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Oxidation Behavior of $TiAl_3$/Al Composite Coating on Orthorhombic-Ti_2AlNb Based Alloy at Different Temperatures

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This paper reports the oxidation behavior of $TiAl_3$/Al composite coating deposited by cold spray. The substrate alloy was orthorhombic-Ti-22Al-26Nb (at.%). The oxidation kinetics of the coating was tested at 650, 800, and 950 °C, respectively. The parabolic rate constant for the coating oxidized at 650 °C was $k_p = 7.2 \times 10^{-2}\ \mathrm{mg{\cdot}cm^{-2}{\cdot}h^{-1/2}}$ for the tested 1200 h. For the coating oxidized at 800 °C, the oxidation kinetics could be separated into two stages with k_p value of $39.8 \times 10^{-2}\ \mathrm{mg{\cdot}cm^{-2}{\cdot}h^{-1/2}}$ for the initial 910 h and $17.7 \times 10^{-2}\ \mathrm{mg{\cdot}cm^{-2}{\cdot}h^{-1/2}}$ for the stage thereafter. For the coating oxidized at 950 °C, the oxidation kinetics can be separated into three stages with k_p of $136.9 \times 10^{-2}\ \mathrm{mg{\cdot}cm^{-2}{\cdot}h^{-1/2}}$ in the first 100 h, followed by $26.9 \times 10^{-2}\ \mathrm{mg{\cdot}cm^{-2}{\cdot}h^{-1/2}}$ from 100 to 310 h, and $11.8 \times 10^{-2}\ \mathrm{mg{\cdot}cm^{-2}{\cdot}h^{-1/2}}$ from 310 to 1098 h. XRD, SEM, and EPMA were used to study the microstructure of the coating. The results indicated that the oxidation took place throughout the entire coating instead of only at the surface. The aluminum phase in the composite coating was soon oxidized to Al_2O_3 in all tested cases. The aluminum in $TiAl_3$ phase was depleted gradually and oxidized to Al_2O_3 along with the degradation of $TiAl_3$ to $TiAl_2$ and TiAl as the temperature increased and time proceeded. $AlTi_2N$ was also a typical oxidation product at temperature higher than 800 °C. The experimental results also indicated that the protection of the coating was attributed greatly to the interlayer formed between the coating and the substrate.

Keywords cold spray, high-temperature oxidation, orthorhombic Ti_2AlNb alloy, $TiAl_3$/Al composite coating

1. Introduction

Orthorhombic Ti_2AlNb based alloy (orthorhombic-alloy) is one of the promising lightweight materials in future advanced aeroengines (Ref 1). However, experimental evidence has shown that the orthorhombic-alloy with an aluminum content of less than about 25 at.% suffer from poor high-temperature oxidation resistance and interstitials embrittlement (Ref 2-4). Therefore, the orthorhombic-alloy must be protected in order to use at elevated temperatures.

Usually protective coatings were expected to provide effective protection without significant negative influence on the mechanical properties of the alloy (Ref 5). Several coating systems were applied onto the orthorhombic-based alloy. Warrier reported *r*-TiAl alloy coating (Ref 6). The results of mechanical test showed that a *r*-TiAl surface layer was successful in preventing interstitial embrittlement of the orthorhombic alloy during thermal cycling. However, the joint material revealed significant strength reduction (Ref 6). Leyens studied the oxidation protection behavior of the TiAlCr coating and the TiAlCrYN coating to the orthorhombic-alloy (Ref 7). Both type of coatings provided excellent environmental protection for orthorhombic titanium alloy at 750 °C. However, the expensive cost and low efficiency in preparing of the coating was a great hindrance for wide application of magnetron sputtering. Wang (Ref 8) reported the NiCoCrAlY coating with and without an Al_2O_3/Al interlayer. The results showed that both coatings can improve the oxidation resistance of the orthorhombic-alloy. However, the NiCoCrAlY coating without an Al_2O_3/Al interlayer soon degraded because of severe interdiffusion between the coating and the substrate (Ref 8). The NiCoCrAlY/Al_2O_3/Al multi-layer coating exhibited excellent oxidation resistance under either isothermal or cyclic conditions from 800 to 900 °C. The Al_2O_3 interlayer acted as an effective interdiffusion barrier in the coating system. The $TiAl_3$ was also an ideal high-temperature oxidation-resistant coating system for titanium alloys and titanium aluminides. The most common method to prepare $TiAl_3$ coating was aluminizing (Ref 9-12). It was reported that the $TiAl_3$ coating was so brittle that vertical cracks would be generated at the cooling treatment during preparation (Ref 9). Interdiffusion between the coating and the substrate was of another major concern. It caused severe degradation of the coating within 300 h (Ref 10, 11). Xiang reported that the $TiAl_3$ coating they have prepared on *r*-TiAl could last for more

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than 6200 h at 800 °C (Ref 12). Lately we reported our investigation on $TiAl_3$/Al composite coating on orthorhombic-Ti-22Al-26Nb (at.%) alloy prepared by cold spray (Ref 13, 14). The results indicated that this composite coating has greatly improved the oxidation resistance of the substrate orthorhombic-Ti-22Al-26Nb (at.%) alloy at 950 °C up to 1098 h without any sign of severe degradation (Ref 14).

