



Article Critical Velocity Prediction and Characterization of Bonding Types of High-Velocity, Air-Fuel-Sprayed Titanium Coating on Aluminum Alloys

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Abstract: This study established finite-element models via LS-DYNA software to predict the critical velocity of Ti spray particles under different collision velocities and preheating temperatures. Particle deformation, collision temperature, and bonding types of the Ti coating/Al substrate system were simulated. At the predicted critical velocity (650 m/s) and the corresponding preheating temperature (300 °C), the TC4 titanium coating was fabricated on a 6061 aluminum substrate by high-velocity air fuel (HVAF) spray. The coating's microstructure and phase transition were analyzed by a scanning electron microscope (SEM) equipped with energy-dispersion X-ray spectroscopy (EDS) and transmission electron microscopy (TEM), revealing that critical velocity decreases with increasing particle velocity and preheating temperature. At 650 m/s, the coating was well-bonded to the matrix in metallurgical bonding type, and mechanical interlock and metallurgical bonding coexisted among particles. Experimental results show that the coating is characterized by the metallurgical bonding type, a fusion layer, and recrystallization, which verifies the simulated collision temperatures.

Keywords: Ti alloy coating; HVAF spray; numerical simulation; critical velocity; bonding type

1. Introduction

Aluminum (Al) alloys have been widely used in modern industry due to their excellent and comprehensive performance (e.g., mechanical and anticorrosion properties) [1]. However, the high-temperature strength and wear resistance of Al alloys are poor, limiting their applications in many fields, such as for use as pistons in automobile engines. Many technologies (i.e., microarc oxidation, electroplating, and thermal spray) can provide an improved wear resistance for Al alloys via hard coatings of tungsten, titanium, and tantalum carbides [2]. Titanium (Ti) alloys possess much better mechanical properties (for TC4 Ti alloy, its elastic modulus is about 110 GPa, and hardness reaches $250-350 \text{ HV}_{0.05}$) than Al alloys (elastic modulus and hardness are 68.3 GPa and 30–95 $HV_{0.05}$, respectively, for 6061 Al alloy). Additionally, Ti coatings can endow Al alloys with good resistance to galvanic corrosion, since Ti has a nobler galvanic potential (-0.1 - 0.1 V vs. SCE) in seawater) than Al alloys $(-1 \sim -0.75 \text{ V vs. SCE}$ in seawater) [3]. Therefore, Ti alloys have been used as coating materials to offer antiwear and anticorrosion protection for Al alloys [4,5]. High-velocity air fuel (HVAF) spray has been applied on Al alloy substrates to fabricate coatings that exhibit excellent qualities with low porosity, high bonding strength, and wear/corrosion-resistance properties [6]. Antiwear and anticorrosion Ti coatings can also be successfully fabricated by HVAF spray if non-melting Ti particles, pores, and cracks can be alleviated by deliberately adjusting the spray parameters [7].

Therefore, coating preparation parameters are essentially considered to attain highquality Ti alloy coatings on Al alloys. Among them, one of the most important parameters is critical velocity. Studies [8–10] have reported that a large number of pores form on



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). titanium alloy coatings, attributed to the particles not reaching critical velocity. For spray technologies, the critical velocity of spray particles is always defined with the occurrence of adiabatic shear instability (ASI). At this velocity, the metallurgical bonding between the particles and matrix occurs. Thus, the spray parameters should be adjusted to obtain the critical velocity [11–13]. Many spray parameters can influence the critical velocity of the spray particles [14], for example, material density, melting point, particle shape/size, and initial impact velocity/temperature. It might be challenging to determine some of these parameters via experiments since the spray is quick and continuous in time. In practice, ancillary facilities (such as the 'SprayWatch' diagnostics system [15,16]) monitor spray parameters, such as temperatures and velocities, increasing the spray system's cost and instability. Instead, numerical simulation to obtain the critical velocity of particles can be very feasible, efficient, and economical. Researchers [17–19] analyzed the effective collision velocity between particles and substrate through numerical simulation and found that particle velocity should be controlled at 300–1200 m/s. When the velocity is too high, particles break into debris, resulting in more defects. On the other hand, when the speed is less than 300 m/s, particles bond back when they impact the substrate, and the bonding strength is poor. Meanwhile, the factors that influence critical velocity can also be simulated. For example, Meng et al. [20] used non-linear FEA simulations using Abaqus/Explicit to simulate particle-collision deposition of different materials systems (Cup/Cu, Nip/Cu, and MSp/Cu). They reported that when the collision velocity was greater than 650 m/s, the flattening rate and effective contact area increased. At this (critical) velocity, adiabatic shear instability occurred between the particle and the coating. Li et al. [21] simulated the deposition mechanism of supersonic spraying by ANSYS and found that the density and specific heat of the particles were the main factors that affect the temperature and velocity of the particles. Furthermore, Ye et al. [22] found the larger the granularity of the spray particle, the slower the energy consumption in the deposition process and the longer the deposition time, which affects particles' collision velocity and critical velocity. The preheating of particle/substrate was also found to significantly influence the collision velocity, bonding, and deposition behavior. Such effects could be interpreted by numerical simulations [23,24]. Thus, the consensus is that numerical simulation efficiently predicts critical velocity and its influencing factors, which lightens the experimental burdens and contributes to understanding deformation, bonding, and deposition mechanisms during the spray process.

