

Article

Microstructure and Microhardness of Ni/Al-TiB₂ Composite Coatings Prepared by Cold Spraying Combined with Postannealing Treatment

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Abstract: Ni/Al-TiB₂ composite powders were deposited on the surface of 316L stainless-steel substrates by cold spraying at gas temperatures of 250 and 450 °C, respectively. Then, the as-sprayed coatings were annealed at 650 °C for 10, 20, and 30 h. The experimental results showed that the average porosity of as-sprayed coating dropped from about 0.68% to 0.054% as the cold spraying gas temperature increased. The contents of Ni, Al, and TiB₂ in the as-sprayed coatings were different from that of the Ni/Al-TiB₂ composite powders. The main phase compositions of the as-sprayed Ni/Al-TiB₂ coatings were the same as those of composite powder, consisting only of pure Ni, Al, and TiB₂ phases. TiB₂ as a reinforced particle in the as-sprayed coating could obviously increase the microhardness of the coatings. NiAl₃ and Ni₂Al₃ intermetallic compounds were synthesized in situ in all of the annealed coatings, and the average contents of NiAl₃ and Ni₂Al₃ intermetallic compounds increased as the cold spraying gas temperature increased. The distribution of TiB₂ particle was changed as the annealing times increased, which changed from more comparative uniform distribution to accumulation. The average porosity of the annealed coatings increased as the annealing time increased. The microhardness of Ni/Al-TiB₂ coatings annealed at 650 °C for 10 h was increased remarkably due to the reinforcement role of TiB₂ particles and NiAl₃ and Ni₂Al₃ intermetallic compounds.

Keywords: cold spraying; NiAl intermetallic compounds; TiB₂; microstructure; porosity

1. Introduction

NiAl intermetallic compounds are regarded as high-temperature structure materials, owing to their outstanding properties, such as high creep strength, high melting point (1676 °C), high oxidation and corrosion resistance, low density (5.9 g/cm³), and high thermal conductivity (76 W/mK) [1–5]. However, the inherent shortcomings of NiAl intermetallic compounds, such as poor fracture toughness at room temperature, low ductility at ambient temperatures, and inadequate strength at elevated temperatures, limit their high temperature structural applications [6]. In order to overcome these drawbacks, the NiAl intermetallic composites using reinforcing ceramic particles (e.g., TiC, WC, TiO₂, Al₂O₃, ZrO₂, TiB₂, and CrB₂) as an additive have been prepared to improve their mechanical properties and high-temperature strength [7–17]. Titanium diboride (TiB₂), due to its excellent properties such as high melting point (2900 °C), high hardness (27 GPa), and high elastic modulus (370 GPa), is particularly suitable in this respect due to its inertness towards NiAl [13]. Guo et al. [13] reported that TiB₂ as a reinforcing ceramic material had better distribution characteristics and increased the tensile

strength of an NiAl composite. Yeh et al. [15] found that the fracture toughness of an NiAl composite increased from 4.2 to 5.8 MPa·m^{1/2} and the hardness increased with the decreasing NiAl content for a synthesized TiB₂/TiN-added NiAl composite. Hawk et al. [16] and Bhaumik et al. [17] reported that the hardness of NiAl-TiB₂ composites increased with the increasing volume fraction of TiB₂.

Recently, NiAl intermetallic composite coatings intended for high-temperature, wear, corrosive and erosive applications were prepared by thermal spraying methods such as plasma spraying [18–20], high velocity oxy-fuel (HVOF) spraying [10,21–24], arc spraying [20,25], electro-thermal explosion ultrahigh speed spraying [26], and laser cladding [27,28]. Movahedi [10,19] prepared Ni(Al)-15 wt % (Al₂O₃-13%TiO₂) nanocomposite coatings have been prepared by plasma spraying and HVOF spraying, respectively. The results showed that the microhardness and wear resistance of the nanocomposite coatings were higher than that of NiAl intermetallic coatings. Enayati et al. [22] reported that the microhardness of nanocrystalline NiAl coatings (5.40–6.08 GPa) was higher than that of conventional NiAl coatings. The diffusion mechanism of Ni/Al composite coatings deposited by arc spraying and plasma spraying technologies was investigated after heat treatment [20]. Hou et al. [26] reported that the addition of TiB₂ to NiAl coatings increased the hardness (20 wt % TiB₂, 1057 HV_{0.2}). The microstructure, tribological properties, and wear mechanism of NiAl coatings that were in situ synthesized by laser cladding were studied by Yu et al. [27,28]. In research on thermal sprayed or laser-cladded NiAl coatings, oxides commonly appeared in the NiAl intermetallic coating during spraying due to the high flame temperature, which modified the coating compositions and deteriorated the properties of the coatings [29].

Cold spraying is a novel, emerging process for preparing coatings or bulk materials in solid state due to its low processing temperature [30]. In this process, the high kinetic energy of the sprayed particles that are accelerated to a high velocity (300–1000 m/s) results in severe plastic deformation onto a substrate to form a high degree of bonding and a dense coating [31,32]. Compared with thermal spraying, the composition of the sprayed particles can be retained in the coating with little oxidation and decomposition in cold spraying [33]. Therefore, metal [34,35], alloy [36], or cermet [37] coatings deposited by cold spraying have been studied by many researchers. However, due to the intrinsic brittleness of NiAl intermetallic compounds at low temperatures, plastic deformation is difficult to achieve with cold-sprayed NiAl intermetallic compound particles [38,39]. In recent years, some researchers have reported that metal powder mixtures (e.g., Ti/Al, Fe/Al, and Ni/Al) and ball-milled Ni/Al-Al₂O₃ composite powder can be deposited on substrates to prepare dense cold-sprayed coatings, and intermetallic compounds can be formed by post-annealing treatment [38–44]. However, there are few reports on the characterization of cold-sprayed Ni/Al-TiB₂ composite coatings at various gas temperature and the influence of phase transformation on Ni/Al-TiB₂ coatings via different annealing times. Due to the critical particle velocity influenced by cold spraying gas temperature and particle characteristics [33,34], the reduced content of particles in the coatings would affect the annealed intermetallic compound compositions. Thus, in this study, we fabricated Ni/Al-TiB₂ intermetallic composite coatings by cold spraying combined with a postannealing method to investigate the microstructure and microhardness of Ni/Al-TiB₂ coatings.

2. Materials and Methods

2.1. Powder and Coating Preparation

Commercially available Ni (99.8 wt %, D₁₀ = 20.8 µm, D₅₀ = 30.5 µm, and D₉₀ = 44.7 µm; BGRIMM Advanced Materials Science & Technology Co., Ltd., Beijing, China), Al (99.0 wt %, D₁₀ = 15 µm, D₅₀ = 35.5 µm, and D₉₀ = 75.3 µm; BGRIMM Advanced Materials Science & Technology Co., Ltd., Beijing, China), and TiB₂ powders (99.5 wt %, D₁₀ = 1.32 µm, D₅₀ = 4.66 µm, and D₉₀ = 27.3 µm; Weifang Bangde Special Materials Co., Ltd., Beijing, China) were used as starting materials in this study. The size distribution of raw powders was measured by a laser diffraction meter (Malvern Mastersizer 2000, Malvern instrument Ltd., Scotland, UK). The Ni/Al-TiB₂ composite powders were prepared by

a ball milling method with a ball-to-powder weight ratio of 2:1 at a rotation speed of 100 rpm for 1 h. The volume fraction of Ni, Al and TiB_2 particles in the composite was 31.6, 48.4, and 20 vol %, respectively. Figure 1 shows the surface and cross-sectional morphologies and the size distribution of Ni, Al, and TiB_2 powders. Ni and Al powders with a spherical morphology were manufactured through electrolytic and gas atomization processes, as shown in Figure 1a,d and Figure 1b,e in SEM back-scattered electron (BSE) imaging mode, respectively. TiB_2 powders produced by a carbothermic process presented an angular morphology, as shown in Figure 1c,f. The Ni-Al/ TiB_2 composite powders are shown in Figure 2 in SEM-BSE imaging mode.

