma Giken, JP) mounted on the 5-axis robot arm (4600, ABB, CH). The spraying parameters are summarized in **Table 6.1**. The morphology captured by SEM and the size distribution of the powder analyzed by ImageJ [248] are presented in **Fig. 6.1**. Powder feeder instability, possibly due to nozzle clogging, occurred in the trial spraying with He gas. The cold-sprayed plates were face-milled (STC 800, Starrag, CH) to obtain 2 mm thick coatings, then cut into three-point bending test subsize specimens with high-pressure waterjet (5555, OMAX, US). The IDs of specimens were laser marked (YLP-K20-CS, Han's Laser, CN) to avoid the vaporization and contamination of ink during heat treatment.

Table 6.1. Cold spray process parameters.

Parameter	Group He	Group N ₂
Carrier Gas	He	N ₂
Gas Pressure	3 MPa	7 MPa
Gas Temperature		900°C
Feedstock powder	Ti6Al4V (Gas-atomized, Plasma Giken, JP); d_{avg} : 4.78 μ m	
Substrate	CP-Ti; sprayed area: 150 x 120 x 5 mm	
Nozzle Material		SiC
Nozzle Divergent Section Length		300 mm
Nozzle Throat Diameter		2 mm
Nozzle Traverse Speed		0.8 m/s
Spraying Loops		14
Toolpath	Horizontal snake pattern with a stepping distance of 1 mm. U-turn sections were positioned 40 cm away from the side edges of the substrates to prevent thick-porous deposition induced by the deceleration and acceleration of the nozzle.	

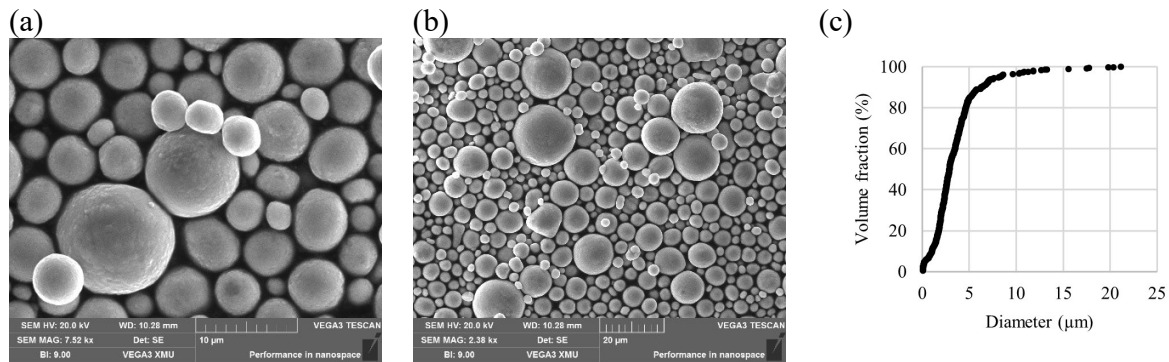


Fig. 6.1. SEM images of Ti6Al4V feedstock powder at magnification of (a) 7520x, (b) 2380x, and (c) size distribution measured at 2380x.

6.2.2 Multi-Step Heat Treatment

MSHT-VAC was performed in a vacuum sintering furnace (Vesta, Shimadzu, JP), while MSHT-THP was performed in a tubular furnace (KTL-1200, LAB Technology, CN) with a safety pressure limit of 121 kPa and an exhaust gas tube connected to a water bottle to cool and visualize the released gas. Quartz boats were used to contain specimens in the quartz tube. The coating side of the specimens was facing down, allowing the weight of the substrate to hold the coating in place and prevent delamination. The temperature-time profiles of MSHT in both atmospheric settings are plotted in **Fig. 6.2**. The tubular furnace was first evacuated using a rough vacuum pump at 7kPa, followed by manual pumping of Ar gas to 111 kPa. The heat-up rate was as slow as 3.1°C/min to prevent delamination of coatings due to a mismatch in CTE. The safety valve was set at 117 kPa to release gas when the gas expanded up to the limit. After the temperature reached 950°C, a continuous hydrogen flow at 111 kPa was fed into the tubular furnace. A one-off purge of Ar replaced the remaining hydrogen gas beyond the hydrogen charging stage. The gas supply was stopped in the cooling process afterwards. The safety valve was triggered occasionally if the desorbed hydrogen from samples reached the pressure limit of 117 kPa. The internal pressure eventually dropped to ~55 kPa after the samples were furnace-cooled to room temperature.

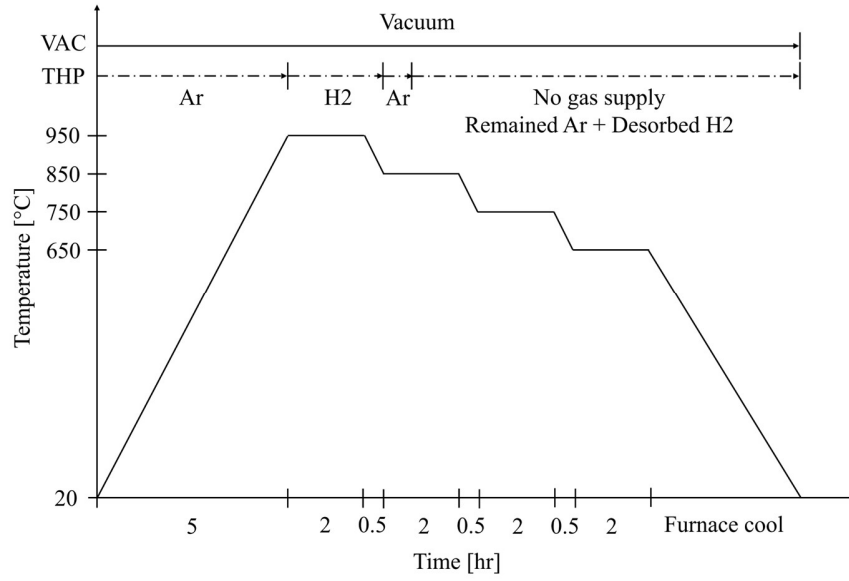


Fig. 6.2. Temperature-time profiles of the MSHT-VAC and -THP settings modified from [214].

6.2.3 Three-Point Bending Test

The ASTM D790-17 [285] three-point bending test was conducted with the universal testing machine (Alliance RT/50, MTS, US) at a test speed of 0.1 mm/min ($4.375\text{E-}5 \text{ s}^{-1}$ for sprayed specimens and $3.125\text{E-}5 \text{ s}^{-1}$ for substrate only). The transducer of the load cell had an accuracy of 0.001 kN and 0.001 mm. A standard metric steel ruler was used to measure the geometries of samples to the nearest mm. The setup of the bending test and the dimensions of the specimen are shown in **Fig. 6.3**. The coating was subjected to the loading pin in a compressively loaded configuration [66]. This setup was chosen instead of tensile-loaded bending because the cold-spray-repaired section of the component would be more susceptible to damage than the other side of the substrate in the real-world operation. The fracture morphologies were observed with SEM (VEGA 3, Tescan, CZ). The flexural stress-strain curves were calculated with the following equations:

$$\text{Flexural stress: } \sigma_f = \frac{3PL}{2bd^2} \quad (6.1)$$

$$\text{Flexural strain: } \varepsilon_f = \frac{6Dd}{L^2} \quad (6.2)$$

$$\text{Bending modulus: } E_B = \frac{L^3 m}{4bd^3} \quad (6.3)$$

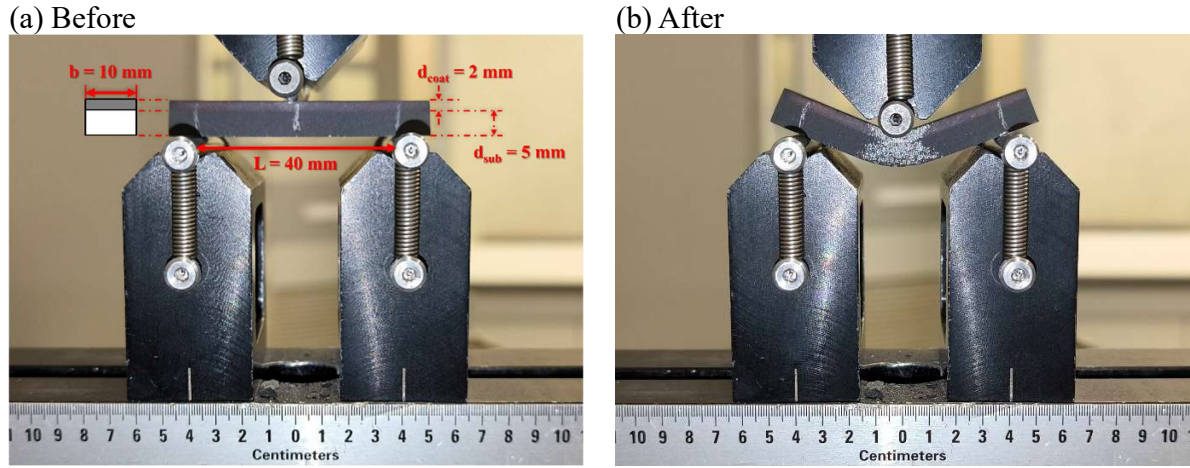


Fig. 6.3. Photos of the setup of the three-point bending test (a) before and (b) after the test.

6.2.4 Characterization

The low-power laser cleaning (CL 100, CleanLASER, DE) was used to remove surface impurities, including oxides, on the XRD coating samples, which were challenging to grind with grit paper. The sample phases were then analyzed by an X-ray diffractometer (SmartLab 9kW, Rigaku, JP) with parallel beam focusing, $\text{CuK}\alpha$ radiation source ($\lambda = 1.54 \text{ \AA}$). The scan was within the range of $2\theta = 20\text{--}90^\circ$. The dwell time was 5 seconds with an increment of 0.02 degrees. The peaks of the spectra were recognized with the open-sourced tool Profex [235].

Samples were waterjet cut into slices with a thickness of 1-3 mm for microstructural characterizations after the three-point bending test. The sample slices in the epoxy resin holder were ground using a semi-automatic grinder polisher (Abramin, Struers, DK) and SiC paper, progressing from 120 to 2000 grit. They were then polished with $0.05 \text{ }\mu\text{m}$ Al_2O_3 polishing suspension to achieve a mirror finish. The cross-sectional microstructure of samples was captured

with a digital microscope (VHX-5000, Keyence, Japan). HV0.5 Vickers microhardness test (TUKON 1102, Wilson Hardness, US) was performed on the cross-section of coatings near the top surface and interface boundary with a dwell time of 10 seconds.

The sample slices were then removed from the epoxy resin holder with a vice and cleaned in an ultrasonic cleaner with a mixture of distilled water and ethanol (10:1) for 30 minutes. To prevent the influence of heat, the cleaned sample slices were dried with compressed air, then stored in sealed bags with dehumidifying packs. The SEM (VEGA 3, Tescan, CZ) equipped with EDS (AZtec, Oxford Instruments, UK) was used to perform line-scan analysis across the coating-substrate interface. The sample slices were then immersed in a weakened variant of ASTM E407-23 etchant #218 (3 g NH_4F , 4 mL HCl , 100 mL water) for 1 min to characterize the microstructure of phases [286].

6.3. Results & discussion

6.3.1 Flexural Properties

The three-point bending test results of cold-sprayed specimens are presented in **Fig. 6.4a**, where the ultimate flexural strengths and moduli are summarized in **Table 6.2**. In general, coatings sprayed with lighter and faster He gas are considered stronger than those sprayed with N_2 gas; however, the subsequent SiC nozzle clogging and powder feeder instability led to severe underperformance in this study. The brittle as-sprayed coatings, N_2 - and He-AS, failed at around 1% and 3%, respectively. The N_2 -VAC was the only specimen exhibiting ductile deformation without fracture. The bending load was stopped at an 18.5% strain, as the sample almost touched the side edges of the pin holder, as shown in **Fig. 6.3b**. The crosshead had displaced 4 mm at its UFS of 887 MPa. This performance was comparable to that of the SLM-MSHT Ti6Al4V by Li et

al. [214], which achieved a UTS of 953 MPa and an elongation of 21.8% in the tensile test. However, the same MSHT in vacuum could not make the He-VAC ductile. The UFS of He-VAC was 422 MPa at a strain of 1.328%, followed by an oscillating curve, as the coating collapsed due to loose compaction failure, a phenomenon commonly observed in conventional powder metallurgy. Hence, the effectiveness of ductility enhancement on cold-sprayed Ti6Al4V is critically limited by the quality of the as-sprayed material. The addition of hydrogen supply to MSHT did not improve the performance of either the N₂ or He sprayed samples, but rather deteriorated them, weakening them to a greater extent than their as-sprayed states, as indicated by the plotted graph at approximately 30 and 40 MPa, respectively. In fact, the N₂ and He sprayed coatings did not fall apart like a sandcastle as the He-VAC, but well adhered to the substrates after the samples were split in half. This phenomenon is unexpected as CP-Ti is considered to be ductile and less susceptible to hydrogen-related damage than its alloys. Thus, the bulk CP-Ti and Ti6Al4V samples were also extensively tested.