For sprayed coatings, bonding strength is an essential factor in assessing the deposition's success under different parameters [25–27]. Bonding strength is mainly influenced by bonding types (i.e., mechanical interlock, metallurgical bonding, and both). Notably, bonding mechanisms of coatings are associated with bonding types, in addition to ASI, local melting, and interface diffusion. Although analytical models can offer such information to interpret the bonding mechanisms, the experimental observation of bonding types is urgently needed. For a spray system, bonding type is strongly related to whether critical velocity is reached or not because the occurrence of local melting and ASI at the critical velocity determines the effective adhesive and cohesive bonding. Accordingly, the spray parameters that influence the critical velocity also affect the bonding types in which metallurgical bonding is always desirable. Thus, it is meaningful to characterize the bonding types of coatings by experiments involving the spray parameters under which critical velocity is predicted by numerical simulation. In this work, we first predicted the critical velocity of Ti alloy particles on Al substrate under different collision velocities and preheating temperatures by numerical simulation using LS-DYNA software. Then, we simulated the deformation and collision temperatures that significantly affect the bonding types in three deposition cases (i.e., single-particle, single-layer, two-particle/two-layer, and multi-particle/multi-layer). Finally, we verified the different bonding types via experiments by characterizing the TC4 Ti alloy coatings on 6061 Al alloy substrate using HVAF spray using the optimum collision velocity and preheating temperature obtained by the numerical simulation.

2. Materials and Methods

2.1. Simulation Model and Settings

The single-particle model was simplified, as the deposition of spherical particles impacting the substrate facilitates the computer calculation. The finite-element model is shown in Figure 1. The diameter of the Ti particle was 20 μ m, and the aluminum-alloy substrate had a dimension of 0.4 mm \times 0.4 mm \times 0.1 mm. The simulation of particle deposition used ANSYS/LS-DYNA software (ANSYS, Inc., Canonsburg, PA, USA). In particle collisions with the matrix, titanium particles experienced severe plastic deformation, producing a large amount of heat in a short duration and a short-time vacuum environment. The Johnson–Cook plastic material constitutive model [28–30] was used to obtain better simulation results. The Mie–Gruneisen state equation [31] was selected by considering the softening of materials due to temperature and the reinforcement of materials under great strain.



Figure 1. Finite-element model to simulate single-particle collision during HVAF spray.

The type of collision was an erosion of the particles, and the Al base substrate was constrained, as shown in Figure 1. Moreover, the contact surface was a free boundary. The physical properties of the materials (Ti and Al alloys) used in the simulation are given in Table 1.

Tabl	e 1.	Physical	properties	of the	e spraying	particle	(Ti alloy)) and su	bstrate	(Al	all	.oy)
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Materials	Titanium Alloy	Aluminum Alloy
Density (kg/m^3)	4500	2770
Melting point (K)	1952	933
Poisson's ratio	0.35	0.33
Young modulus (MPa)	74	69
Specific heat (J/kg·°C)	612	880
Thermal conductivity (W/m.°C)	7.995	237

2.2. Experimental

The coating of TC4 Ti alloy on the 6061 Al alloy was prepared by a high-velocity air-fuel spray (HVAF) system made by the National Key Laboratory for Remanufacturing, Beijing, China. The chemical compositions of the TC4 (Avic Mette Powder Metallurgy Technology Co., Ltd., Beijing, China) and 6061 Al alloy (Institute of Metal Research, Shenyang, China) are given in Table 2. The spray parameters are shown in Table 3. Before spraying, the 6061 substrates were cleaned with acetone, dried in the air, and then grit-blasted to promote adhesion. The preheating temperature of the substrate was 150 °C, and the preheating temperature for the particles was 300 °C. Critical velocity (650 m/s) was achieved by a series of trials using the orthogonal experimental design in which this velocity was regarded as the 'index'. Table 3 shows the optimum spray parameters to conduct experiments at this critical velocity.