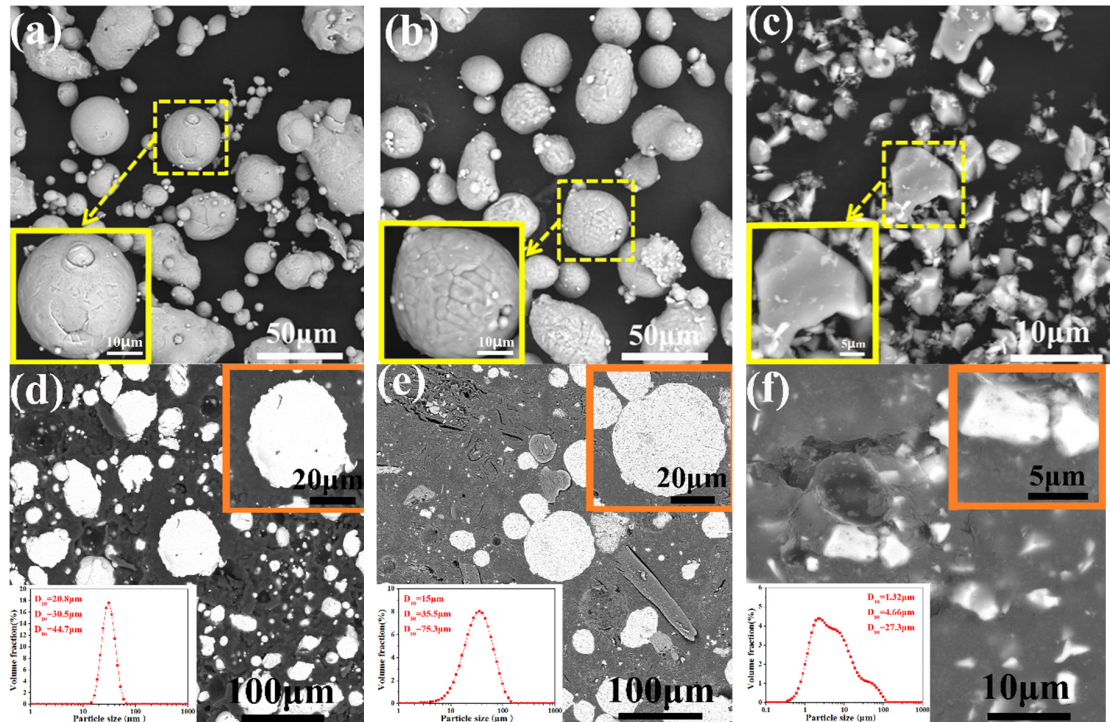


Figure 1. The surface and cross-sectional morphologies of the powders: (a,d) Ni, (b,e) Al, and (c,f) TiB_2 .

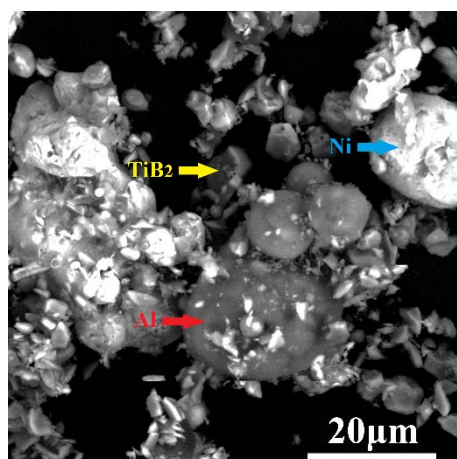


Figure 2. The morphology of Ni-Al/ TiB_2 powders.

The Ni/Al- TiB_2 composite coatings were deposited on the surface of 316L stainless-steel substrates by a cold spray system (CS-2000) developed at Xi'an Jiaotong University. A spray gun with a de Laval type nozzle with a throat diameter of 2 mm was adopted. The divergent nozzle with an exit diameter of 6 mm was 100 mm in length [37]. In this study, nitrogen gas was used as the accelerating and

powder-feeding gases at pressures of 2.0 and 2.2 MPa, respectively. The gas temperature in the gun pre-chamber for depositing the coatings was 250 ± 30 and 450 ± 30 °C. The standoff distance from the nozzle exit to the substrate surface was 20 mm and the traverse speed of the spray gun for coating deposition was 10 mm/s. Scraper powder feeder (Guangzhou Sanxin Metal S & T Co., Ltd., Guangzhou, China) was used for spraying powder feeding. The rotation rate of the scraper powder feeder was 50 r/min. The contents of Ni, Al, and TiB_2 in the Ni/Al- TiB_2 composite coatings were measured by image analysis of five SEM-BSE cross-sectional micrographs.

2.2. Annealing Treatment

In order to form NiAl intermetallic compounds by solid-state diffusion and realize the formation mechanism of the NiAl intermetallic compounds in this study, the as-sprayed Ni/Al- TiB_2 composite coatings were annealed at temperatures of 650 °C for 10, 20, and 30 h using a 1400 multi-channel mixed pipe furnace (SG-GL1400K, Shanghai Institute of Optics and Fine Mechanics, CAS, Chinese Academy, Shanghai, China) at a heating rate of 15 °C/min.

2.3. Microstructure Characterization and Microhardness of Coatings

The morphologies of the cold-sprayed and the annealed composite coatings were analyzed by SEM (VEGA II-LSU, TESCAN, Czech Republic) equipped with energy dispersive spectroscopy (EDS) in BSE imaging mode. The phase constitution transformation of the as-sprayed coatings after annealing treatment was analyzed by XRD (Bruker D8 Advance, Karlsruhe, Germany) with a copper radiation source ($\text{CuK}\alpha$, $\lambda = 1.5418$ Å) operated at 35 kV and 35 mA. The porosity of the Ni/Al- TiB_2 composite and the annealed coatings was measured by the image analysis method (Software Image J, version 1, National institute of health. USA) using five SEM micrographs. The microhardness of the coatings was measured on polished cross sections using an HXD-1000 TM/LCD microhardness tester (Shanghai Precision Instruments Co., Ltd., Shanghai, China) with a 2.94 N load and 20 s dwell time. The microhardness value of the coatings was in the mean of 10 random indents. The surface roughness of the as-sprayed Ni/Al- TiB_2 coatings was measured by a TA620-A surface roughness instrument (Beijing time-top technology Co., Ltd., Beijing, China), and the value was in the mean of five random specimens.

3. Results and Discussion

3.1. Microstructure of the As-Sprayed Ni/Al- TiB_2 Coatings

Figure 3 shows the surface morphologies of the as-sprayed Ni/Al- TiB_2 coatings at different gas temperatures. It can be seen that there are spherical particles which are similar to the original powders on the surface of the coatings. There also appear some hemispherical craters (as indicated by the white hollow arrow), polygonal craters (as indicated by the yellow arrow), and holes formed by the accumulation of particles (as indicated by the green arrow) on the surface of the coatings. The reason for this is that, owing to differences in the Ni, Al, and TiB_2 particle characteristics, the cold spraying critical velocity of the Ni, Al, and TiB_2 particles are different. Moreover, the particles were rebounding off the surface of the coating to form near-spherical or polygonal craters. Nevertheless, due to the low microhardness of the Al material, some Ni particles (as indicated by the blue arrow) were embedded into Al splats to a certain depth and nearly retained a spherical shape similar to that of the original powder. Compared with the surface morphology of the coating sprayed at a 250 °C gas temperature (as shown in Figure 3a), the hole rate of the surface of the coating (as shown in Figure 3b) was 1.54%, which was less than that of the coating sprayed at a 250 °C gas temperature (4.11%). This illustrates that the larger deformation of Al splats could fill the holes due to the higher critical velocity during spraying at 450 °C; therefore, the coating sprayed at 450 °C had a denser microstructure with fewer holes. The average surface roughness values of the coatings (as-sprayed at 250 and 450 °C) were 8.66 ± 0.73 and 6.17 ± 0.88 µm, respectively. The details of the surface roughness values are listed in Table 1.

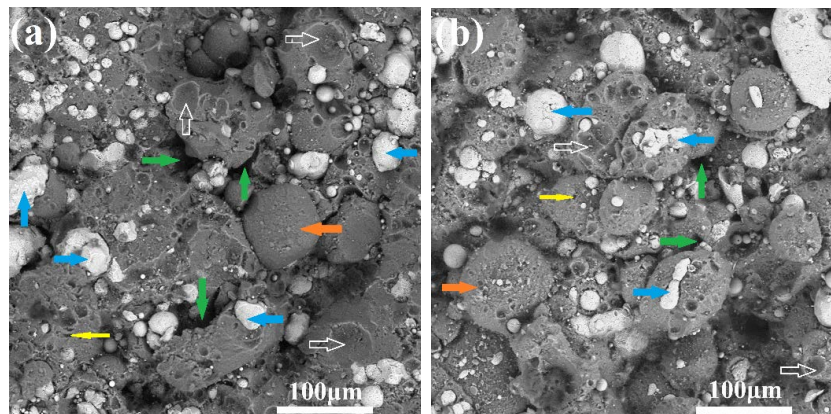


Figure 3. morphologies of the cold-sprayed Ni/Al-TiB₂ coatings at (a) 250 and (b) 450 °C.

Table 1. The details of the surface roughness values of the coatings.