In this paper, we report the oxidation behavior of the $TiAl_3$/Al composite coating prepared by cold spray at different temperatures and the microstructure analysis of the oxidized coating.

2. Experimental Procedure

The nominal composition of the orthorhombic-Ti_2AlNb alloy substrate is Ti-22Al-26Nb-1Mo (at.%), which was provided by Titanium Alloy Division, Institute of Metal Research, CAS, P.R. China. The ingot was cut into Φ 16 × 1 mm buttons. The surface of the buttons were ground and polished with SiC paper up to a 800 grit finish, ultrasonically cleaned in ethanol, dried and pilled before coating.

The powders of the commercial aluminum (Al) and titanium (Ti) (Fig. 1) were sieved to an average size of 20 μm and then premixed in a V-mixer for 48 h. The Ti:Al molar ratio was settled as 1:3. The mixture obtained was dried at 80 °C for 4 h before use.

Cold spraying was carried out on a stationary system, which was manufactured by the Institute of Theoretical and Applied Mechanics of the Siberian Branch of the Russian Academy of Science (ITAM SB RAS). The de laval nozzle was a rectangle exit equipped with a cross section of 2 × 10 mm and a throat of 2 × 2 mm. The stand-off distance, temperature, and gas pressure for cold spraying process was 10 mm, 250 °C, and 1.8 MPa, respectively (Ref 13). The substrates were coated both on flat and side. The thickness of the coating was about 100 μm. The as-sprayed specimens were subjected to heat-treatment under argon gas flow of 40 mL/min. The furnace was heated from room temperature to 630 °C at a heating rate of 3 °C/min and was held at this level for 5 h. The furnace was then cooled to room temperature at its natural rate by switching off its power supply while maintaining the argon gas flow (Ref 13).

Oxidation tests were carried out in static air under quasi-isothermal conditions. The specimens were placed in alumina crucibles. The mass changes of the specimens were measured at regular intervals. The sensitivity of the balance was 10^{-5} g.

X-ray diffraction (XRD) analysis was conducted on D/max-2500pc (RIGAKU, Japan) powder diffractometer. Scanning electron microscopy (SEM-EDS) image was obtained on JSM-6301F (JEOL, Japan), equipped with a schottky field emission cathode. The electron probe microanalysis (EPMA) was obtained on EPMA-1610 (SHIMADZU, Japan).

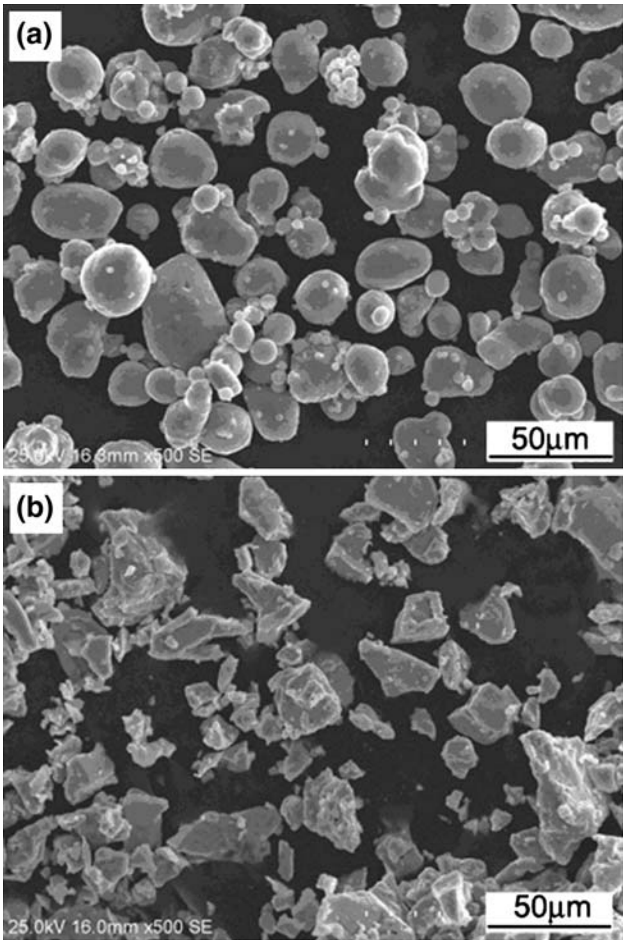

Fig. 1 SEM image of the original powders: (a) Al and (b) Ti (Ref 13)