The three-point bending test results of N₂-VAC, CP-Ti, and Ti6Al4V reference specimens are compared in **Fig. 6.4b**. Concisely, the most ductile sample, N₂-VAC, was far from reaching the wrought or MSHT-THP properties of Ti6Al4V. The bending modulus of the N₂-VAC was only 40 GPa, which was way lower than that of CP-Ti-AS (95 GPa) and CP-Ti-VAC (79 GPa). Beyond the strain of 4%, the stress-strain curve of N₂-VAC almost overlapped with those of CP-Ti-AS and CP-Ti-VAC, which also deformed without fracture. On the other hand, CP-Ti became brittle after MSHT-THP, which failed at 645 MPa and a strain of 1.126%. Hydride formation is unlikely to have contributed to the embrittlement, given the at least 6 hours of degassing time during the cooling stages in MSHT, as well as the absence of β grains. The embrittlement of CP-Ti-THP was caused by over-grown grains and the subsequent rapid reduction of the shielding effect strength

[287]. The reasons behind these mechanical behaviors were further investigated along with the fracture morphologies and other characterizations. In addition, the Ti6Al4V-THP was more ductile than the Ti6Al4V-VAC, with fracture strains of 12.731% and 4.346%, respectively. This means that the MSHT-THP treated parts would also require longer aging times or excessive hardening procedures to regain their wrought strength.

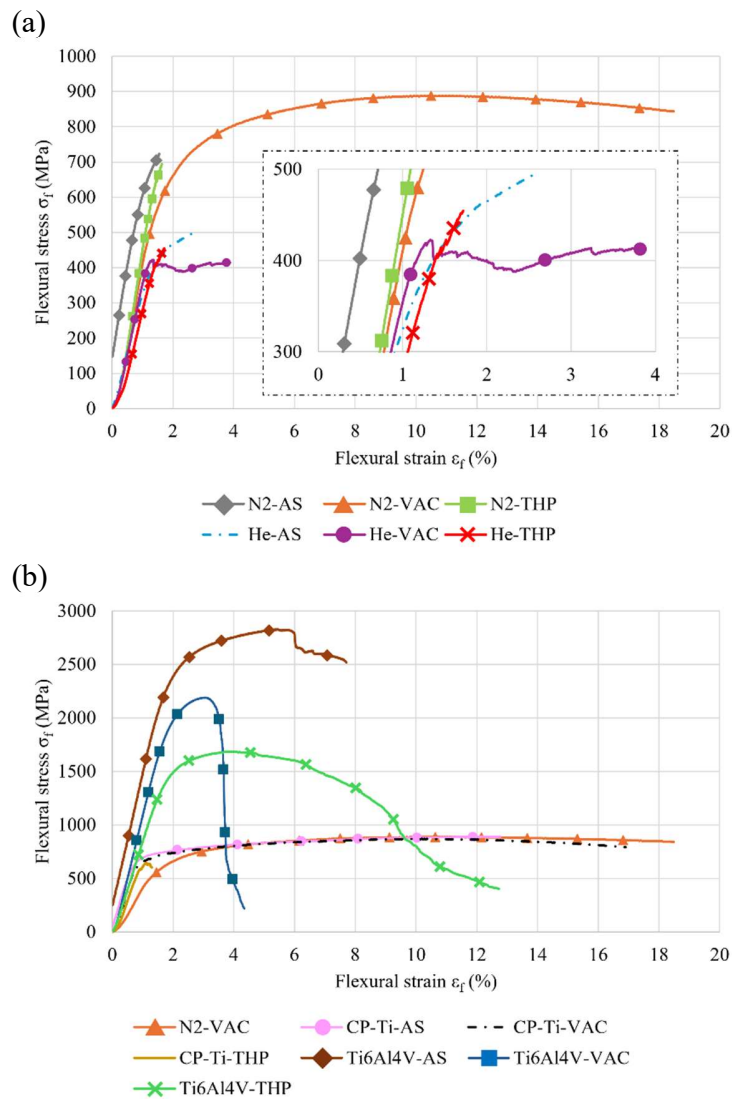


Fig. 6.4. Stress-strain profiles of (a) N₂ and He cold-sprayed Ti6Al4V coatings on CP-Ti substrates, and (b) wrought CP-Ti and Ti6Al4V in as-sprayed, MSHT-VAC and -THP conditions.

Table 6.2. UFS and bending moduli of specimens.

Sample	Ultimate flexural strength σ_{fM} (MPa)	Ultimate flexural strain ϵ_{fM} (%)	Bending modulus E_B (GPa)
N ₂ -AS	722	1.546	52
N ₂ -VAC	887	11.111	40
N ₂ -THP	694	1.635	42
He-AS	496	2.627	32
He-VAC	422	1.328	35
He-THP	454	1.719	28
CP-Ti-AS	891	12.740	95
CP-Ti-VAC	870	9.939	79
CP-Ti-THP	645	1.126	65
Ti6Al4V-AS	2827	5.465	123
Ti6Al4V-VAC	2189	3.056	109
Ti6Al4V-THP	1686	3.858	84

6.3.2 Fracture Mechanisms

6.3.2.1 Fragility of as-sprayed coatings

Fractography of specimens is presented in **Fig. 6.5**. The brittle as-sprayed coatings N₂-AS (**Fig. 6.5a**) and He-AS (**Fig. 6.5d**) struck the surroundings when they were delaminated from the substrates. The cracks only occurred within the coatings, where the CP-Ti substrates bent by only 1-2% in strain. The possibility of coatings delaminating on either one or both sides randomly depended on the defects in the coating-substrate interface of individual specimens. The coatings did not fly off in the study by Tan et al. [65], as the configuration of the three-point bending test loaded on the substrate subjected the coatings to tension and held them in place by supporting pins. The heretofore concept is that tension could break cold-sprayed coatings more easily than compression with the same load [66]. This study found that the debris of compressively bent coatings was actually more dangerous. The SEM image of the coating fracture surface on the He-AS (**Fig. 6.5e**) revealed severe plastic deformation with excess material jetting. In contrast, the particles in the N₂-AS (**Fig. 6.5b**) had less flattening and a smoother surface but with craters by

debonding. The south rim and protruded south pole of the splat with a smooth surface were observed at the bottom of delaminated N₂-AS, as shown in **Fig. 6.5c**. It is considered that the N₂-AS is just reaching critical velocity with very little adiabatic shear [62, 288]. The smooth bottom of splats also reflects the lack of mechanical interlocking, leading to weak adhesion [60]. The bottom of He-AS (**Fig. 6.5f**) was mainly flat with few trenches due to severe deformation above critical velocity and squeezing with surrounding splats. He-AS should be stronger than N₂-AS according to the magnitude of particle deformation, but the high porosity in He-AS induced by nozzle clogging led to a weaker strength, which was reflected in the three-point bending test. The IPB and the coating-substrate interface relies on the ASI, which is insufficient to consolidate coatings with integrity. In brief, the as-sprayed Ti6Al4V deposits should not be used for repairing Ti-aircraft components. In addition to its fragility, the rapid delamination speed of coatings can lead to debris strikes on other parts, resulting in more severe damage. However, it would be feasible as a near-net-shape powder pre-compaction method followed by appropriate heat treatment.

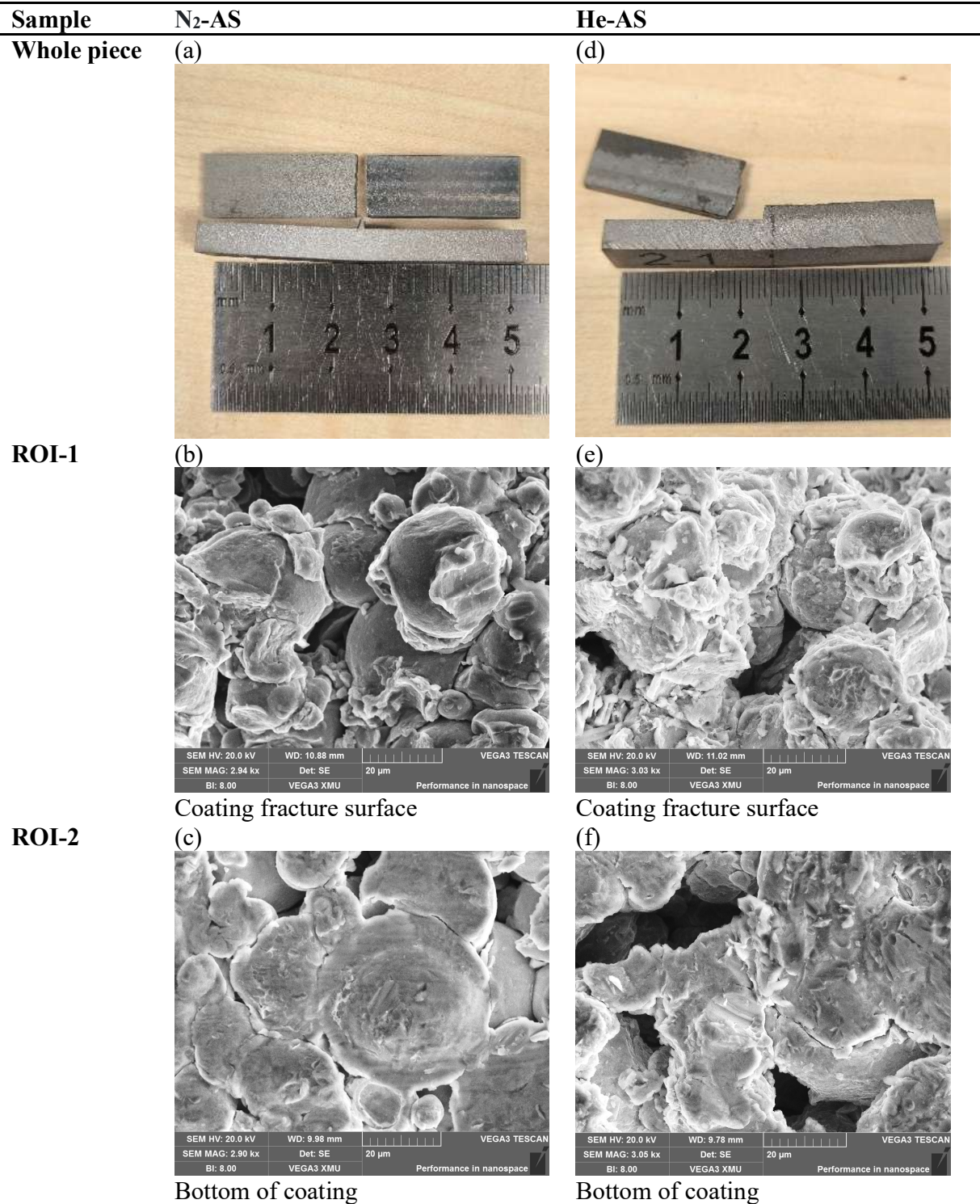


Fig. 6.5. Fracture morphologies of (a-c) N₂ and (d-f) He cold-sprayed Ti6Al4V coatings on CP-

Ti substrates in as-sprayed conditions.

6.3.2.2 Feasibility of ductility and adhesion enhancement

Since N₂-VAC (**Fig. 6.6a**) did not fracture due to its outstanding ductility and adhesion, only the side interface was observed. There was no apparent material squeezing out on the cross-sectional sides, unlike wrought CP-Ti, upon bending to a crosshead displacement of 7 mm. In lieu of that, the oxide debris was peeled off by subjecting it to compression, which also visualized the stress-affected zone of ~5 mm away from the bending load centerline. Although there was no horizontal crack along the coating-substrate interface in **Fig. 6.6b**, there actually were many vertical microcracks across two layers. This indicates that, although the diffusion bonding at the interface has high integrity compared to other samples, the CP-Ti substrate becomes somewhat brittle after the MSHT-VAC process. The cleavage facets through the particles and substrate grains in **Fig. 6.6c** were transgranular cracks denoting brittle fracture. Meanwhile, there were dimples on fracture particles denoting ductile fracture. Hence, it should be defined as a mixed-mode fracture leaning towards ductile fracture [289]. Considering the brittle nature of both cold-sprayed deposit and wrought Ti6Al4V, the ductility of N₂-VAC is superior beyond expectation.