Coating Types	Specimens					Average Value (μm)
	1	2	3	4	5	
Coating sprayed at 250 °C	8.56	9.15	8.78	7.46	9.33	8.66 ± 0.73
Coating sprayed at 450 °C	6.73	7.25	5.36	6.28	5.21	6.17 ± 0.88

Figure 4 shows the cross-sectional morphologies of the as-sprayed Ni/Al-TiB₂ coatings at different gas temperatures. The porosities of the coatings sprayed at gas temperatures of 250 and 450 °C were 0.68% and 0.054%, respectively. This clearly illustrates that the coatings presented a denser microstructure. And there was no obvious micro-crack between coating and substrate. Further, Ni (light) and TiB₂ (as shown by the yellow arrow) were embedded in a matrix of Al (as shown in Figure 4c,d), and there was no obvious gap among the Ni, Al, and TiB₂ phases. Compared with the contents of Ni and Al in the original powder mixture composition (Ni₅₀Al₅₀, at %), the average contents of Ni and Al in the as-sprayed coating at a 250 °C gas temperature were approximately 21.84 ± 2.16 and 70.42 ± 4.37 vol %, respectively; however, those of Ni and Al in the coating at a 450 °C gas temperature were approximately 32.66 ± 1.87 and 54.93 ± 3.61 vol %, respectively. It can be seen that nickel was lost during the spraying process at 250 °C, and the contents of Ni and Al in the coating at 450 °C were nearly the same as those of the feedstock powder. The reason for the loss of nickel is similar to that reported in [43,45,46], and the content of Ni in the coating and the impacting velocity increased as the gas temperature increased. However, the content of TiB₂ in the as-sprayed coating at gas temperatures of 250 and 450 °C was 7.74 ± 0.84 and 12.41 ± 1.13 vol %, respectively. This shows that the content of TiB₂ decreased during cold spraying due to the unique mechanical properties of the TiB₂ material. Nevertheless, the successive incident TiB₂ particles would strike the predeposited splats, consequently tamping the coatings and decreasing the porosity of the coatings.

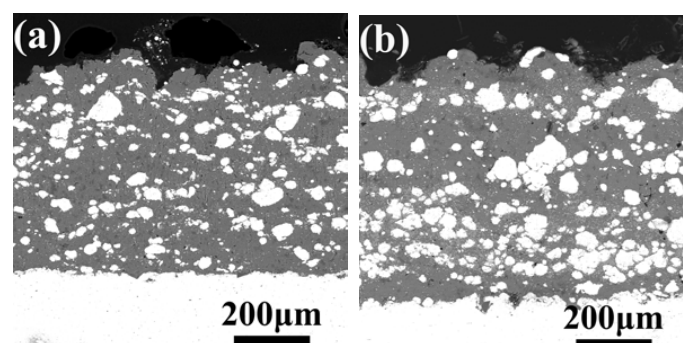


Figure 4. Cont.

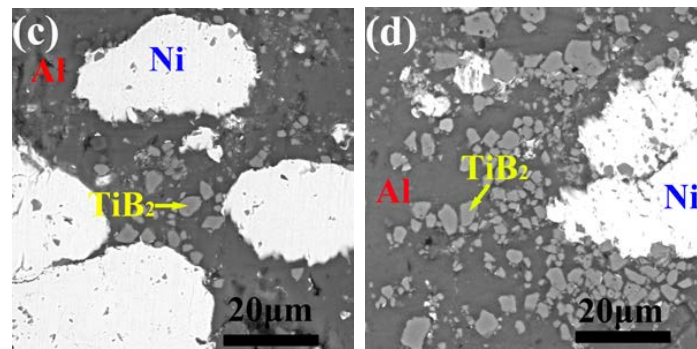


Figure 4. Cross-sectional morphologies of the cold-sprayed Ni/Al-TiB₂ coatings at (a,c) 250 °C and (b,d) 450 °C.

3.2. Microhardness of As-Sprayed Ni/Al-TiB₂ Coatings

The microhardness of the Ni/Al-TiB₂ coatings compared to the cold-sprayed Ni/Al coatings (as shown in Figure 5) under the same spraying process parameters is shown in Figure 6. The microhardness of Ni/Al-TiB₂ coatings was obviously higher than that of the Ni/Al coatings; specifically, the microhardness of Ni/Al-TiB₂ coatings was more than three times that of the Ni/Al coating. The highest microhardness of Ni/Al-TiB₂ coating sprayed at 450 °C was 475.26 ± 31.21 HV_{0.3}. It was also revealed that TiB₂ as a reinforcing ceramic material could increase the microhardness of the Ni/Al-TiB₂ composite coating, and the microhardness of the coating increased as the content of TiB₂ increased.

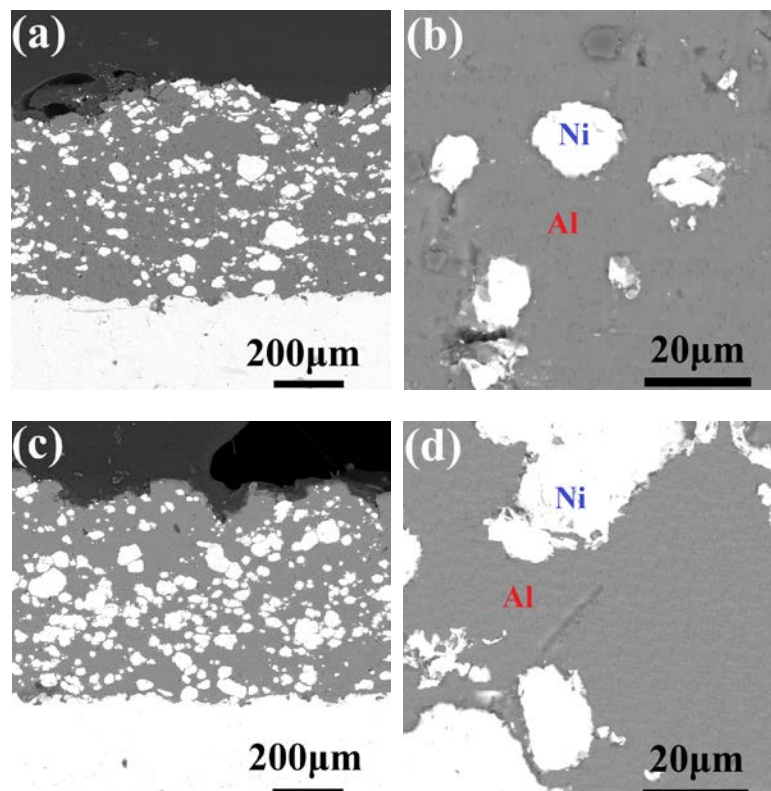


Figure 5. Cross-sectional morphologies of the cold-sprayed Ni/Al coatings at (a,b) 250 °C and (c,d) 450 °C.

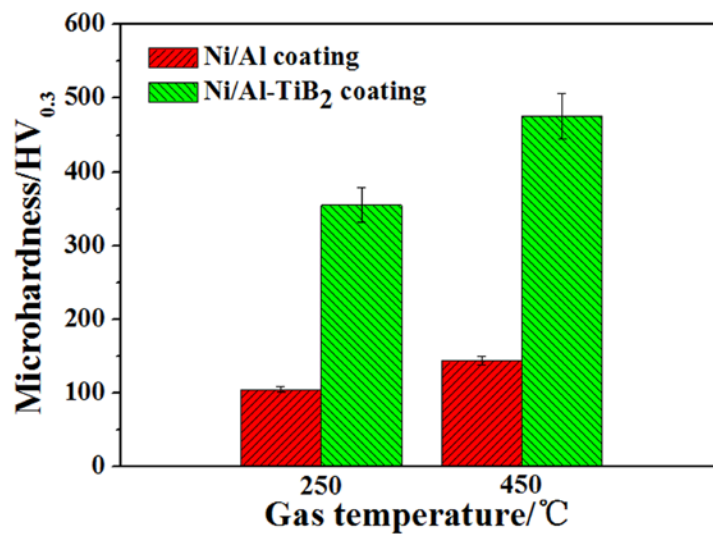


Figure 6. Microhardness of Ni/Al and Ni/Al-TiB₂ coatings.

3.3. Phase Compositions of Feedstock Powder and As-Sprayed Ni/Al-TiB₂ Coatings

Figure 7 shows the XRD patterns of the feedstock powder and the as-sprayed Ni/Al-TiB₂ coatings. The main phase compositions of the as-sprayed Ni/Al-TiB₂ coatings were the same as those of the feedstock powder, consisting only of pure Ni, Al, and TiB₂ phases. Due to the low temperature characteristic of the cold spraying process, no oxides or nickel aluminum intermetallic phases were observed in the coatings. However, due to the high-velocity impact of the particles causing plastic deformation of the substrate and/or previously deposited coating material [35], peak broadening was observed for the as-sprayed Ni/Al-TiB₂ coatings in the XRD analysis. In order to characterize the plastic deformation of particle deposition, the full widths at half maximum (FWHMs) of Ni and Al diffraction peaks were estimated from XRD data and are listed in Figure 8. The FWHMs of the Ni and Al diffraction peaks in the as-sprayed Ni/Al-TiB₂ coatings were larger than those of the feedstock powder, which indicates that Ni and Al particles underwent a certain plastic deformation upon high-speed impact.

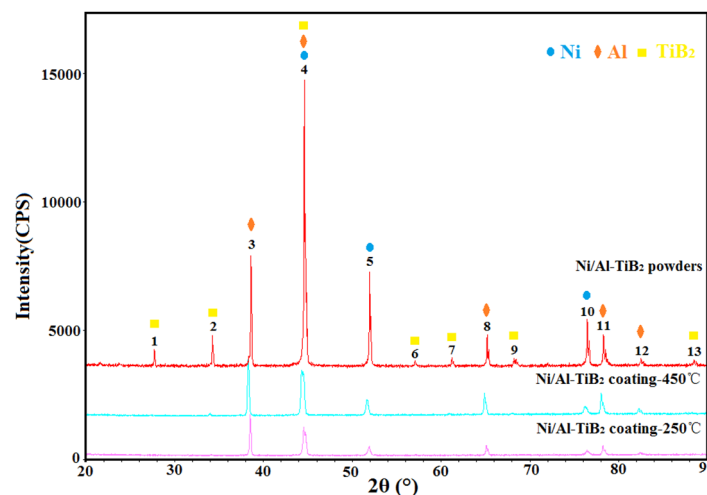


Figure 7. XRD patterns of Ni/Al-TiB₂ feedstock powder and as-sprayed coatings.