3. Results and Discussion

3.1 Oxidation Kinetics of $TiAl_3$/Al Composite Coating

The oxidation kinetics of the $TiAl_3$/Al composite coating was measured in air under quasi-thermal condition at different temperatures. Figure 2 shows the mass change VS time for the coating oxidized at 650, 800, and 950 °C, respectively. It can be seen from the curves that the oxidation behavior of $TiAl_3$/Al composite coating oxidized at relatively low temperature was very different from that oxidized at elevated temperatures. The oxidation kinetics for the coating oxidized at 650 °C was a typical parabolic curve with a total weight gain of 2.41 mg·cm^{-2} in 1200 h. The oxidation kinetics for the coating oxidized at 800 °C experienced much faster weight gain rate than for the coating oxidized at 650 °C. An obvious transition point was observed at 910 h with a total weight gain of 12.1 mg·cm^{-2} for the coating oxidized at 800 °C up to the tested 1154 h. The oxidation curve for the coating oxidized at 950 °C accumulated extremely fast in the initial 100 h. The weight gain for this oxidation period reached 5.78 mg·cm^{-2}, which

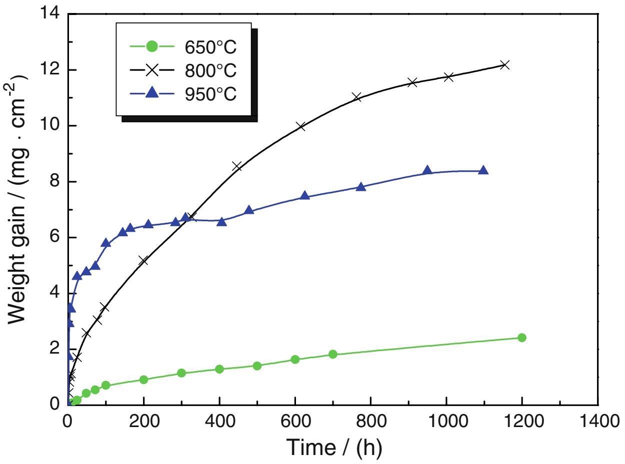

Fig. 2 Oxidation kinetics of the $TiAl_3$/Al composite coatings in air at different temperatures

was the 69% of the total weight gain over the tested 1098 h. After the initial oxidation region, the oxidation weight gain curves became smooth. The total weight gain was 8.73 $mg \cdot cm^{-2}$ for 1098 h, which is even lower than that for the coating oxidized at 800 °C. The weight gain was also plotted against $t^{1/2}$ to describe the growth of the protective oxide scales according to function 1 (Ref 15)

$$\Delta m_t = \Delta m_0 + k_p t^{1/2}$$

where Δm_t is the weight change in $mg \cdot cm^{-2}$, Δm_0 is an offset value as a result of transient oxide formation, k_p is the parabolic oxidation rate constant and can be determined by the slope of the plot of Δm_t versus $t^{1/2}$.

The k_p value was used to evaluate the oxidation rate at different temperatures and at different stages of oxidation. Figure 3 shows the plot of Δm_t versus $t^{1/2}$ at the three tested temperatures. A parabolic kinetics oxidation curve was obtained for the coating oxidized at 650 °C. The k_p value was 7.2×10^{-2} $mg \cdot cm^{-2} \cdot h^{-1/2}$ through the tested 1200 h. For the coating oxidized at 800 °C, the oxidation kinetics was separated into two stages. The initial parabolic kinetics was obtained within 910 h with k_{p1} of 39.8×10^{-2} $mg \cdot cm^{-2} \cdot h^{-1/2}$. The k_{p2} was 17.7×10^{-2} $mg \cdot cm^{-2} \cdot h^{-1/2}$ after first stage. The later rate constant was nearly half of the initial one indicating much lower oxide growing rate after 910 h at 800 °C. The oxide scale grew at 950 °C differed far from those grew at 650 and 800 °C. The initial parabolic rate constant was 136.9×10^{-2} $mg \cdot cm^{-2} \cdot h^{-1/2}$ in the first 100 h, followed by 26.9×10^{-2} $mg \cdot cm^{-2} \cdot h^{-1/2}$ in time scale 100-310 h and 11.8×10^{-2} $mg \cdot cm^{-2} \cdot h^{-1/2}$ in time scale 310-1098 h. The Al content in the $TiAl_3$/Al composite coating was assumed to be the key factor in influencing the oxidation behavior of the $TiAl_3$/Al composite coating, which was far different from those reported for pure $TiAl_3$ (Ref 12). However, the composite coating provided good oxidation protection at all cases from 650 to 950 °C over 1000 h without scaling or observable sign of degradation in spite of those differences in the oxidation kinetics at various temperatures.