On the other hand, He-VAC coating broke into agglomerates and powder after the same MSHT, as shown in **Fig. 6.6d**. The sudden drop of stress from 421 to 404 MPa at a strain of 1.35% in **Fig. 6.4a** indicates the crushing of the coating. The fluctuations around 400 MPa denote the compaction of the loose powder. After terminating the bending test, the powder could be easily shaken off the coating. The collapse of the He-VAC coating, accompanied by agglomerates and fine powder, indicates unevenness in the diffusion bonding process. Zhou et al. [70] suggested that pores can be shrunk or expanded simultaneously by heat treatment, depending on the contact area and strength of interparticle bonding. There are excess weakly bonded particles and unbonded regions induced by nozzle clogging. **Fig. 6.6e** shows the large voids and interlayer cracks on the coating

fracture surface. **Fig. 6.6f** shows a flattened powder remaining on the substrate surface, where the surrounding powder has been crushed and detached by the bending load. When the strong interparticle bonds undergo necking and densifying, the atoms diffuse away from the weakly bonded and unbonded regions. Consequently, the weak interface detaches, and the pores expanded, eventually becoming interconnected. The enhanced strength by diffusion bonding could not overcome the loss due to pore expansion. Therefore, the He-VAC is even weaker than its as-sprayed state, as displayed in **Fig. 6.4a**.

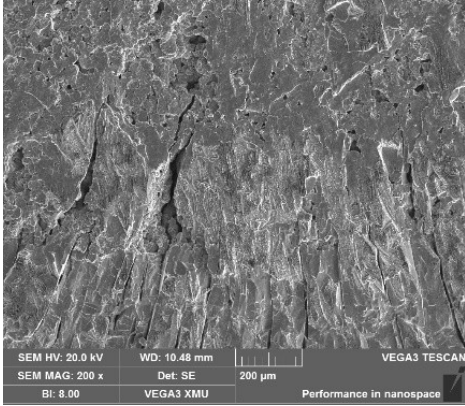
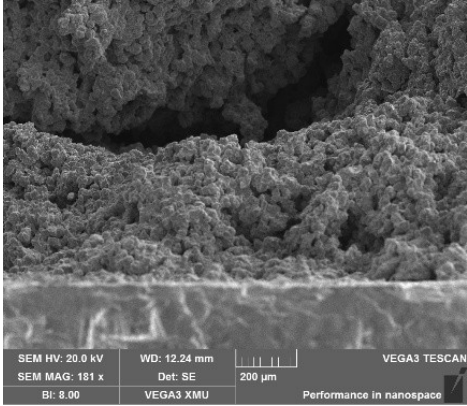
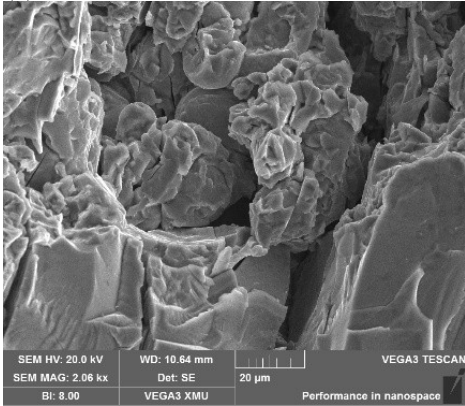
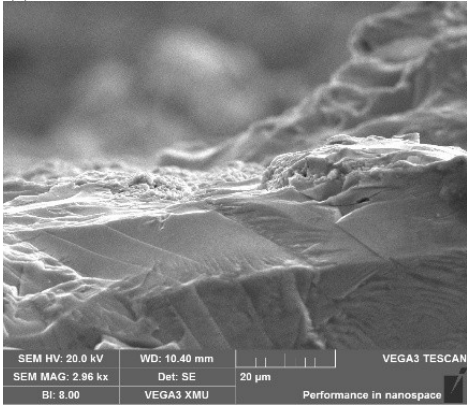
Sample	N ₂ -VAC	He-VAC
Whole piece	(a) 	(d) 
ROI-1	(b) 	(e) 
ROI-2	(c) Side interface 	(f) Coating fracture surface Substrate cut surface 

Fig. 6.6. Fracture morphologies of (a-c) N₂ and (d-f) He cold-sprayed Ti6Al4V coatings on CP-Ti substrates in MSHT-VAC conditions.

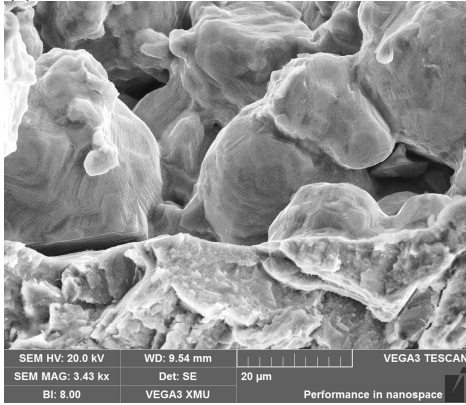
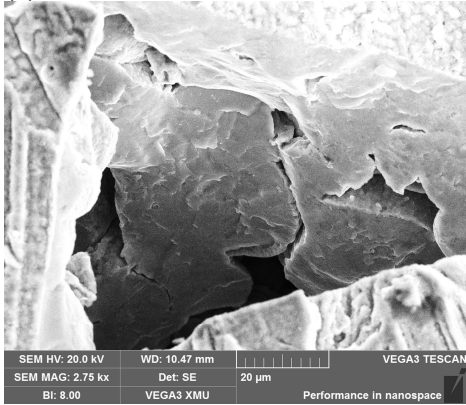
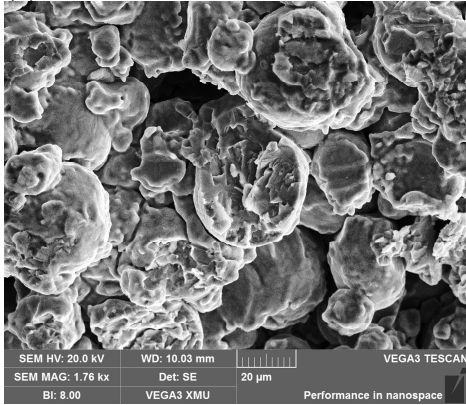
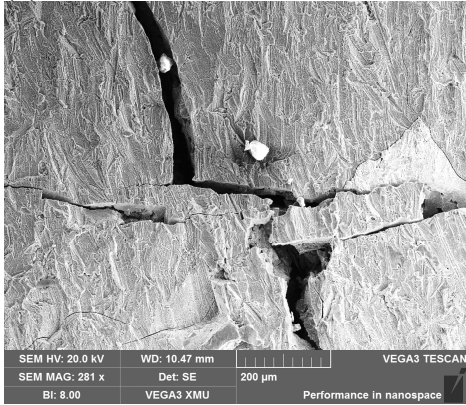
6.3.2.3 Effects of hydrogen on microstructural evolution

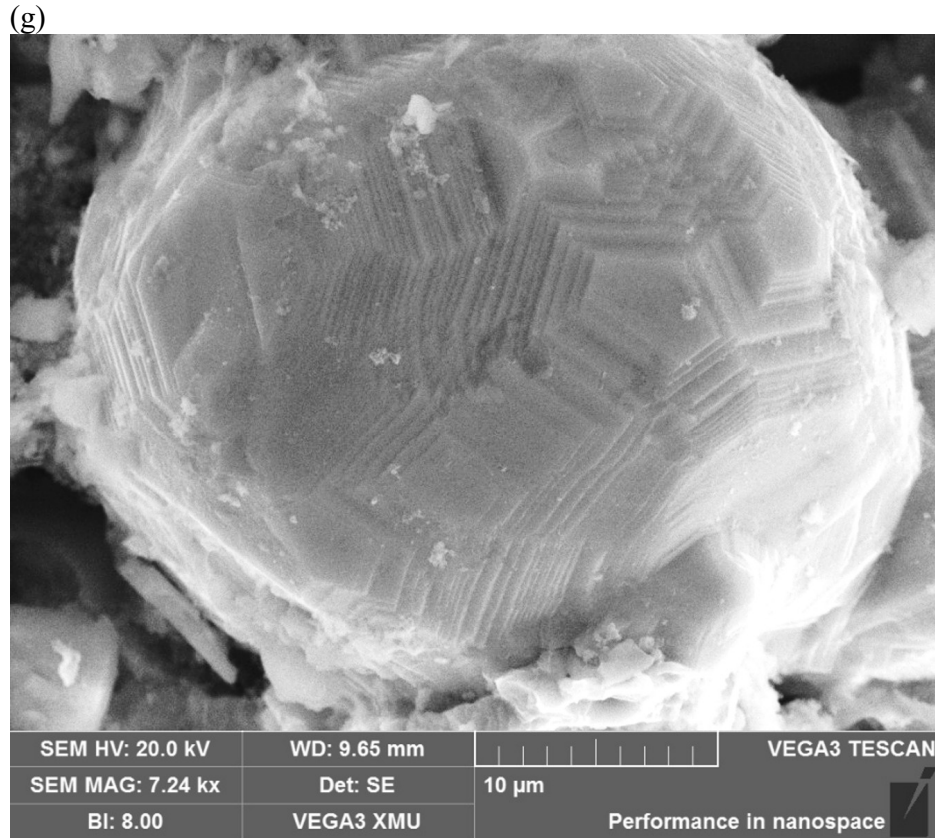
The addition of hydrogen in the MSHT process resulted in the embrittlement of CP-Ti substrates. The crack in N₂-THP (**Fig. 6.7a**) initiated at the bottom of the substrate and propagated across the coating-substrate boundary (**Fig. 6.7b**) but stopped at ~200 µm below the top surface of the coating. Although the energy dissipation rate was fast, the coating was still able to hold the sample from splitting into pieces. The oxide on the cross-sectional sides of the coating, where the oxide on the substrate was peeled off slightly, whereas the oxide on the substrate remained intact without material extruding from the compressed region. The zoomed-in image of the side interface in **Fig. 6.7c** showed the void formed after debris fell off, where the fracture was neatly across the horizontal centre plane of particles. The absence of a fully equiaxed structure could be deduced from this transgranular damage. Although the grain morphology could not be confirmed with this fractographic image, the necking at strong interparticle bonds demonstrate that diffusion bonding is triggered to strengthen the coating and enhance adhesion. The microhardness test and microstructure analysis in the later sections would further elucidate the impact of hydrogen charging in MSHT.

He-THP was divided into half with very coarse grains on the substrate, as shown in **Fig. 6.7d**. The coating could not withstand the energy dissipation since the He-sprayed coatings with nozzle clogging were more porous than the N₂-sprayed coatings. **Fig. 6.7e** shows the interparticle necking and dimples on the fractured particles, indicating that the heat treatment enhanced the ductility. There are actually weak bonds and unbonded regions in the surroundings, but it is surprising that hydrogen charging avoided the coating from detaching rapidly or collapsing into powder. The fracture surface at the coating-substrate interface in **Fig. 6.7f** shows there are turtle shell layer patterns on the intact particles in addition to diffusion bond necking, which are not seen at the

upper region of the coating. The particles at the coating-substrate interface underwent more severe deformation, allowing them to store energy and proceed with static recrystallization during heat treatment [290]. A similar pattern was observed on the N₂-sprayed Ti6Al4V heat treated at 1000°C for 4 hours by Vo et al. [14]. Still, those GB were curvy, possibly because the globularization of α grains did not have time to recrystallize into major-equiaxed structure. The recrystallization dynamics of both N₂- and He-THP samples are benefited from lower β transformation temperature by hydrogen charging and longer recrystallization time in MSHT. A closer look at the Ti6Al4V particle in the He-THP coating (**Fig. 6.7g**) reveals the presence of twins in the pentagonal α_2 Ti₃Al grains. The surface pentagons had a height of $\sim 5 \mu\text{m}$, then enlarged layer-by-layer. Heat treatment at 950°C or near β -transus temperature is known to form pentagonal α_2 grains on deformed Ti6Al4V, i.e., hot-compressed, cold-sprayed, and THP [205, 291-293]. These α_2 grains, in larger sizes, generally contribute to lower strength and higher ductility, whereas vice versa [291]. Indeed, both N₂- and He-THP samples might have higher flexural strength than the as-sprayed and MSHT-VAC counterparts if the CP-Ti substrates remained ductile. The embrittlement of CP-Ti in the MSHT-THP process would be elaborated in the analysis of the etched microstructure. Nevertheless, this study would be the first to capture the morphology of pentagonal α_2 grains in Ti6Al4V particles, thanks to the excess unbonded regions due to nozzle clogging.