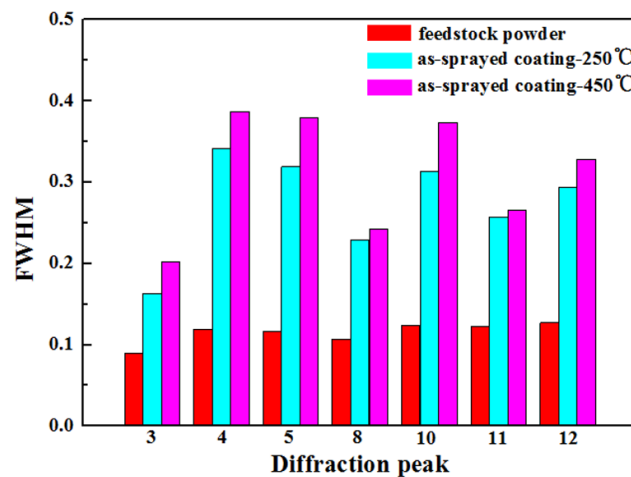


Figure 8. Full widths at half maximum (FWHMs) of the diffraction peaks of the feedstock powder and the as-sprayed coatings.

3.4. XRD Patterns of the Annealed Ni/Al-TiB₂ Coatings

In order to clarify the microstructure evolution of the annealed Ni/Al-TiB₂ coatings at different annealing times, compositional analysis was carried out by XRD. Figure 9 shows the effect of annealing time on the XRD patterns of the annealed Ni/Al-TiB₂ coatings. This confirmed that there was no oxidation phase in the annealed coatings, and NiAl₃ and Ni₂Al₃ intermetallic compound formation actually occurred in all of the annealed coatings. Further, the content of the Al phase decreased, which was evident from the intensity of the diffraction peaks of Al phase, and the diffraction peaks of Al phase disappeared completely after annealing treatment at 650 °C for 30 h. This indicates that the Al phase completely transformed into NiAl₃ intermetallic compounds.

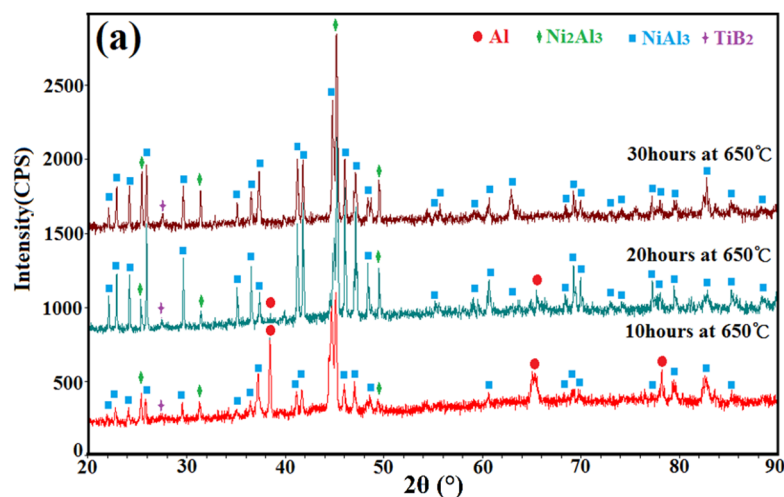


Figure 9. Cont.

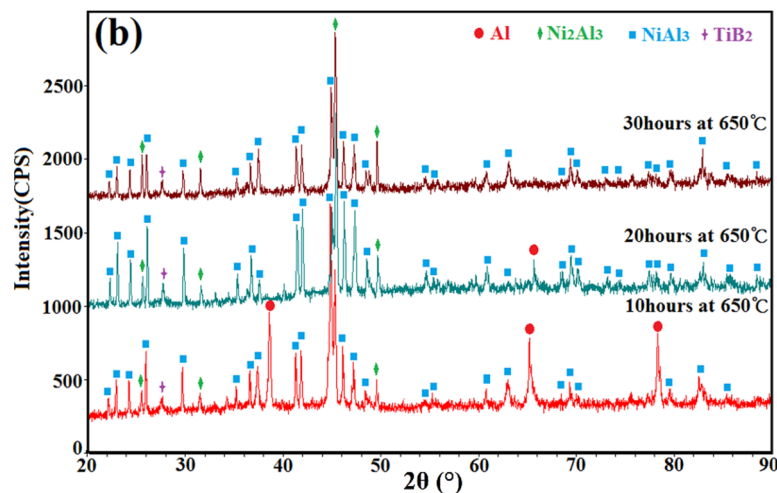


Figure 9. XRD patterns of the annealed Ni/Al-TiB₂ coating at different annealing time: (a) Ni/Al-TiB₂ coating as-sprayed at 250 °C and (b) Ni/Al-TiB₂ coating as-sprayed at 450 °C.

3.5. Microstructure, Composition and Porosity, and Microhardness of the Annealed Ni/Al-TiB₂ coatings

Figures 10–15 show the cross-sectional backscattered SEM morphologies and compositions of the annealed coatings at 650 °C for 10, 20, and 30 h, respectively. It can be seen that the coatings (as-sprayed at gas temperatures of 250 and 450 °C) annealed at 650 °C for 10 h (as shown in Figures 10 and 11) presented a denser microstructure with a small number of pores or cracks. There was no obvious micro-crack between the annealed coating and substrate. Furthermore, there was no interaction between the annealed coating and the substrate. Like the XRD analysis results, the EDS analysis revealed that NiAl₃ and Ni₂Al₃ intermetallic compounds appeared in the coating. This demonstrates that a solid-state diffusion reaction occurred between Ni particles and the Al matrix in the coating. However, larger Ni particles (as indicated by the purple arrow in Figures 10b and 11b) did not fully react with the Al matrix to form intermetallic compounds. By increasing the annealing time at 650 °C to 20 h, the microstructure of the annealed coatings (as-sprayed at gas temperatures of 250 and 450 °C) changed compared with the coating annealed at 650 °C for 10 h, and evident pores and cracks appeared. In addition, there was only a small amount of the Al phase in the coating (as indicated by the red arrow in Figures 12b and 13b), which illustrates that the bulk of the Al matrix reacted with Ni to form intermetallic compounds. After annealing at 650 °C for 20 h, a light gray layer (as marked by the red dotted line in Figures 12b and 13b) was observed between the interface of the coating and the substrate, and FeAl₃ intermetallic compounds (as indicated by the blue arrow in Figures 12b and 13b) were detected based on the EDS analysis. By close examination of the microstructure of the annealed coating at 650 °C for 30 h (as shown in Figures 14 and 15), both micrographs show the same set of NiAl₃ and Ni₂Al₃ intermetallic phases. In addition, as the annealing time increased, the content of the Ni₂Al₃ phase in the coating increased, the FeAl₃ intermetallic compound reaction layer between the coating and the substrate became thicker, and there was no Al phase in the annealed coating, as revealed by EDS and XRD. Therefore, the annealing treatment time clearly had a significant influence on the microstructure and composition of the coatings. By comparing all of the annealed coatings, it can be found that the TiB₂-reinforced phase was comparatively more distributed in the coating after annealing at 650 °C for 10 h; however, as the annealing time increased (30 h), the continuous diffusion between Ni and Al led to the continuous formation and growth of NiAl intermetallic compounds. This resulted in the accumulation of the TiB₂-reinforced phase at the interface of the NiAl₃ intermetallic compounds (as marked by the green dotted line in Figures 14c and 15c).