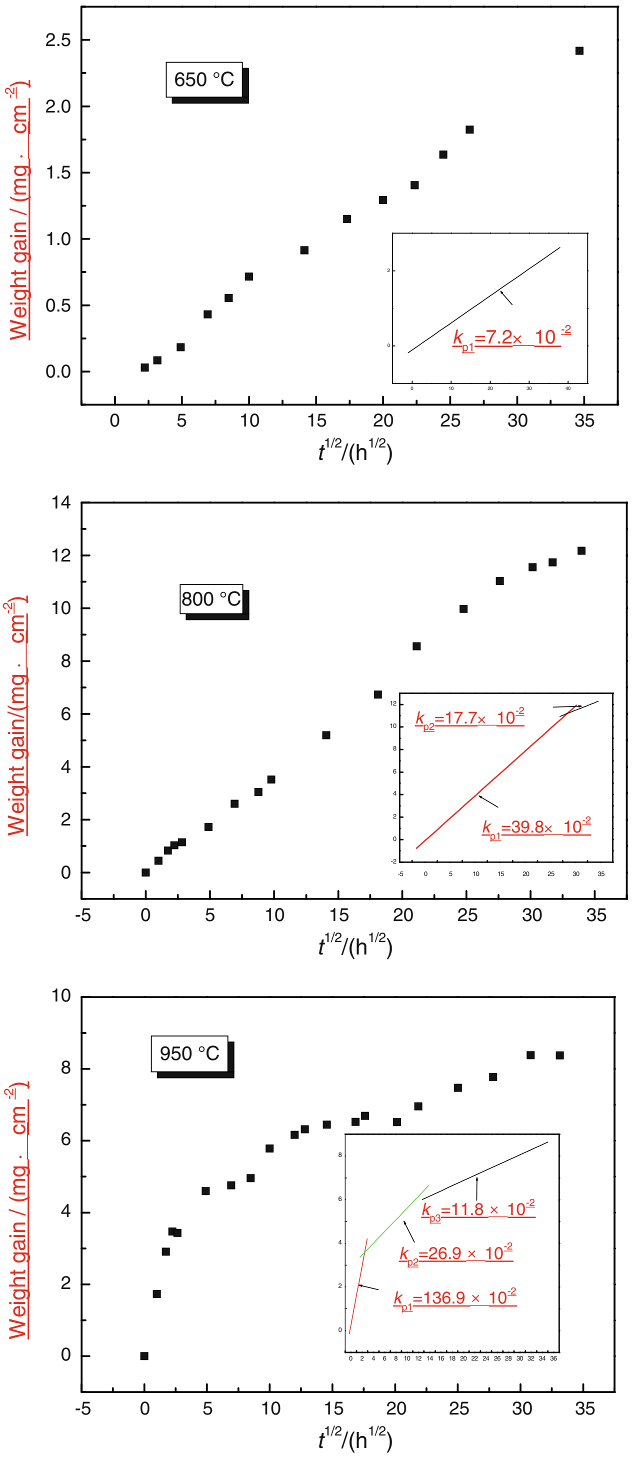

Fig. 3 Plots of weight gains against $t^{1/2}$ for the $TiAl_3$/Al composite coating in air at different temperatures

3.2 Microstructure of the Oxidized Coating

Figure 4 shows the cross-sectional microstructure of the oxidized $TiAl_3$/Al composite coating at different temperatures. Figure 4(a) shows the cross-sectional image of the coating before oxidation. The SEM image shows that the

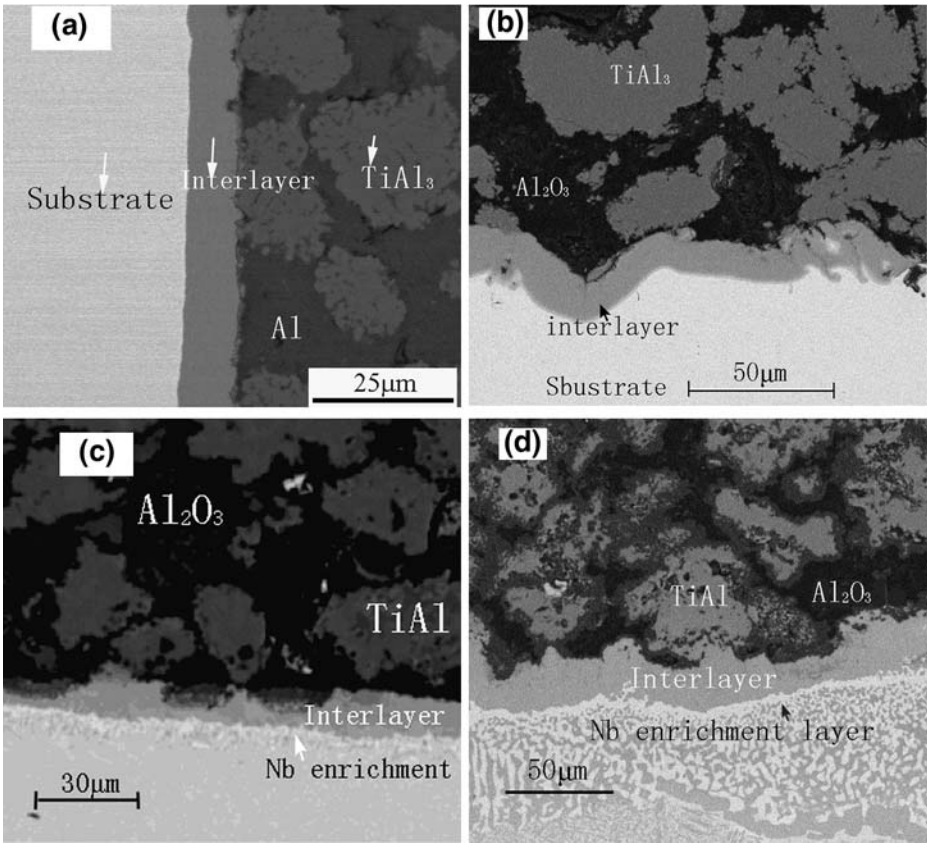

Fig. 4 Microstructure of the $TiAl_3$/Al composite coating on orthorhombic-Ti-22Al-26Nb oxidized for about 1000 h: (a) fresh coating; (b) 650 °C; (c) 800 °C; and (d) 950 °C