Sample	N ₂ -VAC	He-VAC
Whole piece	(a)	(d)
ROI-1	(b)	(e)
ROI-2	(c)	(f)
	Side interface	Coating fracture surface
	(c)	(f)
	Side interface	Interface fracture surface





Particle near the interface fracture surface in He-VAC

Fig. 6.7. Fracture morphologies of (a-c) N₂ and (d-g) He cold-sprayed Ti6Al4V coatings on CP-Ti substrates in MSHT-THP conditions.

6.3.3 Pore structure evolution

This study used a relatively time-saving and accessible OM method to characterize the porosity of samples. The ROIs, with a total height of ~1350 μm, were located directly above the coating-substrate boundaries, as shown in **Fig. 6.8**. The magnification was set at 200x to strike a balance between minimizing the influence of local porosities and preventing image curvature at low magnification. The N₂- (**Fig. 6.8a**) and He-sprayed coatings (**Fig. 6.8d**) had porosities of 5% and 28%, respectively. Despite the varied spraying parameters, the porosity of N₂-AS was similar to that of 5.6% reported by Lett et al. [205] and 5-12% reported by Vo et al. [14]. Heretofore, the use of He as carrier gas has been preferred to obtain higher particle speed and dense coatings. The

glass spraying nozzle is required to propel a stable He jet and deposit a dense coating of hard metals [294], but the metal powder would wear out the nozzle within half an hour. On the other hand, using a ceramic nozzle with He gas would lead to nozzle clogging or powder feeder instability, resulting in porous coatings, as in this study. Nitriding powder could be a solution, but the stock powder and necessary nitridation instruments might not be readily available [213]. The preference for using N₂ is primarily an economic concern about the cost of He gas rather than a stability concern of the solid-gas dynamics. Although the high porosity of He-sprayed coatings enables the morphology observation of pentagonal α_2 grains, the structural repair in real-world engineering would demand dense deposits and sustainable processing. The previous three-point bending test had already demonstrated that neither N₂- nor He-sprayed coatings could be qualified for structural repair in their as-sprayed state. Thus, the navigation of hard metals cold spraying should be a compaction stage instead of a direct forming process. In the light of practicality, N₂ carrier gas and a ceramic nozzle would be adequate for cold spraying hard metals and proceeding with post-spray treatments.

Unlike literature reporting reduced porosity after heat treatment [13, 14, 197-200, 204, 205, 208, 295], the porosity of samples increased dramatically after heat treatments in this study, as shown in **Fig. 6.8b** and **e**. This is referred to as the “arrested contraction stage” during heat treatment by Zhou et al. [70]. The detachment of weakly bonded surfaces leads to the expansion of pores with rising temperature. If the coatings are dense enough, the detachment would be negligible. For the porous coating, it would undergo a “free contraction stage” to slowly close the pores and evolve into a bulk piece. However, the MSHT-VAC does not use high pressure like HIP to compress the voids. The atomic diffusivity at 950°C might be sufficient to facilitate diffusion and recrystallization of grains. However, the evolution of pore structure was still in the middle of the

“arrested contraction stage”. Hence, the porosities of N₂- and He-VAC were about double that of their as-sprayed conditions. THP is supposed to reduce the porosity of Ti alloy castings and builds, where the rise of porosity has not been reported [26, 27, 296]. The porosities of N₂-THP in **Fig. 6.8c** and He-THP in **Fig. 6.8f** are similar to their corresponding MSHT-VAC counterparts. Hence, the hydrogen charging has a limited influence on the porosity at the OM scale.

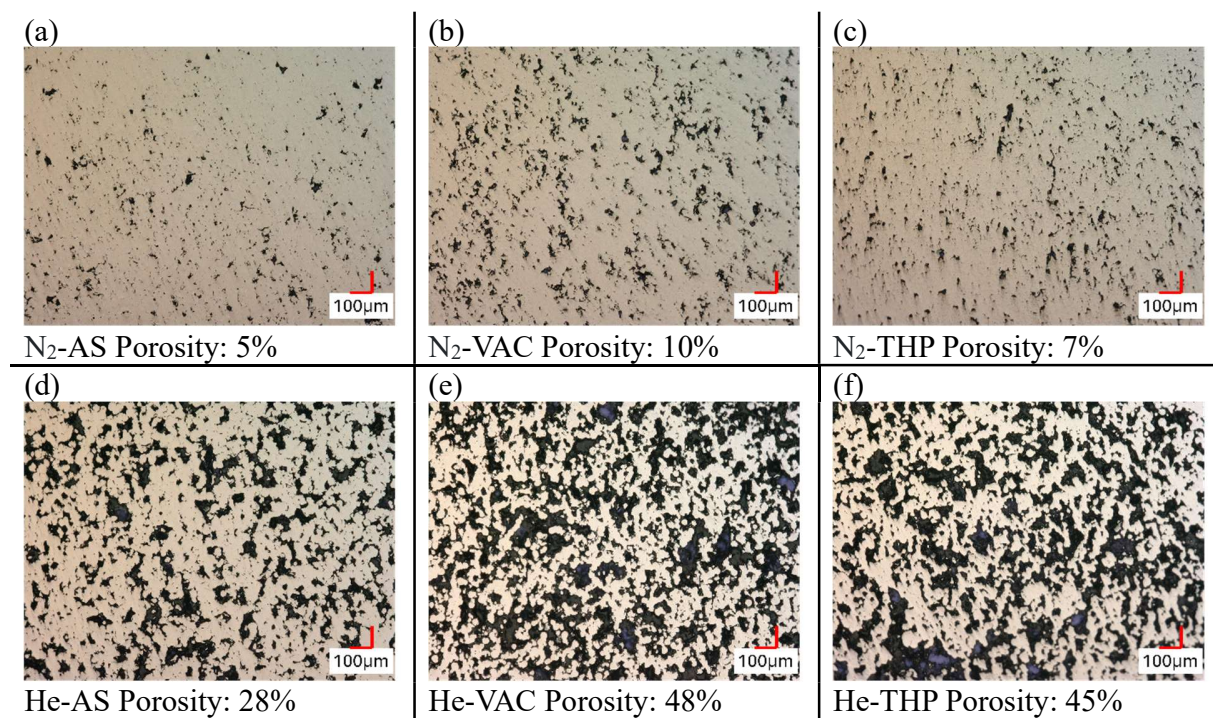


Fig. 6.8. OM images of the (a-c) N₂- and (d-f) He-sprayed coatings in AS, MSHT-VAC and -THP conditions with porosity measurement at magnification of 200X.

Despite the cause of the rise in porosity by THP remaining unclear, the effects of both MSHT-VAC and THP on the coating-substrate boundaries were significant. The coating-substrate boundaries of N₂-AS and He-AS were apparent, as shown in **Fig. 6.9a** and **d**, respectively. The flat boundaries indicate the bonding is mostly metallurgical rather than mechanical intermixing [60], which aligns with the characterization in **Fig. 6.5**. The coating-substrate interface of N₂-VAC exhibited a blurry diffusion bonding with a height of about 20-40 μm, as shown in **Fig. 6.9b**. This

diffusion bonding prevents the coatings from delaminating, even after being bent from flat to 140°. There were grinding artifacts on the substrate, where the grains of CP-Ti had not yet appeared. The charging of hydrogen results in a more textured diffusion bond. It reveals the large lamellar α grains in the CP-Ti substrate, as shown in **Fig. 6.9c**. Sun et al. [287] stated that the accelerated ductile-brittle transition of CP-Ti began at a grain size of $\sim 50\text{ }\mu\text{m}$ with fracture elongation of 30%, which decreased further to 12.5% at a grain size of $107.7\text{ }\mu\text{m}$. The lamellar α grains after MSHT-THP had grown larger than the cold-sprayed particles and the $50\text{ }\mu\text{m}$ scale bar. Hence, it was reasonable that the MSHT-THP samples with CP-Ti substrate were severely embrittled and broke in half at a strain of 1%, as shown in **Fig. 6.4a** and **b**. On the other hand, **Fig. 6.9e** shows that the interfacial diffusion bond between a few particles and substrate in He-VAC is only about $10\text{ }\mu\text{m}$ thick. The adhesion was just enough to hold the near-substrate layer on the substrate when the coating at the upper region was crushed into powder and agglomerates. The necking at the coating-substrate interface proves that hydrogen charging improved the diffusion bonding of the He-sprayed coating, as shown in **Fig. 6.9f**. However, the lamellar α grains could not be seen with the grinding artifacts. Thus, the grain structures were studied extensively using EDS line scans and SEM images of etched microstructures.

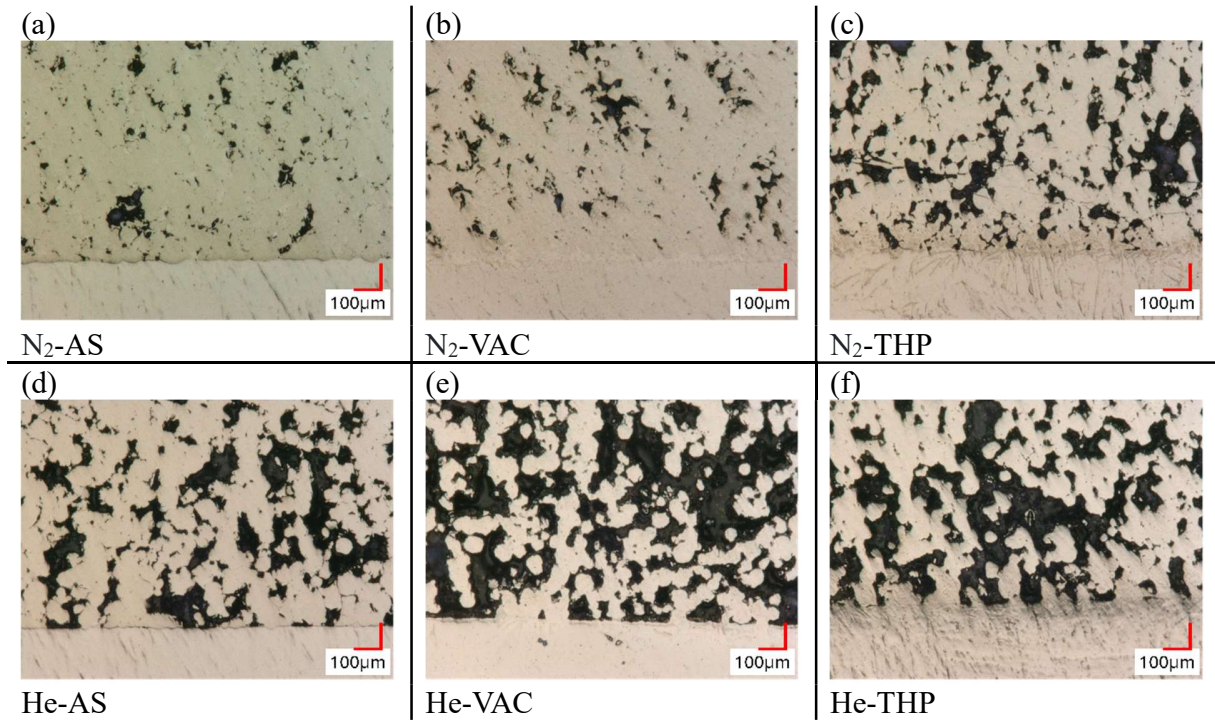


Fig. 6.9. OM images of the coating-substrate interface of (a-c) N₂- and (d-f) He-sprayed coatings in AS, MSHT-VAC and -THP conditions at magnification of 500X.

6.3.4 Relationship between ductility and microhardness

The Vickers indenter targeted two regions of the coatings: (1) “-coat” denoting ~500 μm below the top surface, and (2) “-int” denoting the first layer of particles on the coating-substrate interface. The microhardness results of coatings were presented in **Fig. 6.10a**. The microhardness ranges of N₂-AS at -coat and -int were 184±72 and 179±39 HV, respectively. On the contrary, those of He-AS were 128±32 HV and 140±48 HV, respectively. N₂-AS was harder than He-AS reasonably, since it had more stable deposition and higher density. The stable mean values, along with large variations in microhardness at different coating thicknesses, matched the measurement by Tan et al. [65] on cold-sprayed Ti6Al4V coatings, which reported a value of 370±50 HV. The deposited powder in this study did not undergo severe work hardening to achieve such high hardness. Indentations were attempted on the feedstock powder, but the powder detached from the epoxy

resin holder during retraction. Thus, the microhardness of the feedstock powder was not available for comparison. The indentation was also conducted on the CP-Ti substrates as well as CP-Ti and Ti6Al4V reference bars for comparison, as shown in **Fig. 6.10b**. All as-sprayed coatings were way softer than the wrought Ti6Al4V reference bar with a microhardness of 375 ± 7 HV.

