



# Formation of NiAl Intermetallic Compound by Cold Spraying of Ball-Milled Ni/Al Alloy Powder Through Postannealing Treatment

Qiang Zhang, Chang-Jiu Li, Xiu-Ru Wang, Zhi-Liang Ren, Cheng-Xin Li, and Guan-Jun Yang

(Submitted May 13, 2008; in revised form July 23, 2008)

Ni/Al alloy powders were synthesized by ball milling of nickel-aluminum powder mixture with a Ni/Al atomic ratio of 1:1. Ni/Al alloy coating was deposited by cold spraying using N<sub>2</sub> as accelerating gas. NiAl intermetallic compound was evolved in situ through postspray annealing treatment of cold-sprayed Ni/Al alloy coating. The effect of annealing temperature on the phase transformation behavior from Ni/Al mechanical alloy to intermetallics was investigated. The microstructure of the mechanically alloying Ni/Al powder and NiAl coatings was characterized by scanning electron microscopy and x-ray diffraction analysis. The results show that a dense Ni/Al alloy coating can be successfully deposited by cold spraying using the mechanically alloyed powder as feedstocks. The as-sprayed alloy coating exhibited a laminated microstructure retained from the mechanically alloying powder. The annealing of the subsequent Ni/Al alloy coating at a temperature higher than 850 °C leads to complete transformation from Ni/Al alloy to NiAl intermetallic compound.

**Keywords** annealing, cold spraying, intermetallics, mechanical alloying, NiAl

## 1. Introduction

The NiAl intermetallic compounds, owing to their superior properties such as high-melting point, high-creep strength, low density, high corrosion, and oxidation resistance, are regarded as promising candidates for the development of the next generation high-performance high-temperature structural materials (Ref 1, 2). These characteristics have resulted in the widespread use of NiAl-based bond coats in TBC systems.

The diffusion process is generally utilized to fabricate NiAl on Ni-based superalloy by diffusing Al, either as a separate thermal treatment or combined with the aluminizing step. The aluminizing is performed using a pack cementation (Ref 3-5) or a chemical vapor deposition (CVD) process (Ref 6-8). Although these methods have

successfully generated nickel aluminide layers, the processes are complex. These reaction-diffusion methods result in significant interdiffusion of the materials added to the surface and the underlying substrate alloy. This can compromise the coating if substrate alloy elements, such as W, Ta, Ti, or S, are able to diffuse from the substrate into the nickel aluminide layer (Ref 8, 9).

To address these difficulties, thermal spraying was employed to deposit NiAl coat using NiAl intermetallic as feedstocks (Ref 10-12). However, oxidation during spraying modified the compositions of materials. Cold spray emerged as a new coating process. A coating is formed through plastic deformation of spray particles in solid state during impact in cold spraying. The temperature of spray particles prior to impact is much lower than their melting point and spray materials experience little microstructure change, oxidation, or decomposition. Therefore, the deposition of many metals such as Ti (Ref 13), Zn (Ref 14), Cu (Ref 15), Fe/Si alloy (Ref 16), Fe/Al alloy (Ref 17), MCrAlY (Ref 18), and Ni/Al composite (Ref 19) have confirmed the feasibility to coating. However, it is difficult to directly deposit intermetallic compounds alloy due to their low-temperature brittleness. In previous report (Ref 17), cold spraying of Fe/Al alloy followed by postannealing has been employed to successfully fabricate FeAl intermetallic coating.

In this paper, fabrication of NiAl intermetallic compound coating was investigated through postannealing treatment of cold-sprayed Ni/Al alloy coating.

## 2. Experimental Materials and Procedures

The commercially available Ni (99.8 wt.%, 89 μm, Jinchuan Group Ltd., Jinchang, China) and Al (99.5 wt.%,

This article is an invited paper selected from presentations at the 2008 International Thermal Spray Conference and has been expanded from the original presentation. It is simultaneously published in *Thermal Spray Crossing Borders, Proceedings of the 2008 International Thermal Spray Conference*, Maastricht, The Netherlands, June 2-4, 2008, Basil R. Marple, Margaret M. Hyland, Yuk-Chiu Lau, Chang-Jiu Li, Rogerio S. Lima, and Ghislain Montavon, Ed., ASM International, Materials Park, OH, 2008.