Materials Elements and Compositions (wt.%)									
TC4	Ti	V	Al	С	Fe	0			
101 -	Bal.	3.82	5.83	0.023	< 0.03	< 0.02			
6061	Al	Mn	Mg	Zn	Fe	Cu	Cr	Si	Ti
	Bal.	0.15	0.8–1.2	0.25	0.7	0.15-0.4	0.04–0.35	0.4–0.8	0.15

Table 2. Chemical compositions of TC4 and 6061 Al alloy.

Table 3. Parameters of TC4 coating by HVAF spray on 6061 Al alloy substrate.

Air Pressure (PSI)	Propane Pressure (PSI)	Ar (L/min)	H ₂ (L/min)	Spray Distance (mm)	Powder Feeding Rate (g/s)	Scan Rate (mm/s)
85	73	35	25	8	1500	23

The microstructure of the Ti powders and coatings was characterized by a scanning electron microscope (FEG-250 SEM, Quanta, New York, NY, USA) equipped with energydispersion X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, JEM-2100/HR, Hitachi High-Tech Corporation, Tokyo, Japan). TEM samples were prepared by mechanical thinning and an ion-milling process. The coating foil TEM samples were prepared by the focused ion beam (FIB) lift-out technique.

3. Results and Discussion

3.1. Simulation Results and Discussion

3.1.1. Critical Velocity Prediction

The real critical velocity of the spray particles depends on various factors, e.g., particle/substrate temperature, oxidation of the particles, particles size, and particle physical properties. Based on the results reported by previous studies [32,33], the following empirical formula to calculate the critical velocity of Ti alloy particle was used in this study:

$$V_{\rm c} = 667 - 14\rho + 0.08T_{\rm m} + 0.16\mu - 0.4T_{\rm pt} \tag{1}$$

where V_c is the critical velocity (m/s), ρ is the density (g/cm³) of TC4 alloy, T_m is the particle melting point (°C), μ is the ultimate strength (MPa) of the particle, and T_{pt} is the preheating temperature (°C) of particles.

Figure 2 shows the results of the critical velocities of the Ti particles at different particle preheating temperatures based on Equation (1). In Figure 2, the calculated critical velocities decrease with increasing preheating temperatures. The declined critical velocity indicates that the deposition of particles is easier at higher preheating temperatures, possibly because the particles at high temperatures soften and produce much more intensive plastic deformation [24]. As a result, the bond between the particle and the substrate can also be improved.

In addition, the critical velocity of spray particles can also be estimated by a method proposed by Saeed Rahmati et al. [34]. Simulation results reported that the critical velocity was obtained when the collision velocity of particles (V_{co}) decreased to zero. As V_{co} reaches zero, the surface adhesive energy of the particle is higher than the rebound energy, achieving an effective bond between the particle and the substrate. The critical velocities of Ti alloy particles at different preheating temperatures were also obtained using this method, as shown in Figure 3. With increasing preheating temperature (T_{pt}), the spray velocity decreases to achieve the zero-collision velocity of particles. Specifically, the critical velocity (i.e., the spray velocity when $V_{co} = 0$) for Ti alloy particles at 20, 100, 300, and 500 °C is 850, 700, 650, and 650 m/s, respectively. The results are consistent with the

results in Figure 2, except that the V_c (=650 m/s) using this method is larger than the V_c (=601.17 m/s) calculated via Equation (1) at a preheating temperature of 500 °C.



Figure 2. Results of the calculated critical velocities of Ti particles at different particle preheating temperatures based on Equation (1).



Figure 3. Critical velocities of Ti alloy particles at different preheating temperatures based on the method proposed by Saeed Rahmati et al. [34]. (a) 20 °C, (b) 100 °C, (c) 300 °C and (d) 500 °C at different spray velocities.

Previous results [17–19,35] of simulations and experiments also concluded that a jet outflow forms when the collision velocity reaches the plastic impact velocity. The jet gets elongated and sharper with increasing collision velocity. This condition is considered the onset of adiabatic shear instability (ASI), and the corresponding collision velocity can be regarded as the critical velocity. Critical velocities at different preheating temperatures were obtained based on this criterion. The simulated shapes of a single Ti particle on the Al alloy substrate at different preheating temperatures and collision velocities after 35 ns collision are shown in Figure 4. At 20 °C, no jet can be observed when the collision velocity is less than 800 m/s. A gap exists along the boundary between the particle and the matrix, leading to the rebound of the particle and poor adhesion. An apparent jet appears along the edge when the collision velocity reaches 850 m/s. Moreover, with increasing velocity, the ASI phenomenon of the matrix becomes more pronounced. Accordingly, the critical velocity of titanium alloy particles is about 850 m/s at 20 °C. Similarly, the critical velocity at 100, 300, and 500 °C is about 700, 650, and 650 m/s, respectively, consistent with the results in Figures 2 and 3.