The microhardness difference of N₂-VAC between the two regions (193 ± 28 and 160 ± 11 HV) is significantly smaller than the rest of the heat-treated coatings. The equiaxed microstructure throughout the N₂-VAC almost eliminates the anisotropy of the cold-sprayed coating by reducing the peening effect along the buildup. On the other hand, the near-top regions of N₂-THP and He-THP exhibited 100 HV harder on average than their corresponding near-substrate regions. The disparity in He-VAC was even broader, reaching 170 HV. If the substrates were thinner or machined off, these coatings would be more prone to delamination, cracking, or buckling [297]. It is noted that there is a large deviation of microhardness in the same region of all coatings except N₂-VAC. The deformation of particles during the cold spray process results in uneven strain distribution and a hardening effect across the particles [59]. Heat treatment, including thorough diffusion bonding and recrystallization, would be necessary to minimize the deviation. Nanohardness test would reflect the local strength of coatings better than microhardness. However, the high porosity of the coatings in this study increases the risk of bending the nano-indenter; therefore, only the microhardness test was conducted. Despite this, the microhardness test provides additional evidence that the MSHT-VAC and -THP could soften bulk Ti6Al4V but have an adverse effect on CP-Ti. The microhardness of CP-Ti increased from 139 ± 3 HV to 231 ± 8 HV after MSHT-THP, which led to brittle fracture in the bending test. However, the microhardness test could not reliably reflect the overall integrity. Ti6Al4V slightly dropped from 375 ± 7 HV to 369 ± 8 HV after MSHT-VAC, but the UFS dropped drastically from 2827 MPa to 2189 MPa

according to **Fig. 6.4b**. Hence, minimally invasive tests, such as indentation, should not replace bulk mechanical tests for evaluating the performance of these modified microstructures.

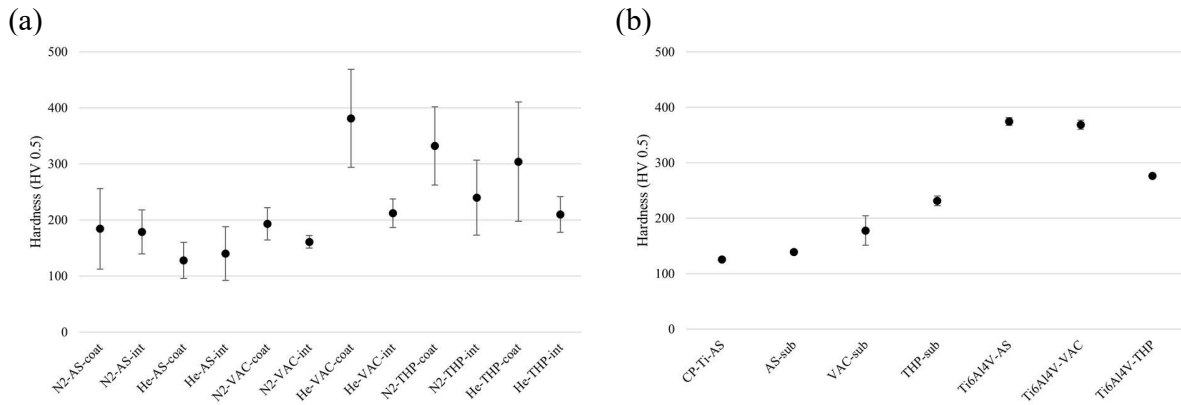


Fig. 6.10. Vickers Microhardness of (a) coatings, (b) CP-Ti substrates and Ti6Al4V reference specimens.

6.3.5 Phase precipitation in the recrystallized microstructures

The XRD patterns of samples are plotted in **Fig. 6.11**. Concerning the inhalation hazard of the feedstock Ti6Al4V powder, the Ti6Al4V reference bar was tested instead. On the contrary, the width changes of peaks could not be used to evaluate the evolution of crystallite, lattice strain, and other defects due to cold spray and heat treatments. The as-sprayed samples N₂- and He-AS exhibited an identical spectrum without β phase, which was detected in the Ti6Al4V reference bar. It was assumed the cold-spray process did not induce any phase change [205]. The weaker signal in He-AS was caused by its porous structure. The samples had a similar spectrum after MSHT-VAC with a few notable differences. The first was that the peaks of N₂-VAC shifted by -1° , whereas those of He-VAC shifted by only -0.5° . Lett et al. [205] suggested that the shifting of peaks was associated with the residual stress or interstitial elements. The peaks of oxides were detected at the same angles with similar magnitude [298]. Therefore, the phenomenon involves the redistribution of internal stress, accompanied by improved interparticle and interfacial diffusion

bonding in N₂-VAC. The second significance is the intensity of the <0002> α peak at 38° in N₂-VAC increasing almost as high as the <1011> α peak at 40.5° [299]. This could refer to intensive recrystallization and grain growth of α grains in N₂-VAC, which would be confirmed with the etched microstructure in a later section. Lastly, there was a <110> β peak at 39.6° in He-VAC only. This may reflect that He-VAC does not undergo recrystallization and grain growth as intensely as N₂-VAC, but it still manages to form some detectable β phases. The weak peaks at 37°, 42°, and 61° are considered to be the remaining oxides [300].

After the MSHT-THP process, the overall intensities of both samples were comparable. This meant hydrogen charging could obtain more consistent microstructures despite having a distinctive quality of coatings. Moreover, the intensities of <0002> and <1011> α peaks exchanged with their as-sprayed conditions. Sun et al. [293] conducted in-situ synchrotron XRD and TGA/DSC characterization on the phase evolution of Ti6Al4V during THP in H₂/Ar atmosphere. A similar change in the XRD spectrum was observed in Ti6Al4V during isothermal hydrogenation at 650°C with 0 to 5 % H₂, indicating the formation of the α_2 phase. Further increasing the H₂ concentration up to 100 % did not affect the intensity of the peaks but shifted them towards more minor degrees. It was also noted that the <0002> α peak was replaced by the <1010> α/α_2 peak at 36° when Ti6Al4V was heat treated at 550 °C with H₂ above 35%. In this study, the final holding temperature was 650 °C for 2 hours, and the instantaneous H₂ concentration was not measurable without the necessary instruments. However, it can be predicted that the H₂ concentration is ~5% without apparent peaks shifting in N₂- and He-THP samples. Nevertheless, the conservations of high-<0002> and low-<1011> peaks indicate that there is no change in phase or crystal orientation during the final furnace cooling stage and hydrogen desorption process.

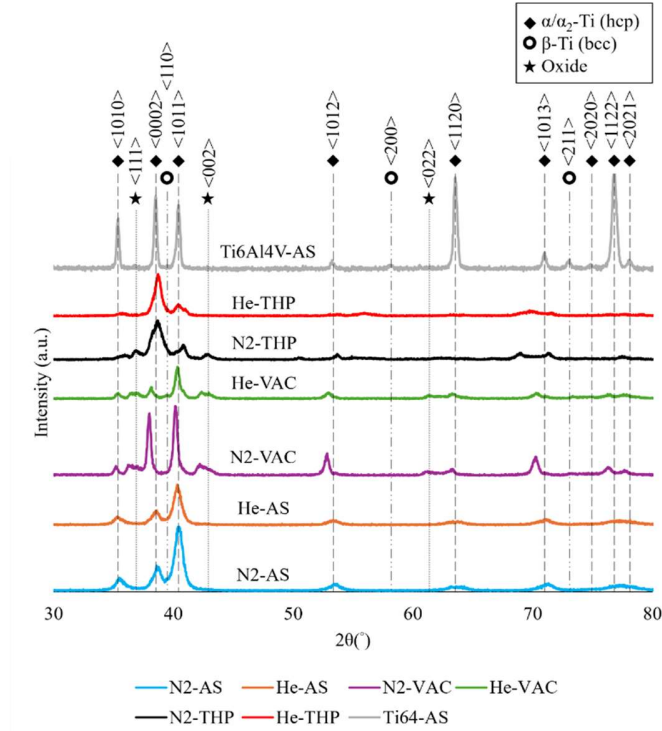


Fig. 6.11. XRD spectrum of coatings and as-received Ti6Al4V reference bar.

6.3.6 Composition profiles at the coating-substrate boundary

The EDS line-scan characterized diffusion bonding at the coating-substrate interface in a more quantified manner than OM. Since the CP-Ti contained a composition of V, indicated by the blue line, the Al signal in red served as the indicator of the effective diffusion zone. The as-sprayed coatings N₂- and He-AS exhibited a steep drop of Al signal from 6 to 0 within a displacement of 5 μm , as shown in **Fig. 6.12a** and **d**. This is sensible as the diffusion bonding would not be triggered without sufficient time and energy. The Al diffusion intervals in N₂-VAC (**Fig. 6.12b**) and N₂-THP (**Fig. 6.12c**) were 40 and 20 μm , respectively, which agreed with the observed range in **Fig. 6.9b** and **c**. The 10 μm diffusion interval in He-VAC (**Fig. 6.12e**) also matched previous OM observations (**Fig. 6.9d**), but the diffusion interval in He-THP was only 5 μm , as shown in **Fig. 6.12f**. It reminds that diffusion bonding is not evenly distributed across the coating-substrate

interface, as there are many weakly bonded and unbonded regions in He-sprayed samples due to nozzle clogging. It is also noted that there are interconnected pore networks for the shiny epoxy resin permeating through the He-sprayed coatings, as shown in **Fig. 6.12d-f**. This means some attacking fluid would be able to penetrate the coatings and further degrade the fragile porous coating. Although porous metallic coatings could be used for some specific functions, more manipulative porous structures could be sprayed with N₂ or air by increasing the standoff distance or reducing the traverse speed [181, 301].

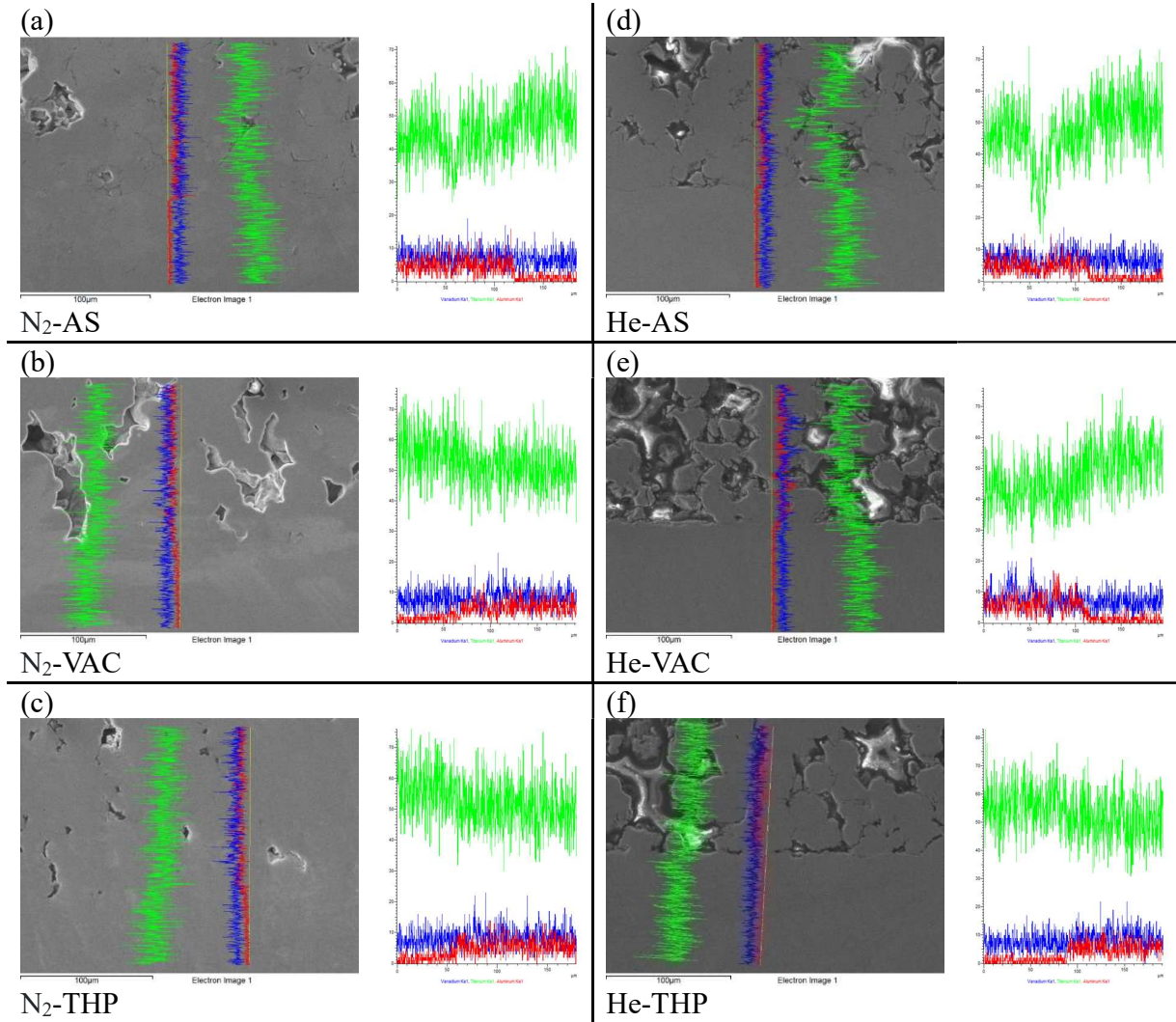


Fig. 6.12. SEM images and EDS line scan profile of unetched (a-c) N₂- and (d-f) He-sprayed coatings in (a and d) AS, (b and e) MSHT-VAC, and (c and f) MSHT-THP conditions.