Qiang Zhang, Chang-Jiu Li, Xiu-Ru Wang, Zhi-Liang Ren, Cheng-Xin Li, and Guan-Jun Yang, State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, P.R. China. Contact e-mail: licj@mail.xjtu.edu.cn.

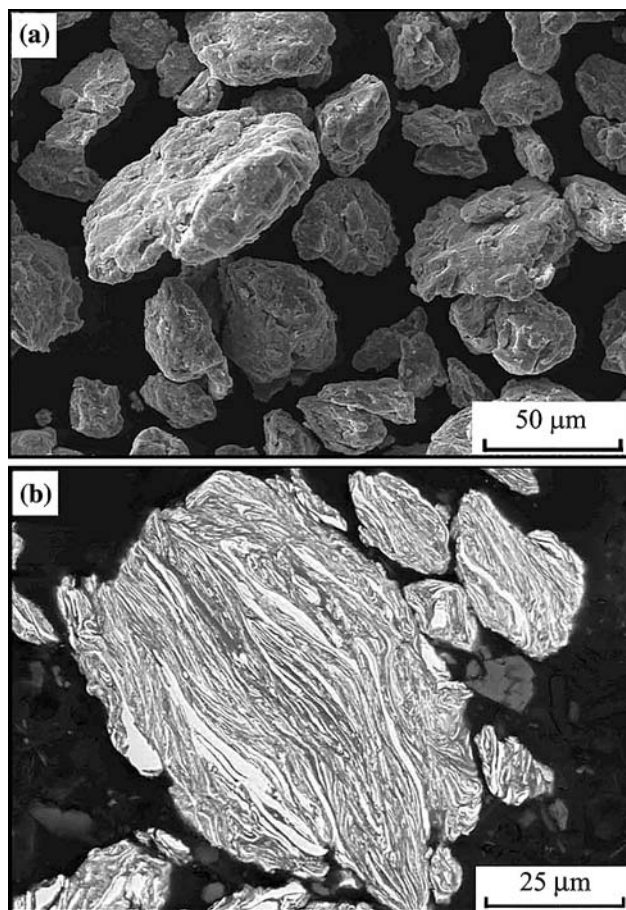
**Table 1 Cold spray conditions**

Driving gas	N <sub>2</sub>
Powders carrying gas	N <sub>2</sub>
Accelerating gas pressure, MPa	2.0
Powders carrying gas pressure, MPa	2.5
Accelerating gas temperature, °C	300
Gun traverse speed over substrate, mm/s	100
Standoff distance, mm	20

74  $\mu\text{m}$ , Youxinglian Nonferrous Metals Ltd., Beijing, China) powders were blended with a Ni/Al atomic ratio of 1:1. The powders were mixed with stainless balls of 6.4 mm in diameter at a ball to powder charge mass ratio of 30:1 and were milled at a rotation speed of 180 rpm in a modified attrition mill (Union Process 01-ST) for 8 h in liquid nitrogen atmosphere. Liquid nitrogen was continuously introduced into the cylinder of the mill during milling operation to ensure complete immersion of the powders in the nitrogen. The cryogenic milled powder was then milled in ethanol to regulate the particle size to be suitable for cold spraying. The milled powder was sieved to a size less than 50  $\mu\text{m}$  and used as the feedstock for spraying deposition. The size distribution of the milled powder was determined by a laser diffraction sizer (MASTERSIZER 2000, Malvern Instruments Ltd., UK). The oxygen contents of the milled powder and corresponding coating were determined using oxygen determinator (Ro-316, LECO, USA). Chemical analysis of the as-sprayed coating was performed using inductively coupled plasma-optical emission spectrometer (ICP) (IRIS-Intrepid II XSP, PE, USA) and all analysis were conducted in triplicate.

The homemade cold spray system which consisted of nozzle, gas heater, and high-pressure gas supply unit was used for coating deposition tests. The setup of the system has been described in detail elsewhere (Ref 13). The particles were accelerated through a De Laval type of nozzle of 100 mm long with a circular cross section with an exit diameter of 6 mm and throat diameter of 2 mm. During cold spraying, all spray parameters were fixed, as shown in Table 1. In the present study, nitrogen gas was used as the driving gas and powders carrying gas. The accelerating gas was operated at a prechamber pressure of 2.0 MPa and a preheating temperature of 300 °C. The standoff distance from the nozzle to the substrate was 20 mm. During deposition, the spray gun was manipulated by a robot at a traverse speed of 100 mm/s relative to the Inconel 738 substrate. The as-sprayed coating was then annealed at different temperatures in a furnace in argon atmosphere at a heating rate of 10 °C/min.