Figure 4. Simulated shapes of a single Ti particle on the Al alloy substrate at the temperature (**a**–**d**) 20 °C, (**e**–**h**) 100 °C, (**i**–**l**) 300 °C and (**m**–**p**) 500 °C at different collision velocities after 35 ns collision.

Meanwhile, the deformation degree of the particle can be estimated by calculating the rate of particle flattening (R_f) and the crater depth (h_c) on the substrate at different preheating temperatures and collision velocities. The rate of particle flattening was employed to characterize the plastic deformation of particles, and the crater depth represents the deformation of the matrix. The following formula calculates the flattening rate:

$$R_{\rm f} = \frac{d_a}{d_b} \tag{2}$$

where R_f represents the flattening rate, d_a is the diameter (major diameter of the ellipsoid) of the particle after the collision, and d_b is the diameter of the spherical particle before the collision. Figure 5 shows the R_f and h_c obtained by analyzing the deformed shapes of particles and substrate in Figure 4. From Figure 5a, the flattening rate, R_f , increases with collision velocity. In addition, R_f increases with an increase in particle temperature at the same velocity, possibly because the particles soften and deform more easily with increasing temperature. Importantly, the deformation of the particles becomes more intensive at the critical velocity at all four temperatures, which can be attributed to the fact that plastic deformation is triggered when ASI occurs. Crater depth has a similar increasing change with temperature and collision velocity, indicating that coordinated deformation occurs between particles and substrate, leading to an effective bond at the critical velocity.



Figure 5. (a) Rate of particle flattening (R_f) and (b) crater depth (h_c) obtained by analyzing the deformed shapes of particles and substrate in Figure 4.

The above simulation results confirm that the deformation of particles becomes more intensive with increasing collision velocity and preheating temperatures. Significantly, at higher preheating temperatures, the softening of the particles contributes to the combination of particles and the matrix, reducing adiabatic shear instability and effectively reducing the critical velocity of the particles. These findings are consistent with the results reported by Yu et al. [23]. Such results indicate that the simulation in this study offers an accurate prediction of the critical velocity of Ti particle sprayed on Al substrate. Further investigations were conducted at this predicted critical velocity to understand the deformation behavior and bonding types of the Ti coating/Al substrate system.

3.1.2. Plastic Strain and Collision Temperature

The results in Figures 2–4 reveal that the critical velocity at 300 and 500 °C is approximate. Moreover, Figure 5 confirms the approximate R_f and h_c at 300 and 500 °C. Considering the cost of increasing preheating temperatures and oxidation of materials at the higher temperature, the optimum preheating temperature of the particle is 300 °C. Therefore, the following sections show the simulation results under a 300 °C preheating temperature and 650 m/s collision velocity.

Figure 6 shows the plastic strain contours of Ti alloy particles at different collision times. Plastic deformation of particles increased with time, increasing contact areas and adhesion between particles and the substrate. Correspondingly, the rebound of particles was restrained. The equivalent plastic strain (PEEQ) at different locations of the titanium alloy particles was obtained by tracking and measuring the corresponding units of the particles, as shown in Figure 6a–d. Figure 6e shows the PEEQ changes with collision time at different regions (i.e., inside, margin, and bottom). It was found that the PEEQ of the particle was the most significant along the edge (margin) and the smallest inside the particle. The biggest PEEQ at the margin is because of a strong pressure wave generated during the collision by the particle, resulting in intensive plastic strain at a high strain rate. When shear stress is big enough, the material becomes completely soft and jets out. After the collision, the flow of fresh metals solidifies, and a metallurgical bond forms. However, the combination between particles and the matrix usually occurs at the bottom of contact rather than at the maximum PEEQ because shear stress is only at the margin region. Still, the normal pressure at the bottom also contributes to the particles bonding to the matrix [36,37].

Figure 6. Plastic strain contours of Ti alloy particles on Al substrate at different collision time (**a**) 10 ns, (**b**) 20 ns, (**c**) 30 ns, and (**d**) 40 ns and (**e**) the equivalent plastic strain (PEEQ) and (**f**) collision temperatures at different locations.

Figure 6f shows the changes in collision temperature with time at different regions (i.e., bottom and margin). It is revealed that when particles come into contact with the matrix, the temperature at the particles' bottom region sharply rises, with the highest temperature reaching more than 1400 K. However, the stable temperature at the margin region reaches 1600 K, which is close to the melting point (1952 K) of titanium alloy. At such a high temperature, plastic deformation is ready to happen due to the softening of the materials, further leading to the thermoplastic rheology. Under such conditions, a metallurgical bond is possible, starting from the bottom to the margin along the boundary between the particle and substrate.