6.3.7 Microstructure evolution

6.3.7.1 Recrystallisation in particles and diffusion bonding at coating-substrate boundary

The pervasive etching artefacts on the as-sprayed coatings N₂- and He-AS hindered the characterization of grains while the CP-Ti substrates remained unharmed, as shown in **Fig. 6.13a** and **d**. Leastwise, the etchant resistance mismatch is noted to be addressed. The etched microstructure revealed the equiaxed microstructure in N₂-VAC with α grains <10 μm and

submicron-thin β laths, as shown in **Fig. 6.13b**. Such a grain structure was consistent across all thickness levels of the coating. On the coating side, 10 μm thick blurry regions indicated the initiation of interfacial diffusion bonding. There was a 30 μm thick diffusion band on the substrate side with a blurry white area and 10-20 μm long β laths at GB. Yin et al. [60] employed a vortex-like mechanical interlocking approach to achieve high adhesion between a Cu coating and an Al substrate, utilizing an interlocking band ~ 50 μm tall. However, it would be challenging to implement on Ti6Al4V due to its hardness and susceptibility to crack initiation during service. Facilitating sufficient diffusion bonding at the coating-substrate interface would be a more suitable approach to hard metal components. Although the coating-substrate interface was seamless, it was observed that there were some interparticle gaps and that the pores had not been sealed yet. If higher density is required, a follow-up HIP heat treatment or other densification work would be needed. Otherwise, the 10% minor pores could be acceptable as long as the mechanical performance of the coating meets the standards and OEM requirements, such as the ASTM C633 bond strength test and the 90° bending test for cold-sprayed Al-Al₂O₃ on AA6061 integrated drive generator housings on commercial aircraft [302].

The interface of N₂-THP in **Fig. 6.13c** showed the first layer of Ti6Al4V particles diffusing to the CP-Ti substrate, then being blocked by the oversized lamellar α grains. The particles above the first layer did not exhibit intense globularization of α grains, but some <10 μm long β laths formed. The large voids in the coating did not seal or spheroidize without the help of a vacuum. On the other hand, the interparticle bonding improved with diffusion, which could not be etched away like in the as-sprayed condition. A similar microstructure was found on He-VAC with excess debris at voids, as shown in **Fig. 6.13e**. The debris at the jetting regions reflected the over-deformation of He-sprayed particles, which could not be softened sufficiently with the MSHT-

VAC treatment. Although He-VAC did not have the white diffusion band like N₂-VAC, there were 10-20 μm long β laths found 50 μm below the coating-substrate boundary. These β laths might slightly harden that region of the substrate, but they cannot provide any adhesion aid for the coating. The hydrogen charging excited the formation of the white diffusion band at the strong-bonding spot along the coating-substrate boundary, as shown in **Fig. 6.13f**. However, the interfacial voids and fractured particles remained unhealed. The particles above the first layer did not form any equiaxed α grains or β laths. Therefore, hydrogen charging can just improve the adhesion of the porous coating. Transformation into integral pieces still relies on heat treatment, which involves higher temperatures, higher pressures, and prolonged time.

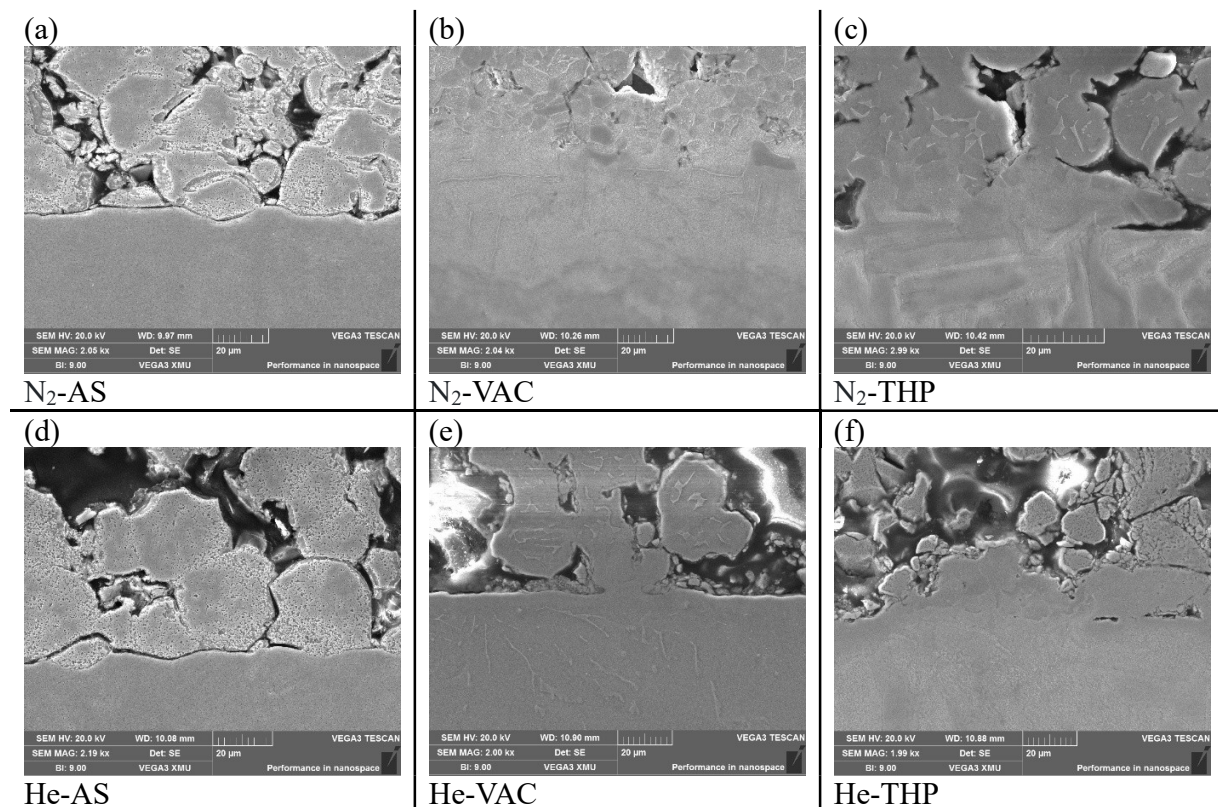


Fig. 6.13. SEM images of the etched coating-substrate interface of (a-c) N₂- and (d-f) He-sprayed coatings in (a and d) AS, (b and e) MSHT-VAC, and (c and f) MSHT-THP conditions.

6.3.7.2 Recrystallisation and grain growth in CP-Ti substrate and wrought Ti6Al4V

The grain structures of CP-Ti in as-received and after MSHT-VAC conditions could not be assessed, as they contained excess etching and grinding artifacts, as shown in **Fig. 6.14a** and **b**. The single α phase in CP-Ti has a more compact and stable passive film than the dual-phase Ti6Al4V, which inhibited corrosion [303]. If the samples were etched for longer period, the coatings would be damaged by over-etching. Providentially, the secondary α laths grew to 200-300 μm and became visible without apparent etching artefacts, as shown in **Fig. 6.14c**. The boundaries of primary α are difficult to be recognized at this stage. This lamellar structure was different from the equiaxed structure in the study by Sun et al. [287]. The addition of hydrogen significantly increases the instability of the grain-boundary interface and led to over-thickening over prolonged time in this MSHT-THP process [304]. It is noticed that the patent by Paramore et al. [305] includes CP-Ti in the definition of titanium materials, which is primarily aimed at refining the microstructure of Ti alloys. The as-received Ti6Al4V reference bar in **Fig. 6.14d** exhibited a lamellar structure after rolling. MSHT-VAC could transform Ti6Al4V bar into an equiaxed structure in **Fig. 6.14e**, as reported by Li et al. [214]. The equiaxed microstructure was further refined after MSHT-THP, which matched the effect of THRM and the bending test results in **Fig. 6.4b** [27, 210-212, 305]. The adverse enlargement of the microstructure and subsequent embrittlement of CP-Ti would be undesirable for aerospace applications, but it might be beneficial with further reduction of V content for fabricating low-neurotoxicity biomedical implants [306]. The disparity of grain growth kinetics between CP-Ti and Ti alloys needs to be explored in future study to prevent mismatch of ductile-brittle transition on cold-sprayed deposit and substrate.

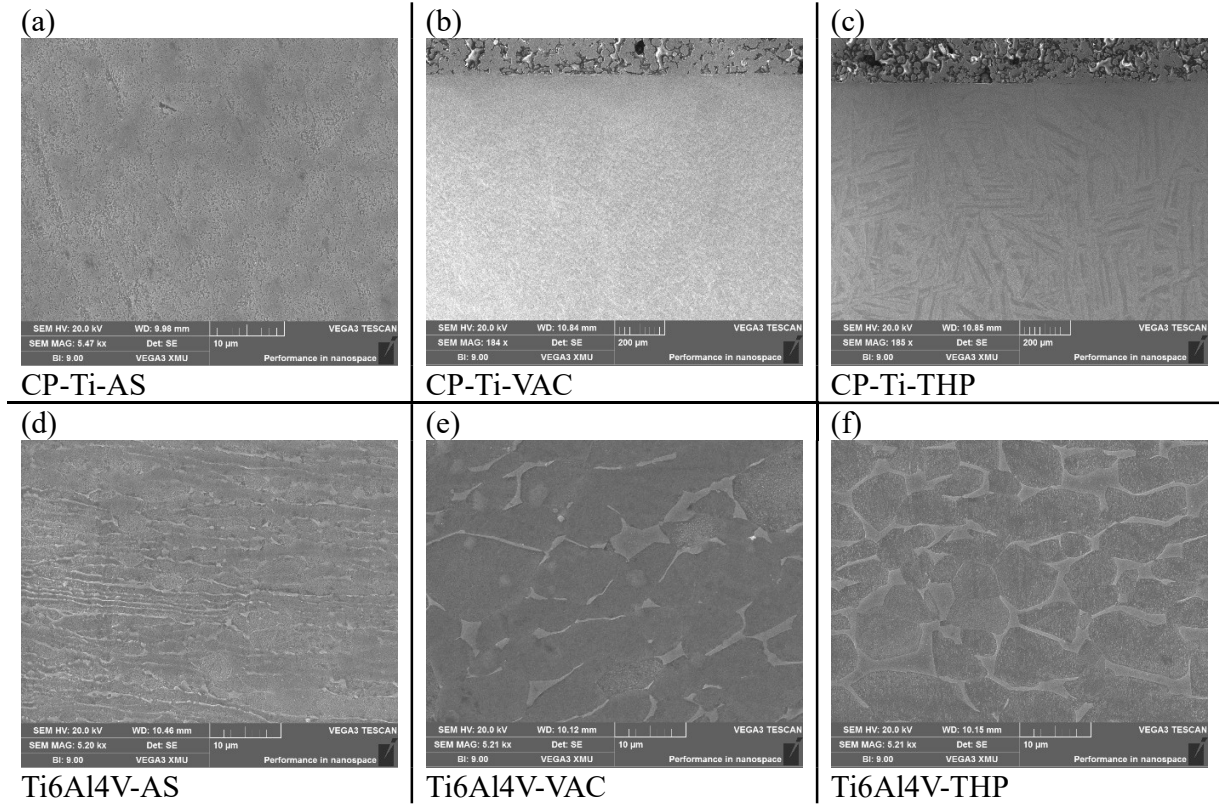


Fig. 6.14. SEM images of etched (a-c) CP-Ti substrates and (d-f) wrought Ti6Al4V in (a and d) as-sprayed, (b and e) MSHT-VAC, and (c and f) MSHT-THP conditions.