The phase structure of Ni/Al alloy powder and as-sprayed coating and annealed coatings were analyzed by x-ray diffraction diffractometer (XRD) (XRD-6000, Shimadzu, Kyoto, Japan) using Cu-K $\alpha$  radiation. The cross-sectional microstructure and compositions of coatings were characterized by a scanning electron microscope (SEM, VEGA II-XMU, TESCAN, Czech) with an energy dispersive spectrometer (EDS).



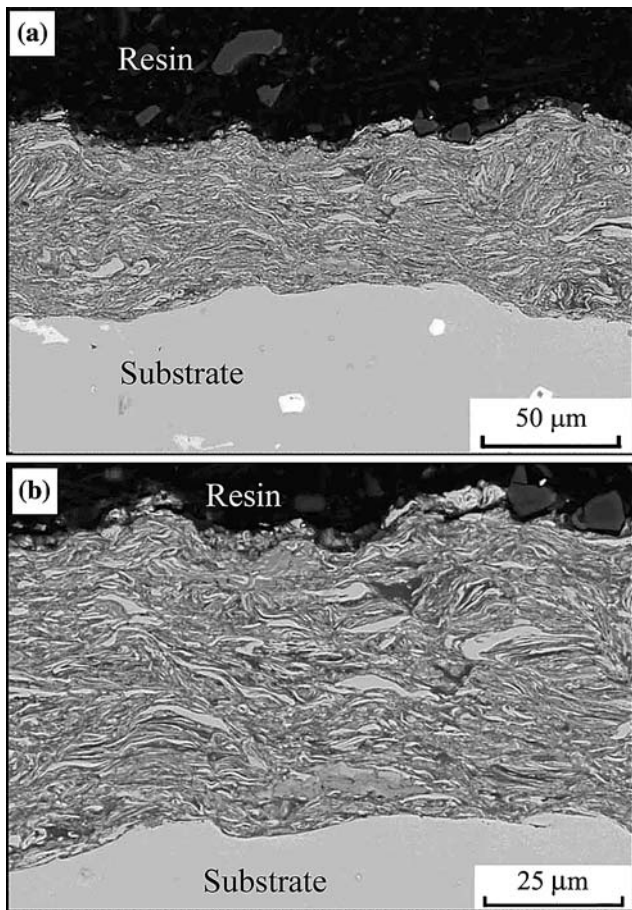
**Fig. 1** Typical morphology (a) and cross-sectional microstructure (b) of the milled powder for 8 h

### 3. Results and Discussion

#### 3.1 Morphology and Microstructure of the Milled Powder

Figure 1 shows typical SEM images of the morphology and cross-sectional microstructure of the powders milled for 8 h. It can be noted in Fig. 1(a) that the as-milled powder presented an irregular morphology, although both Ni and Al starting powder presented a spherical morphology. The milled powder for spray has a mean particle size of 46.2  $\mu\text{m}$ , which was suitable for cold spraying. The powder morphology is typical of milled powders and is generally attributed to the continuous welding and fracturing of particles caused by the collision of balls. It can be noted in Fig. 1(b) that a fine lamellar structure is present in the powder. Two distinguishable regions with different microstructural characteristics can be clearly observed.

The nitrogen, iron, and oxygen contamination were introduced into the powders as a consequence of the ball milling process. The contents of nitrogen, iron, and oxygen were 0.51, 0.14, and 0.75 wt.%, respectively. The presence of iron possibly resulted from the stainless steel balls and stainless steel cylinder. The nitrogen contamination is