Table 1 Results of EDX analysis of interlayer

Item	Interlayer analysis	Al K, at.%	Ti K, at.%	Nb L, at. %	Phase
1	Original (a)	72.30	16.61	11.10	(Ti, Nb)Al_3
2	Oxidized/650 °C 1000 h	76.06	13.96	9.98	(Ti, Nb)Al_3
3	Oxidized/800 °C 1000 h	73.39	16.41	10.20	(Ti, Nb)Al_3
4	Oxidized/950 °C 150 h	48.64	37.07	14.29	(Ti, Nb)Al
	Oxidized/950 °C 300 h	44.52	47.78	7.70	(Ti, Nb)Al
	Oxidized/950 °C 1000 h	47.89	38.81	13.30	(Ti, Nb)Al

(a) See in Ref 13

$TiAl_3$/Al composite coating prepared by cold spray was complex in structure. The irregular $TiAl_3$ phases were embedded in the aluminum matrix (Ref 13). After oxidation, the aluminum phases were oxidized completely to Al_2O_3 (Fig. 4). An interlayer of about 10 μm thickness can be observed between the coating and the substrate in the freshly prepared $TiAl_3$/Al composite coating, which was formed during heat-treatment due to the inward diffusion of aluminum and the outward diffusion of niobium (Nb) (Ref 13, 14). The phase was mainly (Ti,Nb)Al_3 in the freshly prepared coating. The phase was still mainly (Ti,Nb)Al_3 after oxidized over 1000 h at 650 and 800 °C as indicated by the EDX analysis (Table 1, items 1, 2, and 3). The phase in interlayer changed to (Ti,Nb)Al at 950 °C in 150 h; however, this seemed to be the steady phase because it did not change since then and kept with the same phase composition to the tested 1098 h (Table 1, item 4). A possible reason for the difference was thought to be the different diffusion rate at different temperatures. Another subsequence of this difference in diffusion rate was the Nb enrichment below the interlayer. This enrichment was about 50 μm for the specimen oxidized at 950 °C (Fig. 4d) and 10 μm for that oxidized at 800 °C (Fig. 4c), while it was hardly observed for the coating oxidized at 650 °C (Fig. 4b).

3.3 Phase in Coating

Figure 5 shows the XRD patterns of original Ti, Al powders (Fig. 5a) and the deposited coating (Fig. 5b).

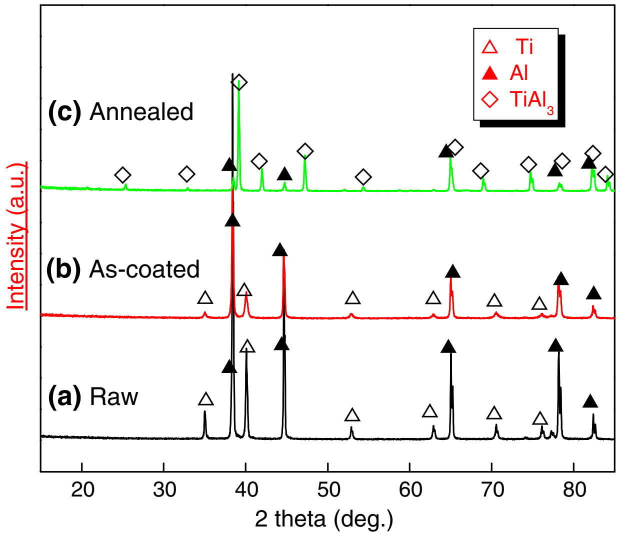

Fig. 5 Phase in the $TiAl_3$/Al composite coating prepared by cold spray before oxidation test

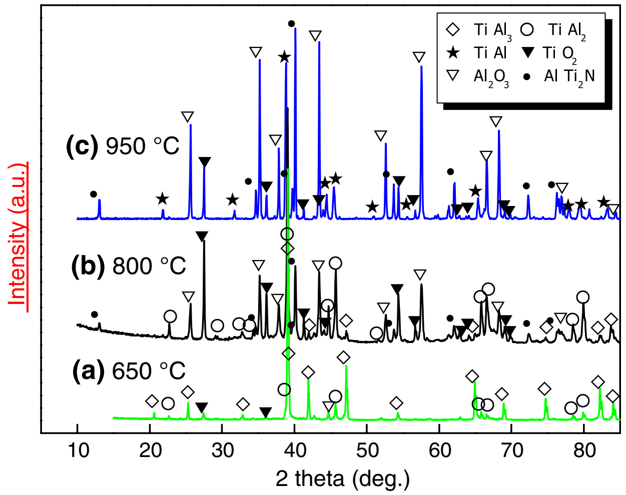

Fig. 6 Phase in the $TiAl_3$/Al composite coating after oxidized for about 1000 h