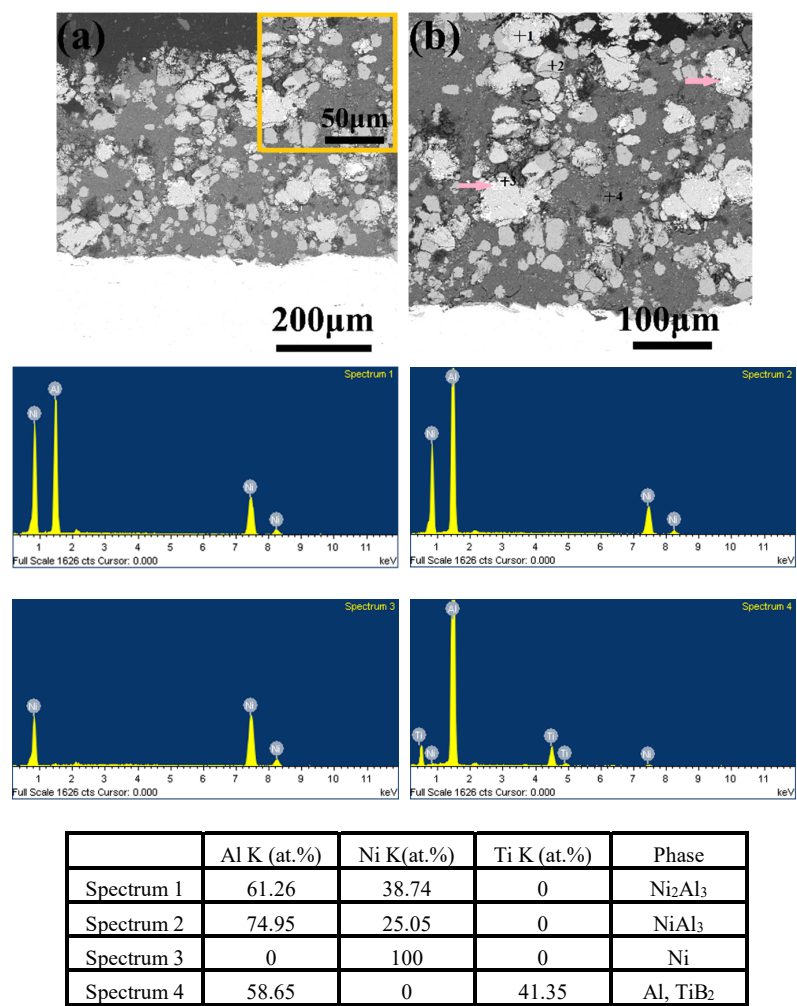


Figure 10. Cross-sectional morphologies and compositions of Ni/Al-TiB₂ coatings as-sprayed at 250 °C and after annealing at 650 °C for 10 h: (a) 200×, and (b) 500×.

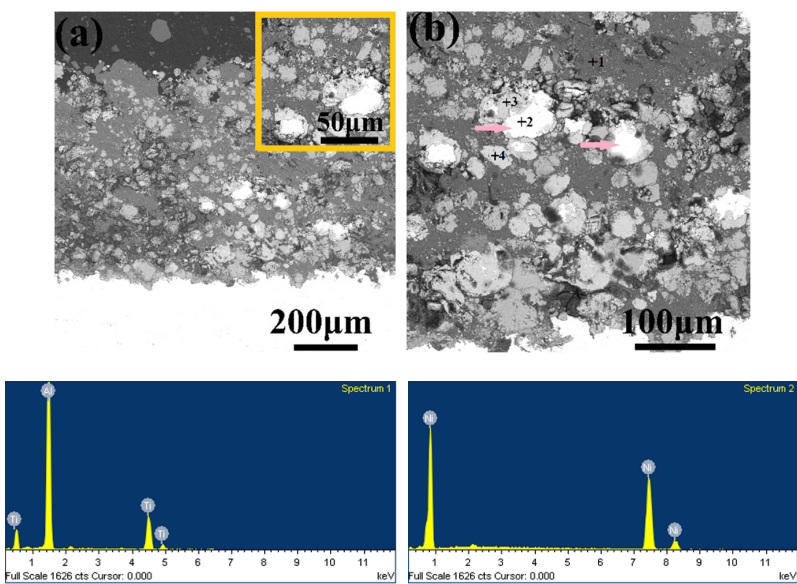


Figure 11. Cont.

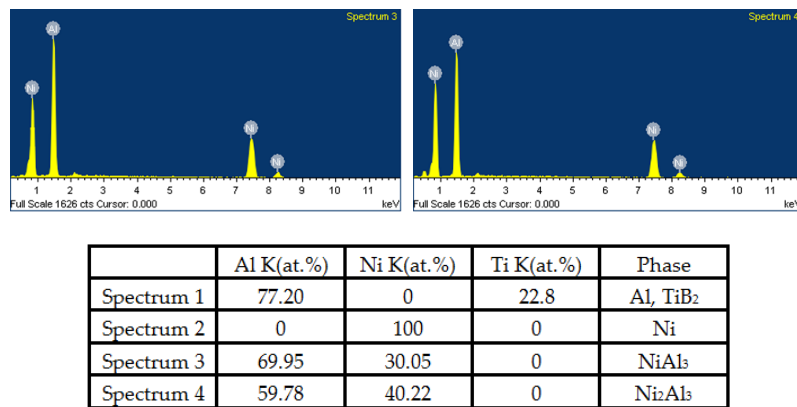


Figure 11. Cross-sectional morphologies and compositions of Ni/Al-TiB₂ coatings as-sprayed at 450 °C and after annealing at 650 °C for 10 h: (a) 200×, and (b) 500×.

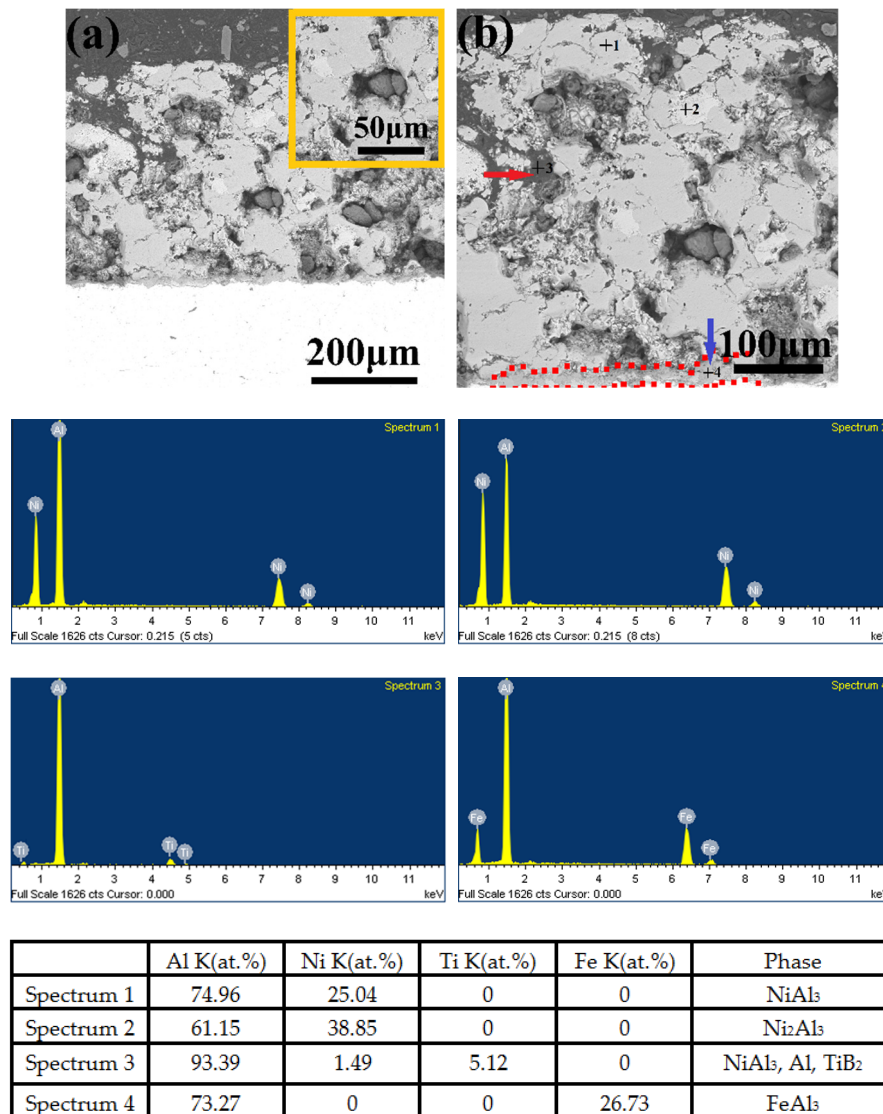


Figure 12. Cross-sectional morphologies and compositions of Ni/Al-TiB₂ coatings as-sprayed at 250 °C and after annealing at 650 °C for 20 h: (a) 200×, and (b) 500×.