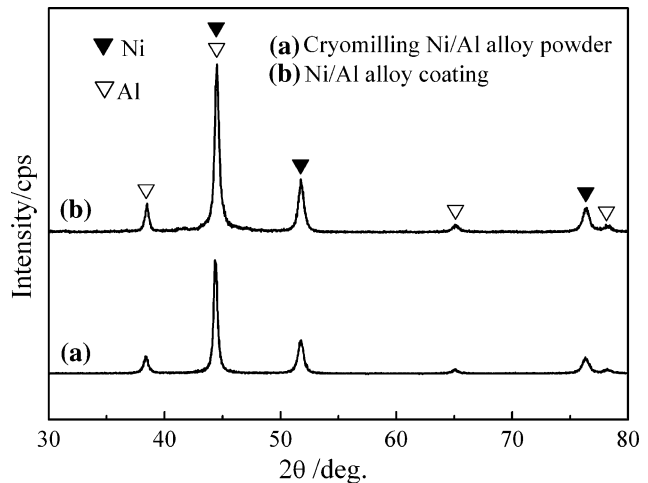


**Fig. 2** Cross-sectional microstructure of cold-sprayed Ni/Al alloy coating observed at different magnifications

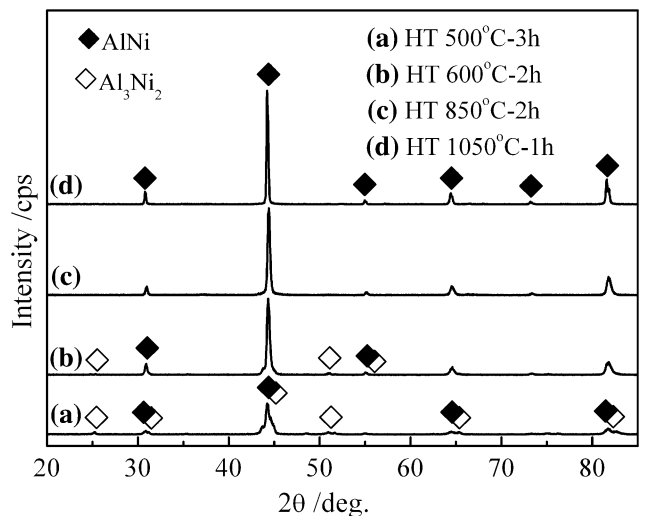
attributed to inclusion during milling from the milling environment. An increase of oxygen concentration is believed to be caused by the incorporation of the leaking air during milling or storage.

### 3.2 Microstructure of Cold-Sprayed Ni/Al Alloy Coating

Figure 2 shows typical SEM images of cross-sectional microstructure of cold-sprayed Ni/Al alloy coating using milled Ni/Al alloy powder. It was observed that the coating exhibited a dense microstructure and some apparent thick layers with a white contrast appeared on the coating microstructure. XRD patterns of the as-sprayed coating and feedstock powder are shown in Fig. 3. Only the peaks of nickel and aluminum were identified in XRD pattern of the ball-milled powder. It is clear that the XRD pattern of the coating is almost the same as that of the milled powder. This fact indicates that the coating and feedstock exhibited the same phase structure and no oxide was identified in the powder and the coating by XRD. The oxygen content of cold-sprayed coating was determined to be 0.78 wt.% using the oxygen determinator, which is similar to that of the powder. Therefore, the particles in flight were subjected to little



**Fig. 3** XRD patterns of the feedstock powder fabricated by ball milling and the as-sprayed coating



**Fig. 4** XRD patterns of the Ni/Al alloy coatings annealed at different temperatures

oxidation. In cold spraying, the particle deposition takes place in a solid state. Consequently, the lamellar structure of the milled powder will be completely retained in the coating, giving a unique effect on the microstructure and properties of the cold-sprayed coating. According to EDS analysis of the coating, the thicker layer in a white contrast was a Ni-rich phase and the fine lamella was a Ni-Al solid solution with high-Al content.