6.4. Summaries

This study investigated the spraying and MSHT parameters to achieve ductile and strongly adherent cold-sprayed Ti6Al4V coatings through interfacial diffusion bonding and tailoring a fully equiaxed microstructure. The key findings are as follows:

1. The N₂-sprayed Ti6Al4V sample after MSHT in vacuum is the only specimen exhibiting ductile deformation without fracture or delamination. Its UFS is 887 MPa at a strain of 11.1%, but its fracture flexural strength and strain are not indexed since the bending was stopped at a strain of 18.5%.

2. Using N₂ carrier gas can deposit coatings stably with low porosity, 5% in this study, which is critical to provide sufficient contact area to facilitate diffusion bonding and tailor a fully equiaxed microstructure during MSHT in vacuum, along with sufficient globularization.
3. MSHT-THP enhances the interfacial diffusion bonding to prevent delamination, but the adversarial effects include the absence of a fully equiaxed microstructure and severe embrittlement in CP-Ti substrates due to excess grain growth.
4. The morphology of twinned-pentagonal α_2 grains in Ti6Al4V particles with turtle shell layer patterns is first captured in a He-sprayed sample after MSHT with hydrogen charging.

Chapter 7: Conclusions and future work

7.1. Conclusions

In this thesis, the interactions of cold-sprayed Ti6Al4V in electrochemical and thermohydrogen environments were thoroughly studied experimentally. The effects of GB networks and porous structures on hydrogen transport were also investigated computationally. The following conclusions can be drawn from this thesis:

1. Hydrogen damage in cold-sprayed Ti6Al4V coatings on CP-Ti substrates under different post-spray heat treatments, including as-sprayed, stress-relieved at 540 °C, and heat-treated at 750 °C, are examined using cathodic charging. The nanocrystalline structure in as-sprayed coatings effectively blocks hydrogen diffusion, while heat treatments promote grain growth, hydride formation, and reduced hydrogen resistance. EBSD revealed dense nanograins acting as permeation barriers. The as-sprayed condition provides the best hydrogen barrier, heat treatment at 750 °C may be used for structural improvements but compromises hydrogen resistance, and stress relieving at 540 °C should be avoided due to increased susceptibility to pitting and coating debonding.
2. Realistic modeling and hydrogen diffusion simulations are conducted on cold-sprayed Ti6Al4V samples after stress-relieving and heat treatment, highlighting the role of GB engineering in mitigating hydrogen damage. A high fraction of special boundaries is essential to trap hydrogen and counteract the fast “short-circuit diffusion” through random boundaries, while recrystallization during heat treatment reduces these special boundaries and weakens hydrogen resistance. The hydrogen mitigation mechanism was explained as hydrogen being forced to take longer diffusion paths when segregated by low-diffusivity special boundaries.

3. The fluid transport properties of cold-sprayed Ti6Al4V are examined with a tsunami-shaped deposit having unique porosity distribution caused by nozzle stoppage. Its 3D porous structure is analyzed using optical microscopy, densitometry, and industrial XCT. Porosity measurements had vast discrepancies depending on the methods, highlighting the need for statistical correlation to assess transport properties reliably. XCT tensor simulations predicted permeability (10^2 – 5×10^4 mD) and diffusivity (10^{-9} – 10^{-7} m²/s) consistently at porosities of ~2.5–30%, with a strong linear relationship between the two. However, permeability and diffusivity deviate widely at porosities below 5%, making exact predictions unrealistic. Instead, power-law bounds with critical porosities at 30 and 40% are proposed for permeability and diffusivity, respectively. Experimental permeability data matches tensor predictions, but diffusivity diverges below 13% porosity due to drastic changes in formation factor.
4. MSHT in vacuum and hydrogen atmospheres are attempted to produce ductile and well-adhered cold-sprayed Ti6Al4V coatings through interfacial diffusion bonding and microstructure modification. It finds that N₂-sprayed samples subjected to MSHT in vacuum are the only ones to show ductile deformation without fracture or delamination, achieving an ultimate flexural strength of 887 MPa at 11.1% strain. The use of N₂ carrier gas enables stable deposition with low porosity (5%), which promotes effective diffusion bonding and globularization for a fully equiaxed microstructure. While MSHT combined with thermohydrogen processing (THP) improves bonding and prevented delamination, it also causes excessive grain growth, loss of equiaxed structure, and embrittlement in CP-Ti substrates. Additionally, unique twinned-pentagonal α_2 grains with turtle shell-like patterns are observed for the first time in He-sprayed samples after MSHT with hydrogen charging.

7.2. Suggestions for Future Research

7.2.1 Hydrogen damage by electrochemical charging

The coatings were deposited in two separate trials according to the recommendation by OEM, and thus the interlayer boundaries were apparent. The sandwich structure of top as-sprayed, middle stress-relieved, and bottom substrate in HT1 group led to anisotropic properties in both mechanical and electrochemical perspectives. Hence, the future cold spray deposition will complete in a single trial to prevent interlayer defects and anisotropy.

The setup of electrochemical hydrogen charging was a simple electrolytic cell without tracking resistivity change throughout the charging period. The strong adhesion and geometries of samples hinder the preparation of thin rod electrodes for conventional electrochemical analysis. Future studies will delaminate coatings from substrates and machines into standard specimens that enable electrochemical measurement.

SEM analysis on etched as-sprayed layer could reveal the grain pattern that EBSD could not index, while intersplat boundaries remain as the challenging area to characterize. However, corrosion resistance varies according to the microstructures by different spraying parameters and post-treatments. When the same etching parameters are used, some coatings with weak resistance exhibit pitting holes along the intersplat boundaries such that the dislocations among the area would be unable to characterize. Etching samples will need tailored parameters to overcome this issue.

7.2.2 Simulation of hydrogen diffusion across the grain-boundary networks

Cold-sprayed coatings contain dense special boundaries, which makes it difficult to create reliable GB maps for modeling. A potential solution is to reconnect interrupted GBs using image

processing but assigning random and special boundaries remains a complex task. TJs also need to be identified, since their diffusivity can be higher than GBs and interstitial sites in nanocrystalline counterparts. Hybrid modelling methods are therefore recommended to improve the accuracy of hydrogen diffusion simulations. If the CSL index method is used to categorize GBs, their energy and hydrogen-related properties must be studied in detail before being applied to GB network models.

Hydrogen diffusivity and solubility values are often taken from literature, but these do not accurately represent cold-sprayed Ti6Al4V grains of various sizes or GBs with different CSL indices. Tools such as im2mesh can generate detailed multi-part models of grains and GBs, but assigning properties in polycrystalline microstructures needs improvement in automatic recognition and user-interface in software. Reliable simulations and 3D extension will require experimental databases under different conditions, including hydrogen charging methods, temperature, and pressure.

Producing standardized cold-sprayed Ti6Al4V samples for hydrogen permeation or atomic probe tomography is difficult. The foils and needles used in these tests bend easily due to the highly deformed microstructure and biaxial stress. Wire-cutting introduces further problems, such as surface recrystallization, loss of special boundaries, and brass oxide contamination. Epoxy resin infiltration into micropores also leads to unreliable hydrogen measurements, and removing the resin with solvents adds further uncertainty. These issues need to be overcome to achieve experimental validation.

7.2.3 Statistical correlation between porosity, permeability and diffusivity

Future research aimed at optimizing the fluid-transport properties of cold-sprayed deposits should encompass material selection, spray process parameters, inspection techniques, post-spray treatments, and the characteristics of the working fluid under operational conditions.

Firstly, coating porosity and bond strength exhibit strong dependence on substrate material. The present study's use of Ti6Al4V powder on a mild-steel substrate reflects the behavior of a hard powder on a moderately ductile substrate; however, systematic investigation of diverse powder-substrate combinations is required to tailor deposit architectures, porous or dense, to specific service requirements.

Secondly, the relationships among porosity, nozzle traverse speed, and standoff distance remain unquantified in the absence of real-time measurements. Future experiments should employ in-situ monitoring of TCP dynamics and evolving deposit geometry to elucidate local formation mechanisms and enable precise control over microstructural development.

Thirdly, current inspection and measurement methods present notable limitations. XCT suffers from finite voxel resolution, water-based Archimedes' density measurements underestimate true porosity due to surface-tension effects, and ultrasonic NDI faces coupling-medium retention challenges in highly porous regions. To address these issues, researchers should (1) scan smaller, precision-cut samples to achieve higher XCT voxel resolution and reduce acquisition times; (2) employ inert gases such as nitrogen or helium in density measurements for gas-environment applications; and (3) develop immersion ultrasonic NDI protocols that maintain coupling integrity while mapping pore morphology, thereby enhancing industrial feasibility.

Moreover, this study did not address the structural integrity of the deposit. Subsequent work will evaluate mechanical performance and microstructural evolution, particularly following post-spray

treatments. Integrating mechanical testing with in-situ XCT imaging will reveal detailed correlations among porosity, microstructure, and mechanical reliability for validating and refining predictive simulations.

Finally, simulations in the present work utilized liquid hydrogen properties, yet hydrogen diffusivity in Ti6Al4V varies significantly with temperature and pressure. This limitation applies broadly to other material-fluid systems. Future simulations will incorporate the actual thermophysical properties of the working fluid under relevant service conditions to ensure predictive accuracy.

7.2.4 Ductility and adhesion improvement by multi-step heat treatment

This study demonstrated that the ductility cold-sprayed Ti6Al4V could be enhanced, but they had not yet regained the strength of wrought material. Since titanium alloys usage in aerospace industry prioritize strength over ductility, it is essential to find the optimal age hardening parameters for cold-sprayed Ti6Al4V after MSHT. In lieu of that, pore expansion during heat treatment remains problematic. MSHT-THP was capable of improving diffusion bonding, but it was ineffective to reduce porosity. Heat treatments were conducted under stable pressure to prevent oxidation and cracking of tubular furnace. The advance in pressure control throughout the MSHT with a suitable furnace might help densify the coatings to near-wrought.

In this work, the bending and delamination of coatings related to thermal expansion were prevented by pressing with the weight of substrate as well as slow heating and cooling rates. However, these measures may be impractical for complex aircraft components, where fixtures must accommodate the geometric constraints and minimize process time. Future research should therefore explore alternative fixation methods and optimization of heating and cooling rates.

The combination of Ti64 coating on CP-Ti substrate in this study cannot represent the combinations of other alloys due to the different diffusivities and melting points of base metals and alloying elements. The heat curve of MSHT cannot be directly applied to other metals without adjusting parameters, such as the temperature of phase changes and recrystallization. Developing comprehensive guidelines for cold-spray repair and post-spray heat treatment requires tailoring of MSHT parameters for each target alloy.

Finally, the Vickers microhardness results showed a poor correlation with the flexural performance of the specimens. A critical reason was the absence of stress-strain data from the conventional microhardness test. Nanoindentation can acquire stress-strain data, but risks indenter damage on hard and porous samples. Profilometry-based indentation plastometry offers the potential to obtain stress-strain data analogous to nanoindentation with the Rockwell microindenter [307]. Notwithstanding, this technique remains novel and requires extensive validation to confirm that its indentation metrics reliably predict bulk mechanical properties.