They were pure Ti and Al after deposited by cold spray. After heat treatment at 630 °C for 5 h, solid reaction (Eq 1) (Ref 16) occurred between Ti and Al, and the newly formed $TiAl_3$ phase appeared in the residual Al matrix (Fig 5c).

$$Ti(s) + 3Al(s) \rightarrow TiAl_3(s) \qquad \text{(Eq 1)}$$

After oxidized at 650 °C for 1200 h (Fig. 6a), the Al content was consumed completely to form Al_2O_3. Most of the $TiAl_3$ phase still remained unoxidized and only part of the $TiAl_3$ transformed to $TiAl_2$ because of preferential Al depletion by forming Al_2O_3 (Eq 2) (Ref 12). Small amount of TiO_2 was also detected in the oxidized composite coating (Fig. 6a)

$$TiAl_3 + \frac{3}{4}O_2 \rightarrow TiAl_2 + \frac{1}{2}Al_2O_3 \qquad \text{(Eq 2)}$$

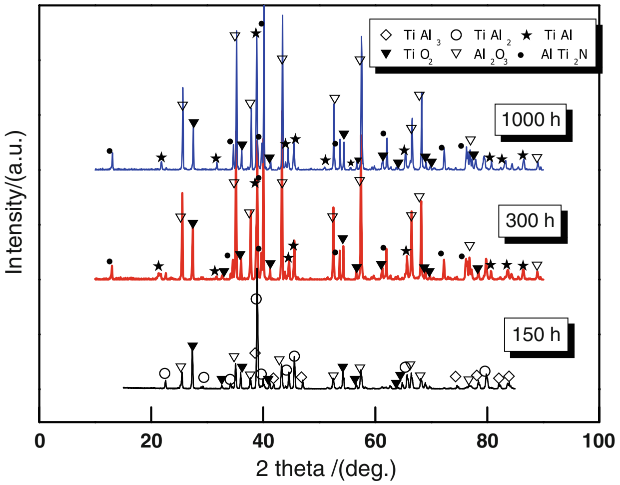

Fig. 7 Phase change in the $TiAl_3$/Al composite coating after oxidized at 950 °C

For the composite coating oxidized at 800 °C for 1154 h (Fig. 6b), the component in the surface became complex. Figure 6(b) shows that there were mainly Al_2O_3, TiO_2, $AlTi_2N$, $TiAl_2$ and small amount of un-oxidized $TiAl_3$. For the composite coating oxidized at 950 °C for 1098 h (Fig. 6c), the oxide in the surface was much similar to those observed at 800 °C except that the phase intensity for Al_2O_3 became the dominate phase. The intensity for TiO_2 reduced much lower. The $TiAl_3$ vanished completely and the TiAl grew as the dominant intermetallics instead of $TiAl_2$ (Fig. 6c).

Further XRD analysis on the coating oxidized at 950 °C revealed that the phase of $TiAl_3$ was oxidized completely within the initial 150 h (Fig. 7) and transformed to correspondence $TiAl_2$. Al_2O_3 and TiO_2 came forth in the coating at the same time. Extending the test to 300 h, both the phase of $TiAl_3$ and $TiAl_2$ consumed transforming to TiAl and $AlTi_2N$. The Al_2O_3 grew much stronger and became the dominant phase while the TiO_2 remained the same as those within 150 h. These seemed to be the steady phase composition and remained unchanged even prolonged the test to 1098 h (Fig. 7).

The phase changing after oxidation could also be revealed by the EPMA map analysis. Figure 8 shows the results of EPMA map analysis of the specimens oxidized at the three tested temperatures. For the $TiAl_3$/Al composite coating oxidized at 650 °C, the oxidation was still restricted to the Al content in the coating with most of the $TiAl_3$ phase untouched. Nitrogen distribution shows no great difference in substrate and in coating indicating no nitride formed at 650 °C. Being oxidized at 800 °C (Fig. 8b), the $TiAl_3$ phase was eroded by oxygen and nitrogen seriously not only at the fringe but also at the inside of the titanium aluminide particle. These became much severe at 950 °C (Fig. 8c), when the titanium aluminide particles were almost mixed with the oxides and nitrides formed. Clearly, the oxidation had taken place throughout the entire coating. It was also reported that the sprayed mixture would suffer

