Effects of Nb and Si on high temperature oxidation of TiAl

JIANG Hui-ren(姜惠仁)[1], WANG Zhong-lei(王中雷)[1], MA Wen-shuai(马文帅)[1],
FENG Xiao-ran(冯晓然)[1], DONG Zi-qiang(董自强)[1], ZHANG Liang(张 亮)[2], LIU Yong(刘 咏)[2]

1. School of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics,
Beijing 100083, China;
2. State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China

Abstract: The isothermal oxidation behavior of TiAl based alloys at 900 ℃ in air with a combination of Nb (5%−10%, mole fraction) and Si (1%−5%, mole fraction) was investigated. The microstructure and the composition of the oxidation scale were studied by using XRD, TEM and EPMA. The results show that the combination of Nb and Si can improve the oxidation resistance of the alloys significantly. The element Si can change the typical microstructure of oxidation scale on TiAl based alloys. In alloys with Si addition, the compact Al_2O_3 forms in the interior side of oxidation scale. When $x(Si) > 3\%$, the Ti_5Si_3 phase forms and the coarse crystal TiO_2 forms on Ti_5Si_3 phase after oxidation. The increase of Nb content in the TiAl based alloys impedes the growth of Ti_5Si_3 phase, and the formation of TiO_2 on surface and on Ti_5Si_3 phase is also impeded.

Key words: TiAl based alloy; niobium silicon alloying; isothermal oxidation behavior; oxidation resistance

1 Introduction

Titanium aluminum (TiAl) and its alloys are promising structural materials for use at high temperatures in aerospace, automobile and gas turbine industries, because of their high elevated-temperature strength and specific strength[1]. However, the commercial application of γ-based alloys is currently limited by their poor oxidation resistance at temperatures above 850 ℃[2].

It was shown that alloying can effectively improve the oxidation resistance of TiAl, e.g. the addition of Nb[3−6], Cr[7], W[8], Mo[9], and Si[10]. Among these elements, Nb improves not only the oxidation resistance of TiAl-based intermetallics, but also the creep resistance and room temperature toughness[11−12]. However, a large amount of Nb addition will densify the TiAl based alloys, and thus limit the applications. And Si addition also improves the oxidation resistance of TiAl based alloys[10], but it will become detrimental to the oxidation resistance with the increase of its concentration due to the formation of Ti_5Si_3 phase. The previous study showed that the combined addition of Nb and Si is more effective for improving the high temperature oxidation resistance of TiAl alloy than alloying with Nb or Si alone[10]. However, the mechanism of the effect of both Nb and Si is not clearly understood.

In this work, the effects of Nb and Si on the oxidation behavior of TiAl based alloys at elevated temperatures are appraised, and the mechanism of oxidation is discussed.

2 Experimental

The experimental alloys were prepared by high purity Ti, Al, Nb and Si powders. The purities of powders were 99.5%, 99.8%, 99.8%, 99.8% (mass fraction), respectively. The TiAl-xNb-ySi alloys had a fixed proportion of x(Ti):x(Al)=1:1 while varied contents of Nb and Si (as listed in Table 1). The ingots were prepared by non-consumable electrode arc melting in an argon atmosphere. Each alloy button specimen with approximately 20 g was remelted and turned over for three times to ensure homogeneity. The buttons were cut by the electrical discharge method for oxidation experiments. The specimens for oxidation tests were about 10 mm×10 mm×1 mm, and their surfaces were

Table 1 Composition of specimens (molar fraction, %)

Sample No.	Ti	Al	Nb	Si
1	47.5	47.5	5	0
2	47.0	47.0	5	1
3	46.0	46.0	5	3
4	45.0	45.0	5	5
5	45.0	45.0	10	0
6	44.5	44.5	10	1
7	43.5	43.5	10	3
8	42.5	42.5	10	5

polished with emery papers up to 1000#, and cleaned with acetone to remove grease.