### 3.3 The Evolution of the NiAl Intermetallic Compound Coating

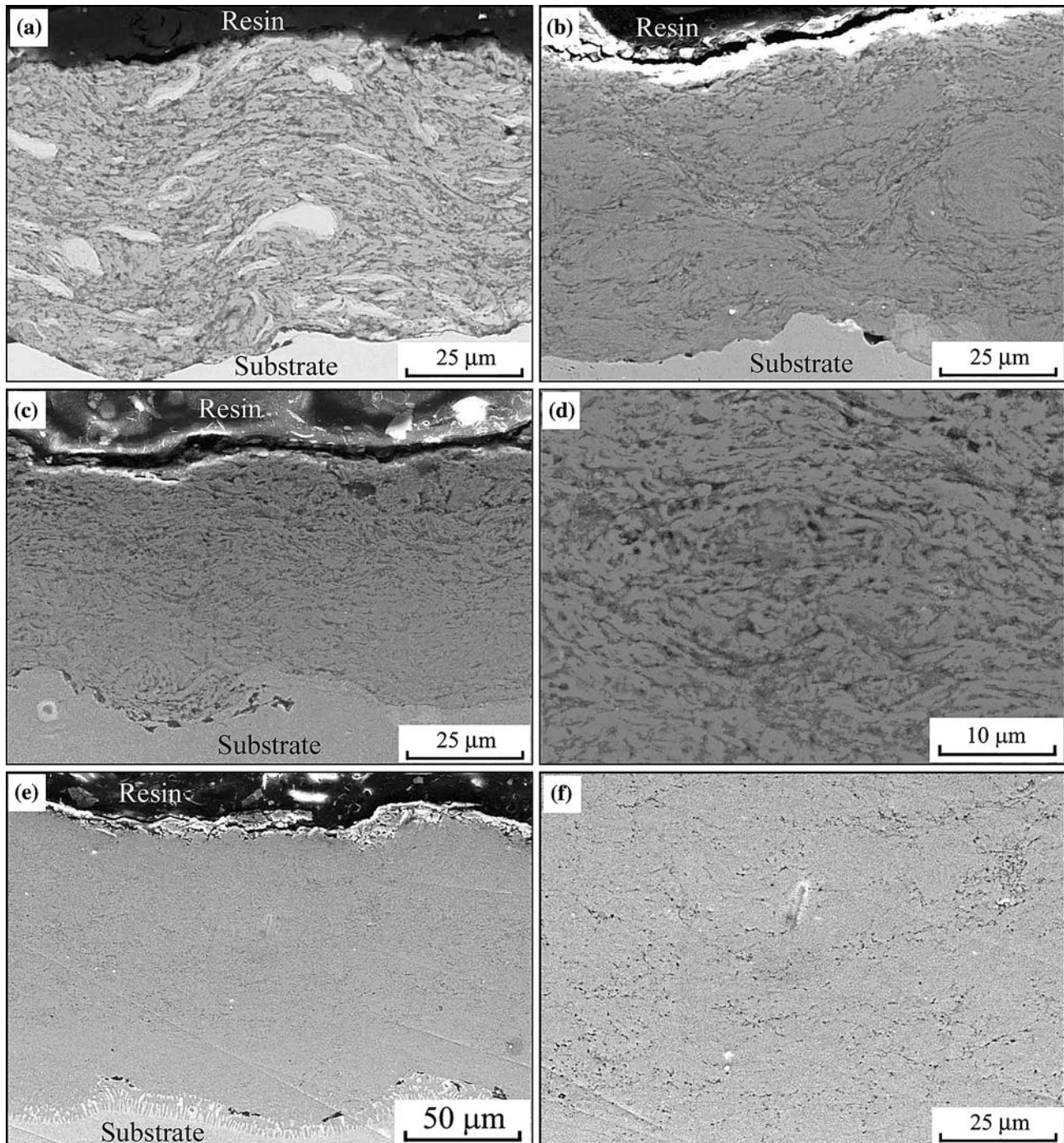
The XRD patterns of annealed Ni/Al alloy coatings are shown in Fig. 4. After annealing treatment at 500 °C for 3 h, Ni and Al peaks completely disappeared and peaks corresponding to  $\text{Ni}_2\text{Al}_3$  and NiAl appeared (Fig. 4a), compared to the as-sprayed NiAl alloy coating (Fig. 3b).



With annealing temperature rising to 600 °C, it can be found from Fig. 4(b) that NiAl became the main phase, only minor Ni<sub>2</sub>Al<sub>3</sub> exists. As the temperature was raised to 850 °C, the diffraction peaks of Ni<sub>2</sub>Al<sub>3</sub> disappeared completely, and only diffraction peaks of NiAl phase were present in the XRD pattern, as shown in Fig. 4(c). This fact indicates that the annealing at temperature of higher than 850 °C completely converts Ni/Al alloy to NiAl

intermetallic compound. As the temperature reached 1050 °C, no additional reaction was detected, and the NiAl phase was present in the coating (Fig. 4d).