3.1.3. Interactions among Particles

Collision temperature can assess the bonds among particles and at the coating/substrate interface. Thus, to confirm the bonding types, the interaction among spray particles and the corresponding collision temperature were simulated by multiple particle deposition. Figure 7 shows the simulation models and the PEEQ maps for different deposition cases (single-layer in Figure 7a, two-particle/two-layer in Figure 7f, and multi-particle/two-layer in Figure 7l) at 300 °C preheating temperature and 650 m/s collision velocity. Generally, plastic deformation happens at this temperature and velocity for the three deposition cases. The deformation and interaction among particles become severe with collision time, and the jet-out phenomenon is apparent along the boundaries among particles and between particles and the substrate. For single-layer deposition in Figure 7a, it was found that mechanical interlocking happens among particles, and no apparent metallurgical bond can be observed. The time-dependent collision

temperatures for points I, II, III, and IV are shown in Figure 7e. The highest temperature was obtained at point III at 12 ns, reaching 945 K, which is far lower than the melting point for the Ti alloy particle. However, this temperature is slightly higher than the melting point (about 933 K) for Al alloy; thus, a metallurgical bond is still possible and mainly relates to the Al substrate. Overall, the single-layer deposition of Ti particles is dominated by mechanical interlocking, although plastic deformation is also severe due to the immense stress on the particles at such a high collision velocity.

Figure 7. Simulation models, PEEQ, and collision temperature for different deposition cases under the condition of 300 °C preheating temperature and 650 m/s collision velocity. (a) Single-layer, (f) two-particle/two-layer (l) multi-particle/two-layer. Plastic strain contours of single-layer case at (b) 10 ns, (c) 20 ns, (d) 25 ns and (e) the collision temperatures at different locations. Plastic strain contours of two-particle/two-layer case at (g) 10 ns, (h) 20 ns, (i) 30 ns and (j) 40 ns and (k) the collision temperatures at different locations. Plastic strain contours of two-particle/two-layer case at (m) 50 ns and (n) the collision temperatures at different locations.

For the two-particle/two-layer deposition in Figure 7b, the severe plastic deformation among the two particles results in thermal softening and plastic flow during impact. In the continuous deposition process (Figure 7g–j), the bottom particle is squeezed by the upper particle, and the flattening rate increases continuously. The highest temperature (curve I in Figure 7k) develops at the boundary between the bottom particle and the substrate, reaching more than 1972 K, which is a higher temperature than the melting point (1952 K) of Ti alloy, which brings about the localized melt of the particles and forms an effective

metallurgical bond with the matrix. At such a high collision temperature, the bottom particle experiences an intensive deformation with a very high particle-flattening rate. In comparison, the collision temperature between the two particles (point II) increases after a 30 ns delay. The final stable temperature reaches 1272 K, which is not high enough to melt the particles. The temperature at point II implies that the bonding between the two particles is mainly a mechanical bond. Overall, in the two-particle/two-layer case, the subsequent particles exert high heat on the substrate, bringing about a metallurgical bond. However, the bond between the particles represents the coexistence of a mechanical bond a metallurgical bond. Similar results can be observed for the multi-particle/two-layer deposition case in Figure 71. The deformation of the bottom particles is more severe than that of the subsequent particles, taking advantage of the continuous impact. Moreover, the collision temperatures also show a high value (higher than the melting point of Ti) between the bottom particles and the substrate and a low value among particles. The collision temperatures further confirm the coexistence of mechanical and metallurgical bonds among particles and the fully metallurgical bond between the coating and substrate.

3.2. Microstructure and Bonding Type of the Coatings

The above simulation results show a correlation between the bonding types (i.e., mechanical interlock and metallurgical bond) and the collision temperatures at the predicted velocity. Experimental observations, including particles deformation and bonding types, were carried out to validate the correlation.

Figure 8a shows the SEM morphology of the TC4 alloy powders. It can be seen that the powders have a smoother surface, with particle sizes ranging from 15 to 45 μ m. The coating surface at different magnifications is shown in Figure 8b–d. In Figure 8b, it can be observed that the spray particles experience intensive plastic deformation, shatter into debris, and form a coating after they impact the substrate. The debris bond with each other by mechanical interlock at region I and by metallurgical bond at region II, suggesting the coexistence of mechanical and metallurgical bonding among particles. Such results are consistent with the simulation results in Figure 7. The details of metallurgical bonding are shown in Figure 8c,d. The SEM morphologies in Figure 8c,d indicate that adiabatic shear instability (ASI) occurs at the preheating temperature and critical velocity, bringing about a good bond among the particles and a compact coating structure.