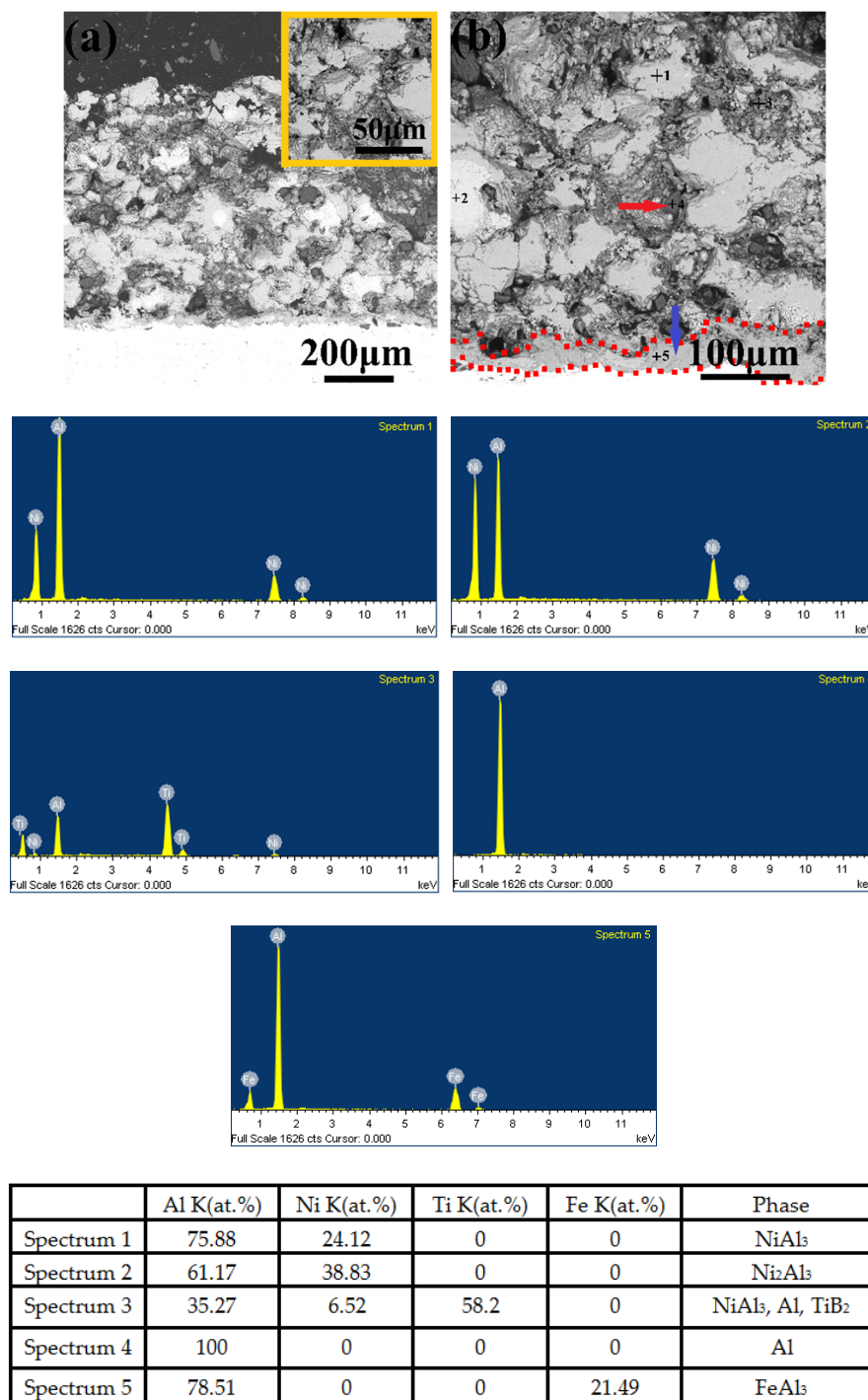


Figure 13. Cross-sectional morphologies and compositions of Ni/Al-TiB₂ coatings as-sprayed at 450 °C and after annealing at 650 °C for 20 h: (a) 200×, and (b) 500×.

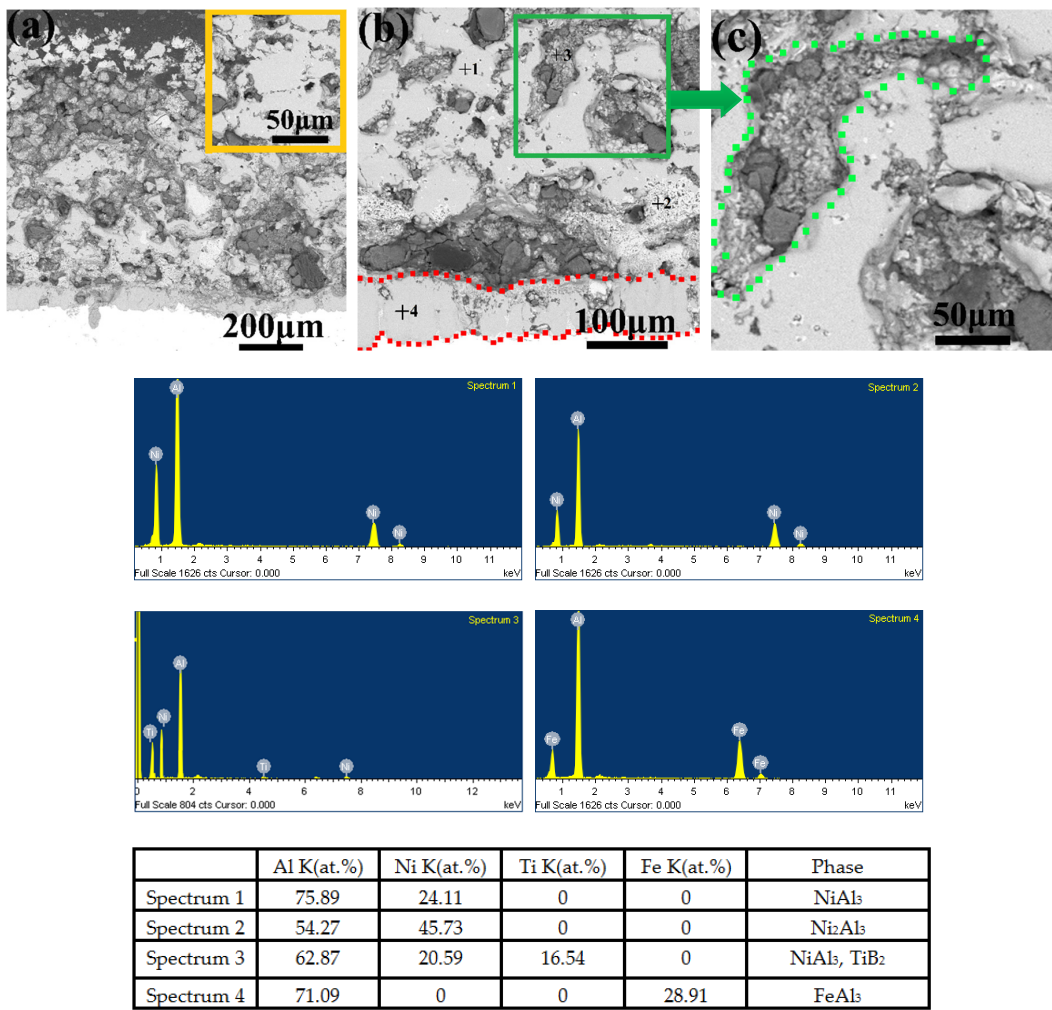


Figure 14. Cross-sectional morphologies and compositions of Ni/Al-TiB₂ coatings as-sprayed at 250 °C and after annealing at 650 °C for 30 h: (a) 200×, (b) 500×, and (c) 1000×.

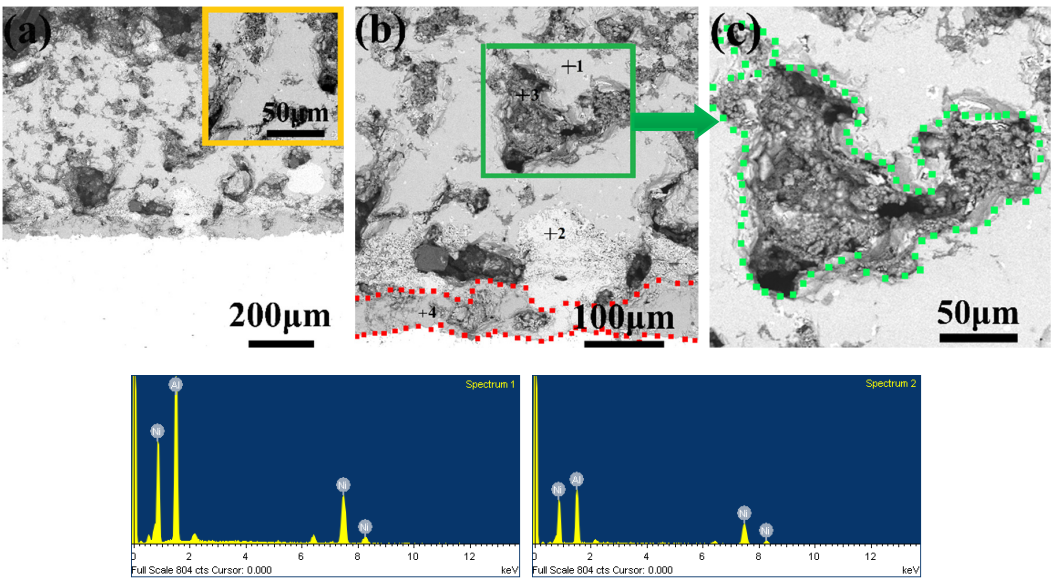


Figure 15. Cont.