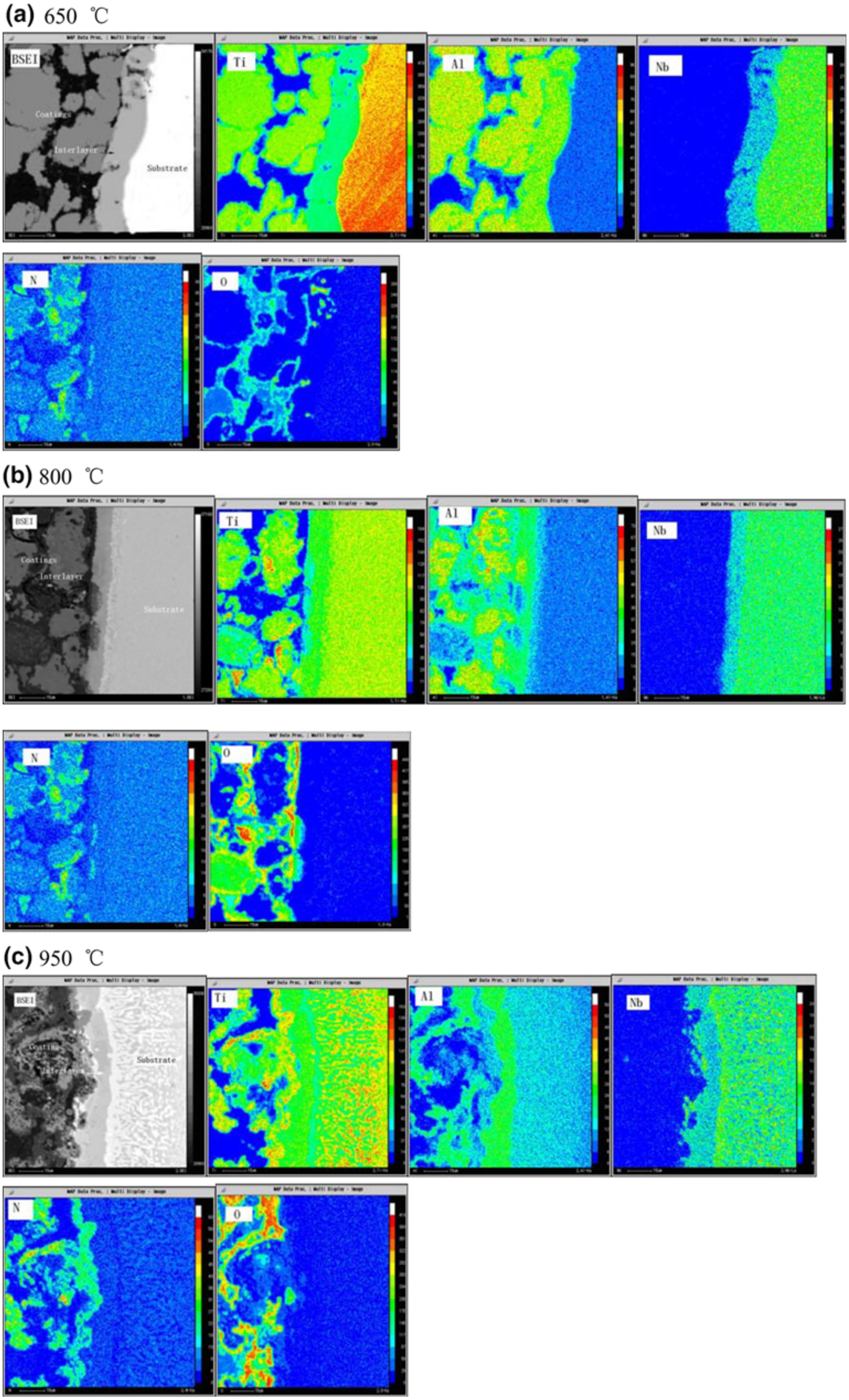

Fig. 8 Elemental mapping of major elements between the coating and the substrate after oxidation for about 1000 h: (a) 650 °C; (b) 800 °C; and (c) 950 °C

from oxidation within the material rather than only at the surface (Ref 16). However, the oxidation was limited to the coating. Further oxidation to the substrate was prevented by the interlayer formed between the coating and the substrate. Neither oxide nor oxygen embrittlement under the $TiAl_3$/Al coating were detected even oxidized at 950 °C for 1098 h (Ref 14). Thus, the coating improved the orthorhombic-Ti-22Al-26Nb high-temperature oxidation resistance significantly as demonstrated by the previous results of oxidation investigation.

4. Conclusion

The oxidation behavior of $TiAl_3$/Al composite coating on orthorhombic-based alloy was reported in this paper. The oxidation kinetics for the coating changed greatly at 650, 800, and 950 °C. The parabolic rate constant for the coating oxidized at 650 °C was $k_{p1} = 7.2 \times 10^{-2}$ $mg \cdot cm^{-2} \cdot h^{-1/2}$ throughout the tested 1200 h. For the coating oxidized at 800 °C, the oxidation kinetics can be separated into two stages with a k_{p1} of 39.8×10^{-2} $mg \cdot cm^{-2} \cdot h^{-1/2}$ in the initial 910 h, and k_{p2} of 17.7×10^{-2} thereafter. For the coating oxidized at 950 °C, the oxidation kinetics can be separated into three stages with k_p of 136.9×10^{-2} $mg \cdot cm^{-2} \cdot h^{-1/2}$ in the first 100 h, followed by 26.9×10^{-2} $mg \cdot cm^{-2} \cdot h^{-1/2}$ from 100 to 310 h, and 11.8×10^{-2} $mg \cdot cm^{-2} \cdot h^{-1/2}$ from 310 to 1098 h.