Figure 9 shows the cross-sectional SEM images of the coating after polishing. Generally, the coating is about 600 μ m in thickness and exhibits good quality without obvious cracks and pores (Figure 9a). Figure 9b illustrates the bonding among particles without the impact of the subsequent particles. It shows typical characteristics of the jets and the molten/unmelted particles, confirming the coexistence of mechanical and metallurgical bonding among particles. In the cross-sectional images in Figure 9c, deformed particles (I) in various shapes can be observed with different flattening rates. However, the magnified cross-sectional image clearly shows the pore distribution among the particles. Moreover, at the boundary of the particles, fusion zones develop a layer (II) to bond the adjacent particles, further confirming that the collision temperature reaches the melting point of TC4, which is in agreement with the simulation results in Figures 6 and 7. In terms of the coating/substrate interface, it is observed that the fusion layer also exists between the bottom deformed particles and the substrate. The gray layer implies that the interface is characterized by complete metallurgical bonding, consistent with the simulation in Figure 7.

The EDS line-scan results in Figure 9d show the changes in elemental (Ti, Al, and V) composition across the interface. At the interface, the three elements change gradually due to the existence of the fusion layer, resulting in elemental diffusion. The amount of Al in the fusion layer at the interface is higher than that of region II, the fusion layer inside the coatings, suggesting the diffusion of Al from the Al substrate. These results confirm metal-lurgical bonding between the coating and the substrate. Another noteworthy phenomenon is that the Ti composition of the fusion layer (II) is lower than that of deformed particles

(I). Such a phenomenon suggests the evolution of different phases and microstructure in regions I and II.

Figure 8. (a) SEM morphology of the TC4 alloy powders and (b–d) SEM morphology of the surface morphology of coatings.

Figure 9. (**a**–**c**) Cross-sectional SEM morphology of TC4 coating and (**d**) EDS line scan across the coating/substrate interface.

With the aim of characterizing the microstructure and phase evolution in regions I and II, TEM images of these two regions are shown in Figure 10. Figure 10a shows the boundary between regions I and II. It is clear that these two regions have a different microstructure, and a distinct boundary can be observed. High-resolution TEM images are shown in Figure 10b,c. The deformed particle (I) in Figure 10b is characterized by needle-like phases (α phase) and primary β phases. The needle-like α phases are formed because the primary α phase experiences distortion and twisting upon impact during spraying. However, such an impact does not induce the phase transition, since the collision temperature inside the particle is not high enough to bring about recrystallization. On the other hand, in region II, the phases in the particle surface experience transition due to the high temperature (Figures 6 and 7) during spray. Thus, the primary β phases decomposes and become the primary and secondary α phases, in addition to some residual β phases, as shown in Figure 10c. Diffraction patterns (the inserted images) show the primary and secondary α phases. The primary α phase (A) has a hexagonal structure (space group: P63/mmc), and the secondary α phase (B) has a cubic structure (space group: Im3m). The delicate isometric crystals, as well as more primary and secondary α phases in fusion regions, play essential roles in developing high-quality coatings with high bonding strength and anticorrosion properties.

Figure 10. (a) TEM images of (I) deformed particles and (II) the fusion layer, (b) the diffraction pattern of needle-like phases (α phase) and primary β phases. (c) the diffraction pattern of primary α phases (A) and secondary α phases (B).

4. Conclusions

The simulation results predict the critical velocity of Ti particles on an Al substrate by HVAF spray, which is associated with the collision velocity and preheating temperature of particles. Critical velocity decreases with increasing collision velocity and preheating temperature. The optimum preheating temperature is 300 °C to achieve the critical velocity of 650 m/s. At 300 °C and 650 m/s, particles experience adiabatic shear instability (ASI) and plastic deformation and exhibit different bonding types, according to the simulation results. The bonding types are well-correlated with the simulated collision temperature. The experimental observations show the representative characteristics of the sprayed Ti coating (i.e., deformed particles, fusion layers, and elemental diffusion). Importantly, experiments confirm that mechanical interlock and metallurgical bonding coexist among spray particles,

and the bond between the coating and the substrate is complete metallurgical bonding. Such observations verify the bonding types determined by the simulated collision temperature under the predicted critical velocity.