The evolution microstructures of the annealed Ni/Al alloy coatings are shown in Fig. 5. At an annealing temperature of 500 °C, the fine bright layer changed to large gray layers, while minor thicker bright layer was still present in the coating and the interface of the thick layer



**Fig. 5** Cross-sectional microstructure of Ni/Al alloy coatings annealed at different conditions: (a) 500 °C, 3 h; (b) 600 °C, 2 h; (c), and (d) 850 °C, 2 h; (e), and (f) 1050 °C, 1 h



was surrounded by the gray layer, as shown in Fig. 5(a). According to EDS analysis, in accord with the XRD data, it was clear that the NiAl phase was present in the coating with deep gray contrast and  $\text{Ni}_2\text{Al}_3$  phase with gray contrast. Some large Ni lamellae with a bright contrast were still present in the core of the deformed particles. This fact is due to insufficient diffusion between Al and Ni. When the alloy coating was annealed at 600 °C, the thick bright layer disappeared; the gray layer and the deep gray layer co-exist, as shown in Fig. 5(b). Based on EDS and XRD analyses, the gray layer and the deep gray layer are  $\text{Ni}_2\text{Al}_3$  and NiAl, respectively.

At 850 °C, it can be noted in Fig. 5(c) and (d) that NiAl became the dominant phase, which is reasonable by taking account of XRD results, although the Ni-rich and Al-rich NiAl phase detected by the EDS analysis presented in the coating. This fact indicates that the heterogeneity of the lamellar structure of the as-milled powder will influence the annealing time which is required to transform the Ni/Al composite alloy into NiAl intermetallics. Under the annealing condition of 1050 °C for 1 h, it is important to note in Fig. 5(e) and (f) that the coating contained a uniform NiAl structure with small amount of  $\text{Al}_2\text{O}_3$  particulates dispersed and a fully dense NiAl was achieved. In addition, a diffusion layer was clearly observed at the interface between NiAl coating and substrate. These results clearly indicate that the reaction process is believed to be controlled via in situ solid-state diffusion. Zhu et al. (Ref 18) also reported that reactive processing of nickel-aluminide intermetallic compounds was controlled by solid-state diffusion. The phase formation sequence during the annealing of Ni/Al alloy coatings in the present study is well consistent with the published results (Ref 20-24).

## 4. Conclusions

A dense Ni/Al alloy coating was deposited by cold spraying using a mechanically alloyed powder as the feedstock. The as-sprayed coating exhibited a laminated microstructure retained from the mechanically alloying powder. The postspray annealing temperature influences significantly the in situ evolution of NiAl intermetallic compound in the Ni/Al alloy coating. The annealing of the subsequent Ni/Al alloy coating at a temperature higher than 850 °C leads to the complete transformation from Ni/Al alloy to NiAl intermetallic compound. The heterogeneity of the as-milled alloy powder microstructure may influence the annealing time needed to completely transform the alloy phase to the intermetallic phase. The high temperature annealing treatment also promotes the formation of a diffusion layer at the interface between the coating and substrate.

## Acknowledgments

The present work is supported by National Basic Research Program of China (Grant No. 2007CB707702),

National Science Fund for Distinguished Young Scholars (Grant No. 50725101).