The microstructure analysis shows that the oxidation took place at the entire coating instead of only at the coating surface. Al in the composite coating was soon oxidized to Al_2O_3 in all tested cases. The $TiAl_3$ in the composite coating was oxidized by Al depleted oxidation. The $TiAl_3$ phase itself degraded to $TiAl_2$ at low temperature and TiAl at elevated temperatures. $AlTi_2N$ was also a typical oxidation product of elevated temperature oxidation. The experimental results indicated that the protection of the $TiAl_3$/Al coating probably comes from the interlayer between the coating and the substrate.

Acknowledgment

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References

1. J.C. Willianms, Intermetallics for Structural Applications Potential, Reality and the Road Ahead, *Structural Intermetallics 1997*, M.V. Nathal, R. Darolia, C.T. Liu, P.L. Martin, D.B. Miracle, R. Wagner, and M. Yamaguchi, Ed., TMS, Warrendale, PA, 1997, p 3-8
2. F.C. Dary and T.M. Pollock, Effects of High Temperature Air and Vacuum Exposures on the Room Temperature Tensile Behavior of the (*O+B2*) Titanium Aluminide Ti-22Al-23Nb, *Mater. Sci. Eng.*, 1996, **208**, p 182-202
3. L. Gauer, S. Alperine, P. Steinmetz, and A. Vassel, Influence of Niobium Additions on High-Temperature-Oxidation Behavior of Ti_3Al Alloys and Coatings, *Oxid. Met.*, 1994, **42**(1-2), p 49-74
4. C. Leyens, Environmental Effects on Orthorhombic Alloy Ti-22Al-26Nb in Air Between 650 and 1000 °C, *Oxid. Met.*, 1999, **52**(5-6), p 475-503
5. C. Leyens and M. Peters, *Titanium and Titanium Alloys*, Wiley-VCH, Weinheim, 2003
6. S.G. Warrier, S. Krishnamurtby, and P.R. Smith, Oxidation Protection of Ti-Aluminide Orthorhombic Alloys: An Engineered Multilayer Approach, *Metal. Mater. Trans.*, 1998, **29**(4), p 1279-1288
7. R. Braun and C. Leyens, Protective Coatings on Orthorhombic Ti_2AlNb Alloys, *Mater. High Temp.*, 2005, **22**(3-4), p 437-447
8. Q.M. Wang, K. Zhang, J. Gong, Y.Y. Cui, C. Sun, and L.S. Wen, NiCoCrAlY Coatings with and Without an Al_2O_3/Al Interlayer on an Orthorhombic Ti_2AlNb-Based Alloy: Oxidation and Interdiffusion Behaviors, *Acta. Mater.*, 2007, **55**, p 1427-1439
9. S.C. Kung, High-Temperature Coating for Titanium Aluminides Using the Pack-Cementation Technique, *Oxid. Met.*, 1990, **24**(3-4), p 217-228
10. K. Zhang, C. Sun, and F.H. Wang, Preparation and Protection of Al Diffusion Coatings on Matrix *r*-TiAl, *Acta. Met. Sin.*, 2006, **42**, p 355-360
11. V. Gauthier, F. Dettenwanger, M. Schütze, V. Shemet, and W.J. Quadakkers, Oxidation-Resistant Aluminide Coatings on r-TiAl, *Oxid. Met.*, 2003, **59**, p 233-254
12. Z.D. Xiang, S.R. Rose, and P.K. Datta, Pack Formatin and Long Term Oxidation Kinetics of $TiAl_3$ Coating on *r*-TiAl, *Mater. Sci. Technol.*, 2005, **21**, p 1111-1118
13. L. Shen, L.Y. Kong, T.Y. Xiong, H. Du, and T.F. Li, Preparation of TiAl-Al Composite Coating by Cold Spraying, *Trans. Nonferrous Met. Soc. China*, 2009, **19**, p 879-882
14. L.Y. Kong, J.Z. Qi, B. Lu, X.Y. Cui, H. Du, T.F. Li, and T.Y. Xiong, Oxidation Resistance of $TiAl_3$-Al Composite Coating on Ti-22Al-26Nb Alloy, *Surf. Coat. Technol.* (submitted)
15. B. Pieraggi, Calculations of Parabolic Reaction Rate Constants, *Oxid. Met.*, 1987, **24**(3/4), p 177-185T
16. Novoselova, P. Fox, R. Morgan, and W. O'Neill, Experimental Study of Titanium/Aluminium Deposits Produced by Cold Gas Dynamic Spray, *Surf. Coat. Technol.*, 2006, **A433**, p 139-143