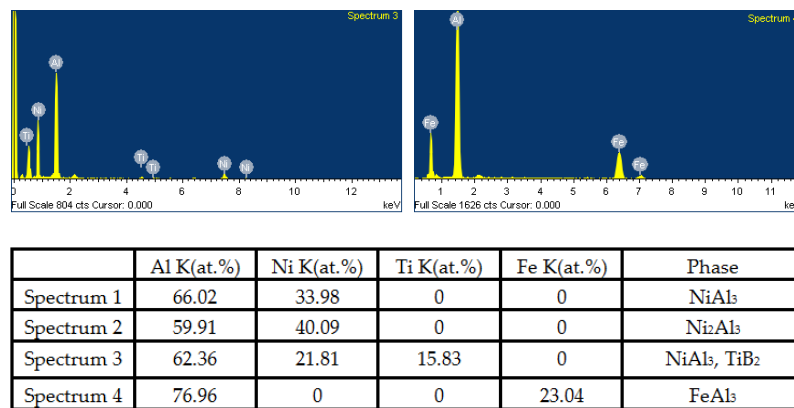


Figure 15. Cross-sectional morphologies and compositions of Ni/Al-TiB₂ coatings as-sprayed at 450 °C and after annealing at 650 °C for 30 h: (a) 200×, (b) 500×, and (c) 1000×.

Figure 16 shows the average porosity of the coatings annealed at 650 °C for 10, 20, and 30 h. Compared with the average porosity of the as-sprayed coatings, that of all of the annealed coatings remarkably increased. In addition, the average porosity of the annealed coatings gradually increased as the increasing annealing treatment time increased from 10 to 30 h. By further examination of Figure 16, it also can be found that the average porosity of the annealed coatings as-sprayed at 450 °C was higher than that of the annealed coatings as-sprayed at 250 °C. The reasons for this phenomenon in this study are that, firstly, porosity can develop during interdiffusion and NiAl intermetallic formation [38,39,41–43,47]. Some pore formation is accounted for by the unbalanced solid-state diffusivity between Ni and Al due to the Kirkendall effect. Secondly, due to the density difference among the various phases (Ni, Al, NiAl₃, and Ni₂Al₃), NiAl intermetallic formation can induce a volume change between products and reactants [39,47], which can result in new intrinsic pores in the coating. Thirdly, the cracks in the coating can be induced by the stress produced by the volume change, which can increase the porosity of the coating. Lastly, the primary reason in this study is that, due to the accumulation of the TiB₂-reinforced phase and the different coefficients of thermal expansion between TiB₂ and NiAl intermetallic compounds, larger pores could form in the coating as the annealing time increased (as shown in Figures 14 and 15). The weakly bound particles (e.g., TiB₂) would fall off from the coating and cause pore production during preparation of the metallographic specimens.

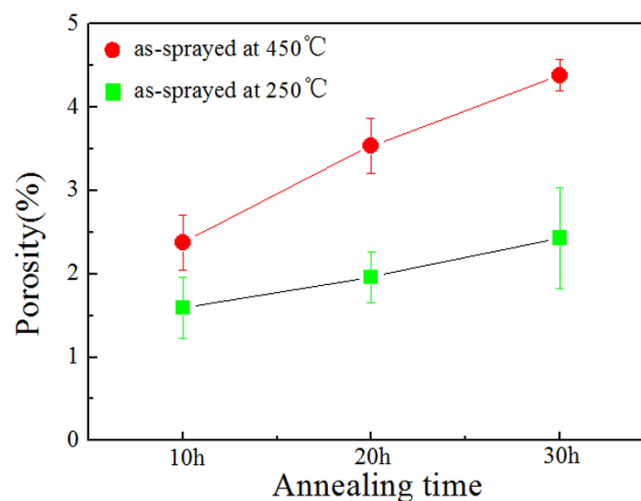


Figure 16. The porosity of the annealed Ni/Al-TiB₂ coatings at different annealing times.

Figure 17 shows the microstructure of the Ni/Al-TiB₂ composite coatings as-sprayed at 450 °C and annealed at 650 °C for 10 and 30 h, as observed in back-scattered mode. It was found that the core shell structure formed in the coating annealed at 650 °C for 10 h (as shown in Figure 17a), and the core shell structure particle contained three different phases in contrast, and the phases with different contrasts were identified using EDS as follows: the Ni phase in light contrast was still present in the core of the core shell structure particle, the Ni₂Al₃ phase in light grey contrast formed closer to the Ni core side, while the NiAl₃ phase in dark grey contrast formed between the Al matrix and the Ni₂Al₃ phase. This core shell structure also illustrated that, because the Gibbs free energy of NiAl₃ intermetallic compounds is lower than that of other Ni-Al intermetallic compounds [44], the NiAl₃ phase formed first through the fast diffusion of Al atoms into Ni particles; then, NiAl₃ and Ni reacted with each other to form a Ni₂Al₃ phase. The diffusion mechanism of Ni-Al intermetallic compounds has been widely reported [5,13,29,40,42,43]. By comparing the cross-sectional morphologies of the Ni/Al-TiB₂ composite coatings (as-sprayed at gas temperatures of 250 and 450 °C) annealed at 650 °C for 10 h, the contents of NiAl₃ and Ni₂Al₃ intermetallic compounds, measured using image analysis of five backscattered SEM images, were clearly different in each annealed coating because of the effect of the cold spraying gas temperature. The results (as shown in Figure 18) show that the average content of the Ni₂Al₃ intermetallic compound in the annealed coatings (as-sprayed at gas temperatures of 250 and 450 °C) was approximately 14.98 ± 1.07 and 20.56 ± 1.77 vol %, and that of the NiAl₃ intermetallic compound was approximately 24.99 ± 0.614 and 30.05 ± 0.389 vol %. The average contents of NiAl₃ and Ni₂Al₃ intermetallic compounds in the annealed coatings as-sprayed at 450 °C were higher than those in the annealed coatings as-sprayed at 250 °C. This phenomenon is attributed to an increase in the average content of Ni and the more intense deformation of incident particles as-sprayed at 450 °C (as shown in Figures 3 and 4). In addition, more TiB₂ particles with a higher velocity continuously impacted the cold-sprayed coatings to form denser microstructures. Therefore, more Ni particles reacted with the Al matrix to form intermetallic compounds and the denser microstructure with lower porosity (0.054%) of the coating as-sprayed at 450 °C made the diffusion length of both Ni and Al atoms decrease.

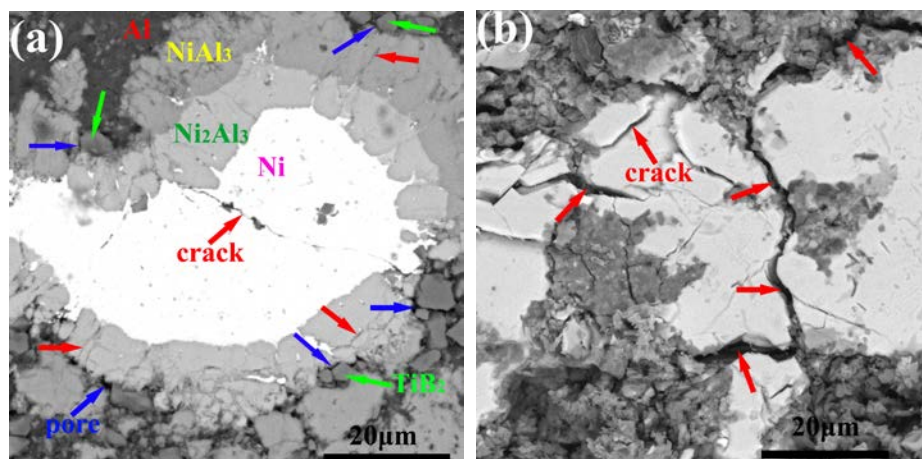


Figure 17. Microstructure of Ni/Al-TiB₂ composite coatings as-sprayed at 450 °C and annealed at (a) 650 °C for 10 h and (b) 650 °C for 30 h.

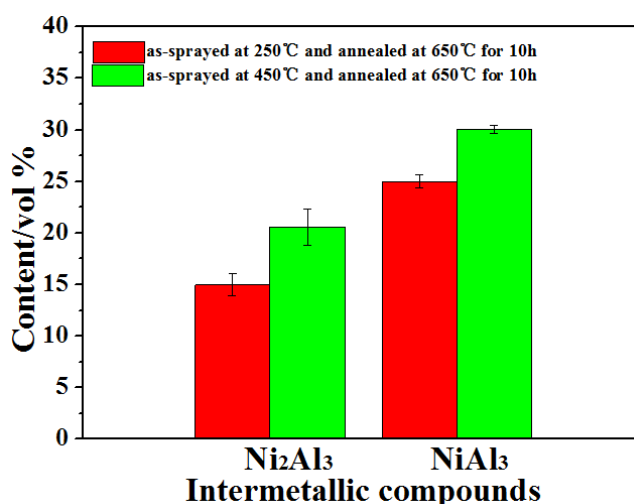


Figure 18. The contents of NiAl₃ and Ni₂Al₃ intermetallic compounds in the annealed Ni/Al-TiB₂ composite coatings.