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References

- Chak, V.; Chattopadhyay, H.; LDora, T. A review on fabrication methods, reinforcements and mechanical properties of aluminum matrix composites. J. Manuf. Processes 2020, 56, 1059–1074. [CrossRef]
- Samodurova, M.; Shaburova, N.; Samoilova, O.; Moghaddam, A.O.; Pashkeev, K.; Ul'yanitckiy, V.; Trofimov, E. Properties of WC–10%Co–4%Cr Detonation Spray Coating Deposited on the Al–4%Cu–1%Mg Alloy. *Materials* 2021, 14, 1206. [CrossRef] [PubMed]
- McCafferty, E. Introduction to Corrosion Science, 1st ed.; Springer: New York, NY, USA, 2009; pp. 56–62.
- Nosova, E.; Baliakin, A.; Galkina, N.; Alekseevet, V. Research of Titanium Covering Effect Received by Selective Laser Melting on Mechanical Properties of Aluminum Alloy Al-6Mg. *Mater. Today Proc.* 2019, 11, 370–374. [CrossRef]
- Wang, C.; Li, J.; Wang, T.; Chai, L.; Deng, C.; Wang, Y.; Huang, Y. Microstructure and properties of pure titanium coating on Ti-6Al-4V alloy by laser cladding. *Surf. Coat. Technol.* 2021, 416, 127–137. [CrossRef]
- da Silva, F.S.; Cinca, N.; Dosta, S.; Cano, I.G.; Guilemany, J.M.; Caires, C.S.A.; Lima, A.R.; Silva, C.M.; Oliveira, S.L.; Caires, A.R.L.; et al. Corrosion resistance and antibacterial properties of copper coating deposited by cold gas spray. *Surf. Coat. Technol.* 2019, 361, 292–301. [CrossRef]
- Li, W.; Cao, C.; Yin, S. Solid-state cold spraying of Ti and its alloys: A literature review. *Prog. Mater. Sci.* 2020, 110, 100633. [CrossRef]
- Hussain, T. Cold Spraying of Titanium: A Review of Bonding Mechanisms, Microstructure and Properties. *Key Eng. Mater.* 2012, 533, 53–90. [CrossRef]
- 9. Hesamodin, J.; Jabbarzadeh, A. Molecular simulation of high-velocity deposition of titanium dioxide nanoparticles on titanium. *Appl. Surf. Sci.* **2021**, 542, 148567–148577. [CrossRef]
- 10. Wong, W.; Irissou, E.; Ryabinin, A.N.; Legoux, J.-G.; Yue, S. Influence of Helium and Nitrogen Gases on the Properties of Cold Gas Dynamic Sprayed Pure Titanium Coatings. *J. Therm. Spray Technol.* **2011**, *20*, 213–226. [CrossRef]
- 11. Zhizhong, W.; Chao, H.; Huang, G.; Bin, H.; Bin, H. Cold spray micro-defects and post-treatment technologies: A review. *Rapid Prototyp. J.* **2019**, *28*, 330–357. [CrossRef]
- Luo, X.-T.; Wei, Y.-K.; Wang, Y.; Li, C.-J. Microstructure and mechanical property of Ti and Ti6Al4V prepared by an in-situ shot peening assisted cold spraying. *Mater. Des.* 2015, 85, 527–533. [CrossRef]
- 13. Li, C.-J.; Li, W.-Y. Deposition characteristics of titanium coating in cold spraying. Surf. Coat. Technol. 2003, 167, 278–283. [CrossRef]
- 14. Assadi, H.; Gärtner, F.; Stoltenhoff, T.; Kreye, H. Bonding mechanism in cold gas spraying. *Acta Mater.* **2003**, *51*, 4379–4394. [CrossRef]
- Chakravarthy, Y.; Bhandari, S.; Chaturvedi, V.; Pragatheeswaran, A.; Nagraj, A.; Thiyagarajan, T.K.; Ananthapadmanaban, P.V.; Das, A.K. Plasma spray deposition of yttrium oxide on graphite, coating characterization and interaction with molten uranium. *J. Eur. Ceram. Soc.* 2015, 35, 623–756. [CrossRef]
- Kang, C.W.; Ng, H.W.; Yu, S.C.M. Imaging Diagnostics Study on Obliquely Impacting Plasma-Sprayed Particles Near to the Substrate. J. Therm. Spray Technol. 2006, 15, 118–130. [CrossRef]
- 17. Lemiale, V.; King, P.C.; Rudman, M.; Prakash, M.; Cleary, P.W.; Jahedi, M.Z.; Gulizia, S. Temperature and strain rate effects in cold spray investigated by smoothed particle hydrodynamics. *Surf. Coat. Technol.* **2014**, 254, 121–130. [CrossRef]
- 18. Ye, H.; Wang, J. Preparation of aluminum coating on Lexan by cold spray. *Mater. Lett.* 2014, 137, 21–24. [CrossRef]
- 19. Klinkov, S.V.; Kosarev, V.F.; Rein, M. Cold spray deposition: Significance of particle impact phenomena. *Aerosp. Sci. Technol.* 2005, *9*, 582–591. [CrossRef]