## References

1. V.K. Sikka, J.T. Mavity, and K. Anderson, Processing of Nickel Aluminides and Their Industrial Applications, *Mater. Sci. Eng. A*, 1992, **153**(1-2), p 712-721
2. C.T. Liu and J.O. Stiegler, Ductile Ordered Intermetallic Alloys, *Science*, 1984, **226**, p 636-642
3. Z. Yu, D.D. Hass, and H.N.G. Wadley, NiAl Bond Coats Made by a Directed Vapor Deposition Approach, *Mater. Sci. Eng. A*, 2005, **394**(1-2), p 43-52
4. J. Angenete and K. Stiller, A Comparative Study of Two Inward Grown Pt Modified Al Diffusion Coatings on a Single Crystal Ni Base Superalloy, *Mater. Sci. Eng. A*, 2001, **316**(1-2), p 182-194
5. M. Chigasaki, K. Otaka, A. Okayama, K. Onisawa, and K. Soeno, Method of Producing Nickel Base Alloy Structure with NiAl Coating, U.S. Patent 4,486,245
6. B.M. Warnes and D.C. Punola, Clean Diffusion Coatings by Chemical Vapor Deposition, *Surf. Coat. Technol.*, 1997, **94-95**, p 1-6
7. Y. Zhang, W.Y. Lee, J.A. Haynes, I.G. Wright, K.M. Cooley, and P.K. Liaw, Synthesis and Cyclic Oxidation Behavior of a (Ni, Pt) Al Coating on a Desulfurized Ni-Base Superalloy, *Metall. Mater. Trans. A*, 1999, **30**(10), p 2679-2687
8. W.Y. Lee, Y. Zhang, I.G. Wright, B.A. Pint, and P.K. Liaw, Effects of Sulfur Impurity on the Scale Adhesion Behavior of a Desulfurized Ni-Based Superalloy Aluminized by Chemical Vapor Deposition, *Metall. Trans. A*, 1998, **29**(3), p 833-841
9. N.P. Padture, M. Gell, and E.H. Jordan, Thermal Barrier Coatings for Gas-Turbine Engine Applications, *Science*, 2002, **296**, p 280-284
10. W.Y. Hua, M.H. Li, and M. Fukumoto, Preparation and Properties of HVOF NiAl Nanostructured Coatings, *Mater. Sci. Eng. A*, 2008, **478**(1-2), p 1-8
11. J.A. Hearley, J.A. Little, and A.J. Sturgeon, The Effect of Spray Parameters on the Properties of High Velocity Oxy-Fuel NiAl Intermetallic Coatings, *Surf. Coat. Technol.*, 2000, **123**(2-3), p 210-218
12. Y. Wang, W. Chen, and L. Wang, Micro-Indentation and Erosion Properties of Thermal Sprayed NiAl Intermetallic-Based Alloy Coatings, *Wear*, 2003, **254**(3-4), p 350-355
13. C.J. Li and W.Y. Li, Deposition Characteristics of Titanium Coatings in Cold Spraying, *Surf. Coat. Technol.*, 2003, **167**(2-3), p 278-283
14. C.J. Li, W.Y. Li, and Y.Y. Wang, Formation of Metastable Phases in Cold-Sprayed Soft Metallic Deposit, *Surf. Coat. Technol.*, 2005, **198**(1-3), p 469-473
15. C.J. Li, W.Y. Li, Y.Y. Wang, G.J. Yang, and H. Fukunuma, A Theoretical Model for Prediction of Deposition Efficiency in Cold Spraying, *Thin Solid Films*, 2005, **489**(1-2), p 79-85
16. C.J. Li, W.Y. Li, W.H. Ma, and H. Fukunuma, Characterization of Microstructure of Nanostructured Fe-Si Coating Deposited by Cold Spraying, *Thermal Spray Solutions: Advances in Technology and Application*, Conference Proceedings, May 10-12 2004 (Osaka, Japan), DVS, Düsseldorf, 2004, p 371-377
17. H.T. Wang, C.J. Li, G.J. Yang, C.-X. Li, Q. Zhang, and W.-Y. Li, Microstructural Characterization of Cold-Sprayed Nanostructured FeAl Intermetallic Compound Coating and Its Ball-Milled Feedstock Powders, *J. Therm. Spray Technol.*, 2007, **16**(5-6), p 669-676
18. Q. Zhang, C.J. Li, C.X. Li, G.J. Yang, and S.C. Lui, Study of Oxidation Behavior of Nanostructured NiCrAlY Bond Coatings Deposited by Cold Spraying, *Surf. Coat. Technol.*, 2008, **202**(14), p 3378-3384
19. H.Y. Lee, S.H. Jung, S.Y. Lee, and K.H. Ko, Alloying of Cold-Sprayed Al-Ni Composite Coatings by Post-Annealing, *Appl. Surf. Sci.*, 2007, **253**(7), p 3496-3502
20. H.C. Zhu and R. Abbaschian, Reactive Processing of Nickel-Aluminide Intermetallic Compounds, *J. Mater. Sci.*, 2003, **38**(18), p 3861-3870

21. L. Farber, L. Klinger, and I. Gotman, Modeling of Reactive Synthesis in Consolidated Blends of Fine Ni and Al Powders, *Mater. Sci. Eng. A*, 1998, **254**(1-2), p 155-165
22. L. Farber, Irena E.Y. Gutmanas, and A. Lawley, Solid State Synthesis of NiAl-Nb Composites from Fine Elemental Powders, *Mater. Sci. Eng. A*, 1998, **244**(1), p 97-102
23. A. Battezzati, P. Pappalepore, F. Durbiano, and I. Gallino, Solid State Reactions in Al/Ni Alternate Foils Induced by Cold Rolling and Annealing, *Acta Mater.*, 1999, **47**(6), p 1901-1914
24. A. Biswas and S.K. Roy, Comparison between the Microstructural Evolutions of Two Modes of SHS of NiAl: Key to a Common Reaction Mechanism, *Acta Mater.*, 2004, **52**(2), p 257-270