Appendices

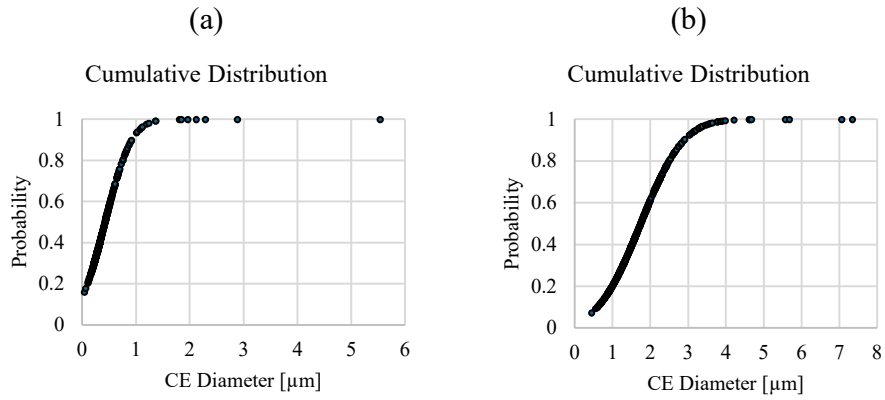


Fig. S4.1. Cumulative distribution of grain size measurement in (a) SR-GB and (b) HT-GB

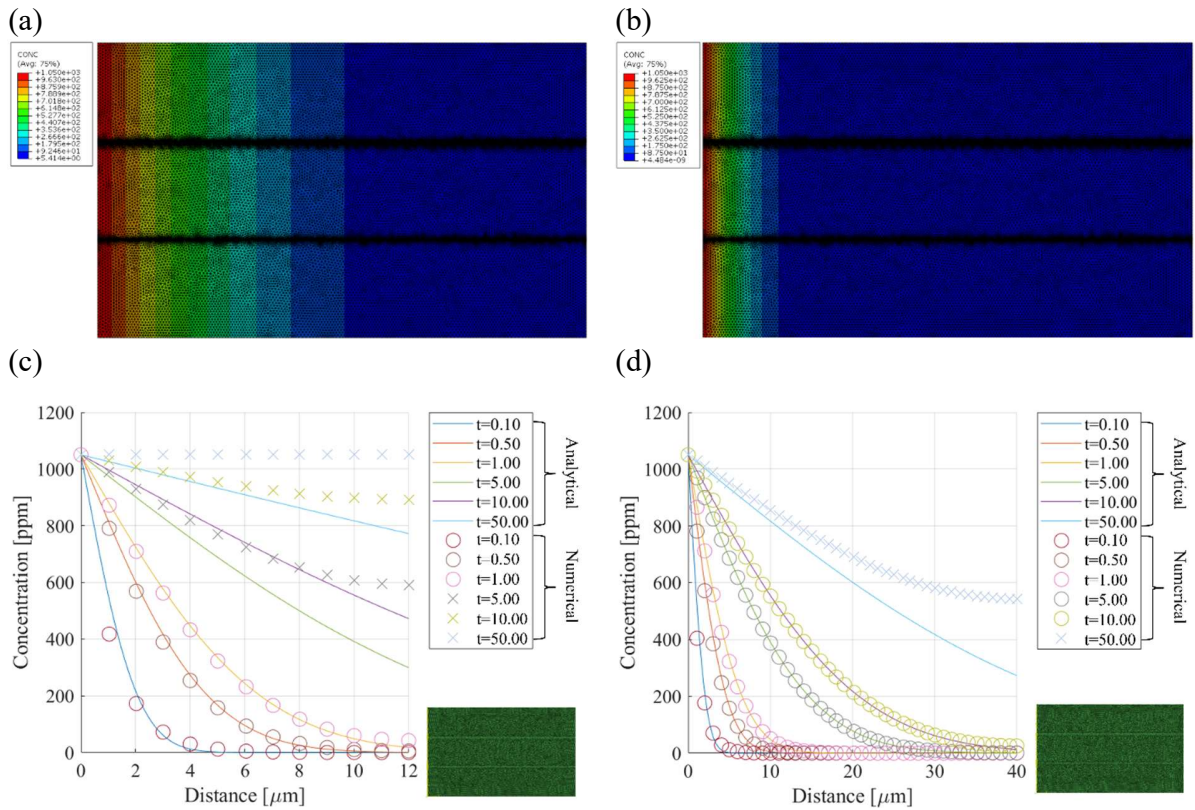


Fig. S4.2. Hydrogen concentration maps in numerical simulations of (a) German 12 μm and (b) German 40 μm wide monocrystal at $t = 0.5$ h. Comparison of analytical and numerical hydrogen diffusion profiles of (c) German 12 μm and (d) German 40 μm wide monocrystal.

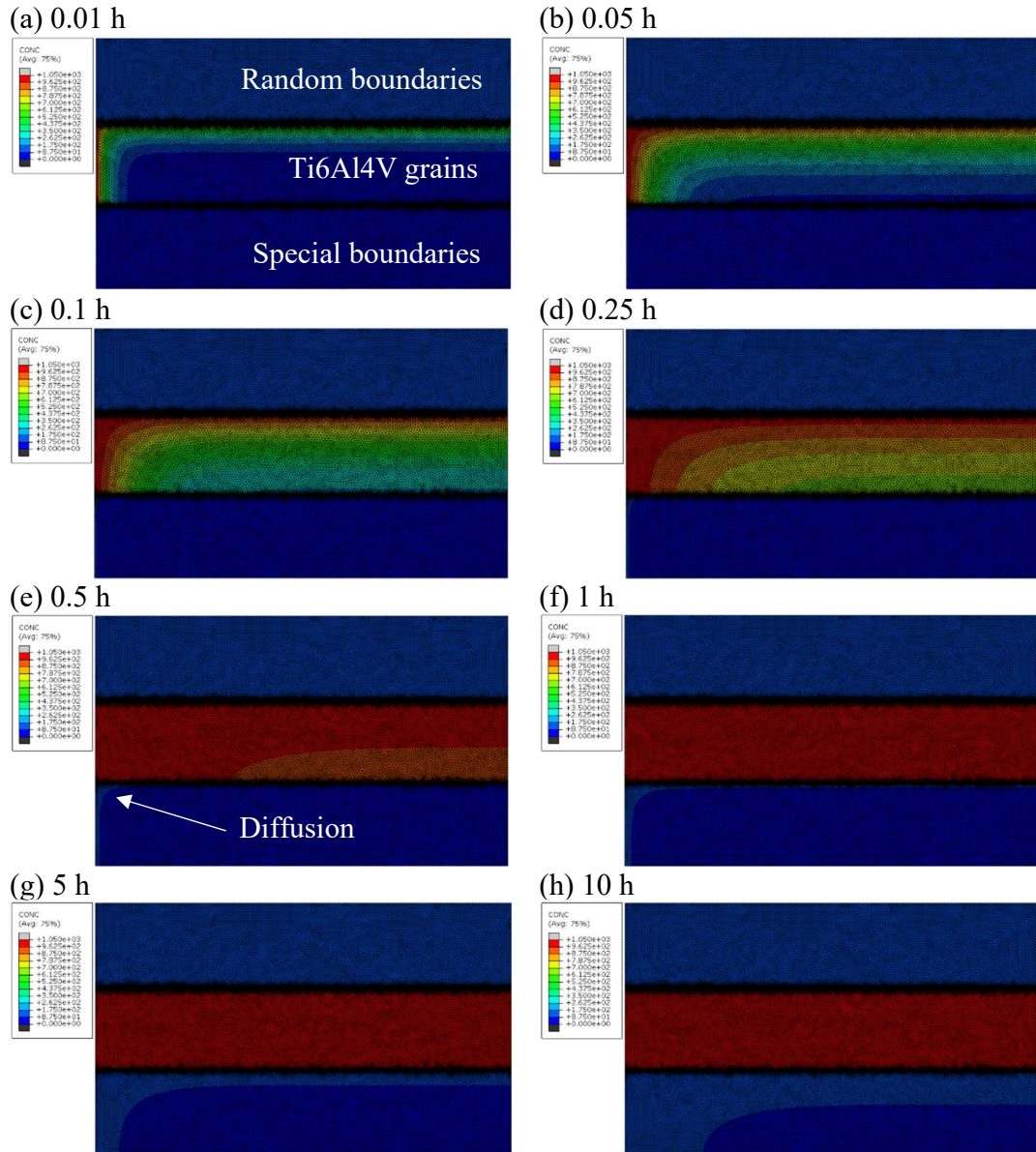


Fig. S4.3. Hydrogen concentration maps in numerical simulations of a 12 μm wide German flag model with hydrogen properties of random boundaries (top), Ti6Al4V grains (middle), and special boundaries (bottom) at $t =$ (a) 0.01 h, (b) 0.05 h, (c) 0.1 h, (d) 0.25 h, (e) 0.5 h, (f) 1 h, (g) 5 h, and (h) 10 h.

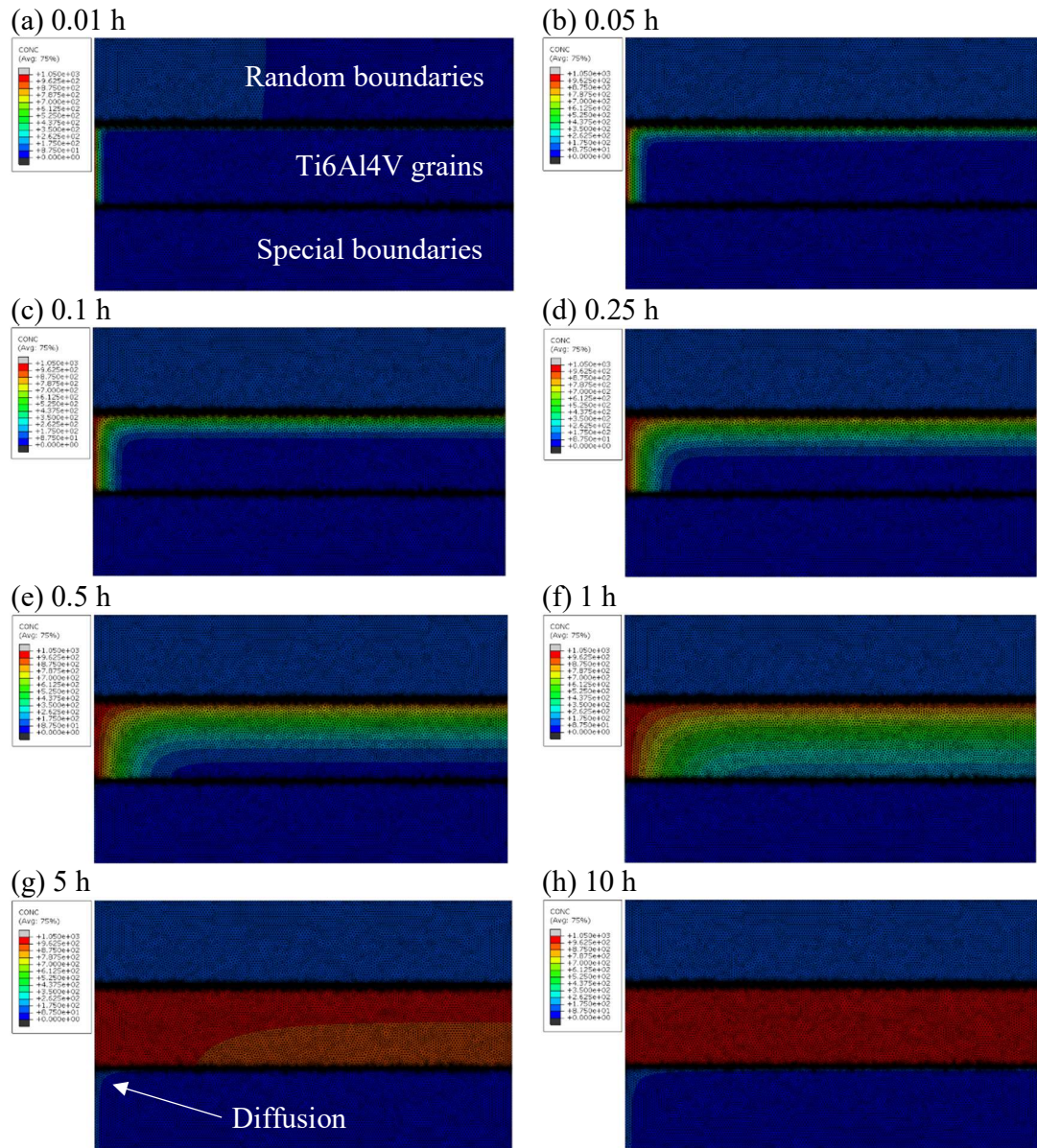


Fig. S4.4. Hydrogen concentration maps in numerical simulations of a 40 μm wide German flag model with hydrogen properties of random boundaries (top), Ti6Al4V grains (middle), and special boundaries (bottom) at $t =$ (a) 0.01 h, (b) 0.05 h, (c) 0.1 h, (d) 0.25 h, (e) 0.5 h, (f) 1 h, (g) 5 h, and (h) 10 h.

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