- 20. Meng, F.; Yue, S.; Song, J. Quantitative prediction of critical velocity and deposition efficiency in cold-spray: A finite-element study. *Scr. Mater.* **2015**, *107*, 83–87. [CrossRef]
- 21. Li, W.Y.; Zhang, D.D.; Huang, C.J.; Yin, S.; Yu, M.; Wang, F.F.; Liao, H.L. Modelling of Impact Behaviour of Cold Spray Particles: Review. *Surf. Eng.* **2014**, *30*, 299–308. [CrossRef]
- 22. Ye, F.; Niu, A.; Guo, A.; Ding, K. Impact Behavior of WC-17Co Particle in HVOF Spraying. J. Tianjin Univ. 2016, 49, 882–887. [CrossRef]
- Yu, M.; Li, W.Y.; Wang, F.F.; Suo, X.K.; Liao, H.L. Effect of Particle and Substrate Preheating on Particle Deformation Behavior in Cold Spraying. *Surf. Coat. Technol.* 2013, 220, 174–178. [CrossRef]
- Li, W.Y.; Yang, K.; Yin, S.; Guo, X.P. Numerical Analysis of Cold Spray Particles Impacting Behavior by the Eulerian Method: A Review. J. Therm. Spray Technol. 2016, 25, 1441–1460. [CrossRef]
- 25. Wang, Y.; Han, Y.; Lin, C.; Zheng, W.; Jiang, C.; Wei, A.; Liu, Y.; Zeng, Y.; Shi, Y. Effect of spraying power on the morphology of YSZ splat and micro-structure of thermal barrier coating. *Ceram. Int.* **2021**, *47*, 18956–18963. [CrossRef]
- Nastic, A.; Jodoin, B.; Poirier, D.; Legoux, J.-G. Particle temperature effect in cold spray: A study of soft particle deposition on hard substrate. *Surf. Coat. Technol.* 2021, 406, 126735. [CrossRef]
- Bolelli, G.; Cannillo, V.; Gadow, R.; Killinger, A.; Lusvarghi, L.; Rauch, J. Properties of High Velocity Suspension Flame Sprayed (HVSFS) TiO 2 coatings. *Surf. Coat. Technol.* 2009, 203, 1722–1732. [CrossRef]
- Semih, A.; Puyuan, W.; Tsai, J.-T.; Chandra, N.; Jun, C.; Byung-Guk, M. A study on droplets dispersion and deposition characteristics under supersonic spray flow for nanomaterial coating applications. *Surf. Coat. Technol.* 2021, 426, 127788. [CrossRef]
- 29. Munagala, V.N.V.; Chakrabarty, R.; Song, J.; Chromik, R. Effect of metal powder properties on the deposition characteristics of cold-sprayed Ti6Al4V-TiC coatings: An experimental and finite element study. *Surf. Interfaces* **2021**, *25*, 58–61. [CrossRef]
- Chakrabarty, R.; Song, J. A modified Johnson-Cook material model with strain gradient plasticity consideration for numerical simulation of cold spray process. Surf. Coat. Technol. 2020, 397, 125981. [CrossRef]
- 31. Singhal, C.; Murtaza, Q.; Parvej. Simulation of Critical Velocity of Cold Spray Process with Different Turbulence Models. *Mater. Today Proc.* **2018**, *5*, 17371–17379. [CrossRef]
- 32. Kim, H.-J.; Lee, C.-H.; Hwang, S.-Y. Fabrication of WC-Co coatings by cold spray deposition. *Surf. Coat. Technol.* **2005**, *191*, 335–340. [CrossRef]
- 33. King, P.C.; Busch, C.; Kittel-Sherri, T.; Jahedi, M.; Gulizia, S. Interface melding in cold spray titanium particle impact. *Surf. Coat. Technol.* **2014**, *239*, 191–199. [CrossRef]
- 34. Rahmati, S.; Jodoin, B. Physically Based Finite Element Modeling Method to Predict Metallic Bonding in Cold Spray. *J. Therm. Spray Technol.* 2020, *29*, 611–629. [CrossRef]
- Fardan, A.; Berndt, C.C.; Ahmed, R. Numerical modelling of particle impact and residual stresses in cold sprayed coatings: A review. Surf. Coat. Technol. 2021, 409, 126835. [CrossRef]
- Nastic, A.; Vijay, M.; Tieu, A.; Rahmati, S.; Jodoin, B. Experimental and Numerical Study of the Influence of Substrate Surface Preparation on Adhesion Mechanisms of Aluminum Cold Spray Coatings on 300M Steel Substrates. J. Therm. Spray Technol. 2017, 26, 1461–1483. [CrossRef]
- Zhu, L.; Jen, T.-C.; Pan, Y.-T.; Chen, H.-S. Particle Bonding Mechanism in Cold Gas Dynamic Spray: A Three-Dimensional Approach. J. Therm. Spray Technol. 2017, 26, 1859–1873. [CrossRef]