Further, cracks (as indicated by the red arrow in Figure 17a) appeared in the Ni and intermetallic compound phases, which were formed by annealing at 650 °C for 10 h, and some pores (as indicated by the blue arrow in Figure 17a) were also present in the coating. As the annealing treatment time increased to 30 h (as shown in Figure 17b), the propagation of cracks clearly changed in the coating, which increased the coating porosity. Guo et al. [13], Wang et al. [41], and Novoselova et al. [43] have also reported that the formation of pores is attributed to the Kirkendall effect, and crack initiation in an annealed coating is induced by the stress caused by volume change. Hence, in this study, due to the different coefficients of thermal expansion between the TiB₂ ($8.1 \times 10^{-6} \text{ K}^{-1}$) and NiAl intermetallic compound ($15.1 \times 10^{-6} \text{ K}^{-1}$) phases [13,48], cracks or pores (as indicated by the blue arrow in Figure 17a) were prone to occur at the interface of the TiB₂ (as indicated by the green arrow in Figure 17a) and NiAl intermetallic compound phases during heating and cooling, and due to the different densities among the Ni (8.9 g/cm³), Al (2.7 g/cm³), and NiAl intermetallic compound (5.9 g/cm³) phases, the transformation of Ni + Al into NiAl₃ or Ni + NiAl₃ into Ni₂Al₃ intermetallic compounds resulted in a volume change. Wang et al. [41] reported that volume changes caused by intermetallic formation may induce tensile stresses around surface and compressive stresses in inner of particles, and tensile stresses became large enough to cause cracking in Fe₂Al₅ as the annealing temperature rose. Biswas et al. [49] also reported that intrinsic pores result from the volume change between products and reactants. Therefore, as the annealing time increased in this study, the more forming amount of the NiAl₃ and Ni₂Al₃ intermetallic compounds induced larger volume change, which caused the presence of the larger micro-cracks (as shown in Figure 17b). Hence, due to the more content of TiB₂ in the as-sprayed coating at gas temperature of 450 °C, and the higher contents of NiAl₃ and Ni₂Al₃ intermetallic compounds in the annealed coating as-sprayed at 450 °C, the average porosity of the annealed coatings as-sprayed at 450 °C was higher than that of the annealed coating as-sprayed at 250 °C (as shown in Figure 16). In addition, the microstructure of Ni/Al coatings sprayed at gas temperature of 450 °C and annealed at 650 °C for 10 h and 30 h was shown in Figure 19. This was similar to the results of Figure 17, the amount of pores and the larger micro-cracks in the annealed Ni/Al coatings increased as the annealing time increased.

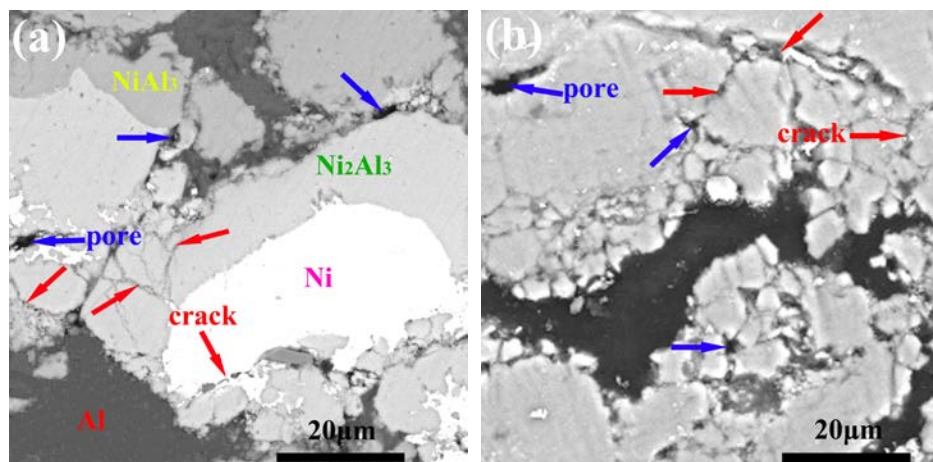


Figure 19. Microstructure of Ni/Al coatings as-sprayed at 450 °C and annealed at (a) 650 °C for 10 h and (b) 650 °C for 30 h.

Figure 20 shows the microhardness of the annealed coatings at different annealing times. It can be seen that the microhardness of Ni/Al-TiB₂ coatings annealed for 10 h was obviously higher than that of the cold-sprayed coatings at 250 and 450 °C (as shown in Figure 5) because of the role of TiB₂-reinforced particles and NiAl₃ and Ni₂Al₃ intermetallic compounds. Further, due to the higher contents of TiB₂-reinforced particles and NiAl₃ and Ni₂Al₃ intermetallic compounds, the microhardness of Ni/Al-TiB₂ coatings annealed at 650 °C for 10 h as-sprayed at 450 °C (701 ± 50 HV_{0.3}) was higher than that of the coating annealed at 650 °C for 10 h as-sprayed at 250 °C (610 ± 27 HV_{0.3}). Furthermore, due to the formation of NiAl₃ and Ni₂Al₃ intermetallic compounds, the microhardness of Ni/Al coatings annealed for 10 h was also higher than that of the cold-sprayed Ni/Al coatings at 250 and 450 °C, but lower than that of the annealed Ni/Al-TiB₂ coatings due to the lack of TiB₂ reinforcement phase. However, as the annealing time increased, the microhardness of all the annealed coatings gradually decreased. The reason for this is that large pores or micro-cracks gradually increased in the annealed coatings.

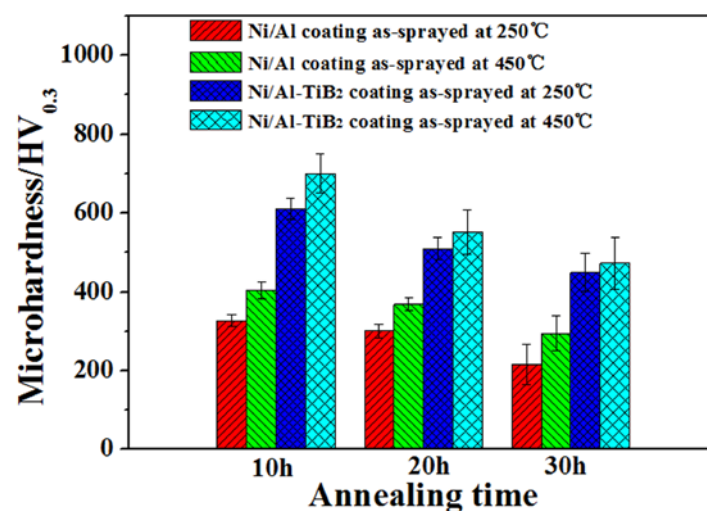


Figure 20. The microhardness of the annealed Ni/Al coatings and Ni/Al-TiB₂ coatings at different annealing times.

4. Conclusions

Ni/Al-TiB₂ composite powders prepared by a ball milling method were successfully deposited on the surface of 316L stainless-steel substrate by a cold spraying method at gas temperatures of 250 and

450 °C, respectively. Then, the as-sprayed coatings were annealed at 650 °C for 10, 20, and 30 h. Based on the results of this study, the following conclusions can be drawn:

- The average surface roughness values of the coatings dropped from 8.66 ± 0.73 to 6.17 ± 0.88 μm as the spraying gas temperature increased.
- The average porosities of the coatings as-sprayed at gas temperatures of 250 and 450 °C were 0.68% and 0.054%, respectively. The average contents of Ni, Al, and TiB₂ in the as-sprayed coating increased as the spraying gas temperature increased. The average contents of Ni, Al, and TiB₂ in the coating as-sprayed at 450 °C were 32.66 ± 1.87 , 54.93 ± 3.61 , and 12.41 ± 1.13 vol %, respectively.
- Owing to the reinforcing role of TiB₂ particles, the microhardness of Ni/Al-TiB₂ coatings was higher than that of Ni/Al coatings. The microhardness of the coatings increased as the spraying gas temperature increased. The highest microhardness of Ni/Al-TiB₂ coatings as-sprayed at 450 °C was 475.26 ± 31.21 HV_{0.3}.
- Due to the low processing temperature of cold spraying, the main phase compositions of the as-sprayed Ni/Al-TiB₂ coatings were Ni, Al, and TiB₂ phases with no oxides or nickel aluminum intermetallic phases. FWHMs of Ni and Al diffraction peaks indicated that Ni and Al particles underwent a certain plastic deformation upon high-speed impact.
- The combined XRD and EDS analysis results for the annealed coatings after annealing at 650 °C for 10, 20, and 30 h revealed that NiAl₃ and Ni₂Al₃ intermetallic compounds were in situ synthesized in all of the annealed coatings.
- By analyzing the microstructure of the annealed coatings, Al phase gradually decreased with the diffusion reaction occurring. Further, TiB₂ particles changed from the comparative more distribution to the accumulation in the coating due to the continuous formation and growth of NiAl intermetallics.
- The porosity of the annealed coatings increased as the annealing times and spraying gas temperatures increased. Due to the increased amount of TiB₂-reinforced particles and NiAl₃ and Ni₂Al₃ intermetallic compounds, it led to larger volume change and much more accumulation of TiB₂ particles to form more pores in the annealed coating as-sprayed at 450 °C.
- The microhardness of Ni/Al-TiB₂ coating as-sprayed at 450 °C and annealed at 650 °C for 10 h was the highest (701 ± 50 HV_{0.3}) compared with the other coatings, however, the microhardness of the annealed coating gradually decreased as the porosity of the annealed coatings increased.

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