The isothermal oxidation tests were performed at 900 ℃ in a box furnace in static air at atmospheric pressure for 24 h. At the end of the test, the specimens were furnace cooled. The phases formed in the scales were identified by Rigaku D/max-2200 X-ray diffractometry (Cu K_α, 40 kV, 40 mA). The morphology of the scale and the distribution of elements were examined by electro-probe micro-analyses(EPMA) (JXA-8100, JEOL) and transmission electron microscope (TEM)(JEM-2100F, JEOL).
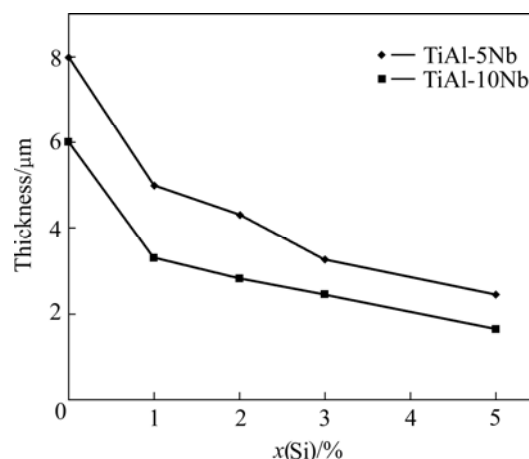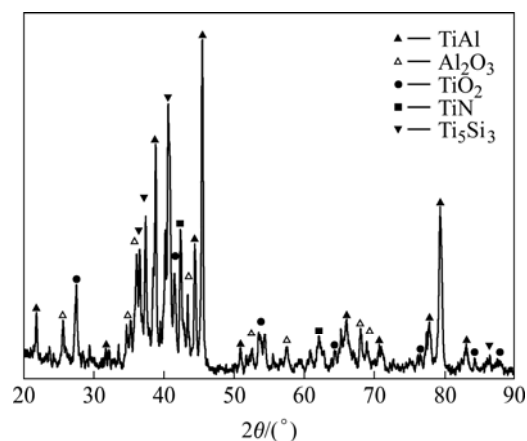
3 Results

3.1 Thickness and phase constitution of oxidation scale

The variation of oxidation scale thickness with Nb, Si content (x(Nb), x(Si)) in the series of TiAl-xNb-ySi is shown in Fig.1. The scale thickness of the alloys increases with the increase of Si content. With the same Si content, the thickness of the scale on the 10Nb alloys is thinner than that on the 5Nb alloys, indicating that Nb addition can further improve the oxidation resistance of the alloys. For these eight alloys, the scale formed on TiAl-10Nb-5Si alloy is the thinnest, and the thickness is about 2 μm, which is thinner than that of the scales on TiAl-10Si alloy[13] and TiAl-15Nb alloy[14]. This means that the combination of Nb and Si results in much better oxidation resistance than the individual element addition.

The XRD pattern obtained from the high temperature oxidized specimen surface of TiAl-10Nb-5Si alloy is given in Fig.2. It is demonstrated that in TiAl-10Nb-5Si alloy, the major oxidation phases are TiO_2 and Al_2O_3, and TiN is also observed, but no Nb oxidation and Si oxidation are detected. Since the oxidation scale is thin, the Ti_5Si_3 phase and TiAl phase from the matrix can be detected in XRD.

3.2 Surface morphologies of alloys before oxidization

Fig.3 shows the back scattered electron images of

Fig.1 Change of scale thickness with Nb and Si contents

Fig.2 XRD pattern obtained from surface of TiAl-10Nb-5Si alloy after oxidizing in air at 900 ℃ for 24 h

the surface morphologies. For TiAl based alloys, when x(Si)=3%, the pin-like additional phases are introduced (Fig.3(a)). As shown in Fig.2, the additional phase is confirmed as Ti_5Si_3 phase. When x(Si)=5%, the rod-like grains of Ti_5Si_3 phase are introduced in the alloys (Fig.3(c)). By comparing Fig.3(a) with Fig.3(b) and Fig.3(c) with Fig.3(d), it can be seen that the increase of Nb addition can refine Ti_5Si_3 phase effectively and let them distribute symmetrically in the matrix.

3.3 Surface morphologies of oxidation scale

Fig.4 shows the surface morphologies of oxidation scale formed on the TiAl based alloys. The SEM observation indicates that the surface morphology of the scale differs for different alloys, which is related to the quantity of the elements addition. It can be seen that as the x(Si) increases, the oxides formed on the alloys become finer and smoother (Figs.4(a) and (c)). When x(Si)>3%, the coarse TiO_2 is formed on the island-like Ti_5Si_3 phase(Figs.4(c) and (d)). When x(Nb) increases from 5% to 10% in alloys, the TiO_2 phases formed on the surface and on Ti_5Si_3 phase all become finer (Figs.4(c) and (d)).
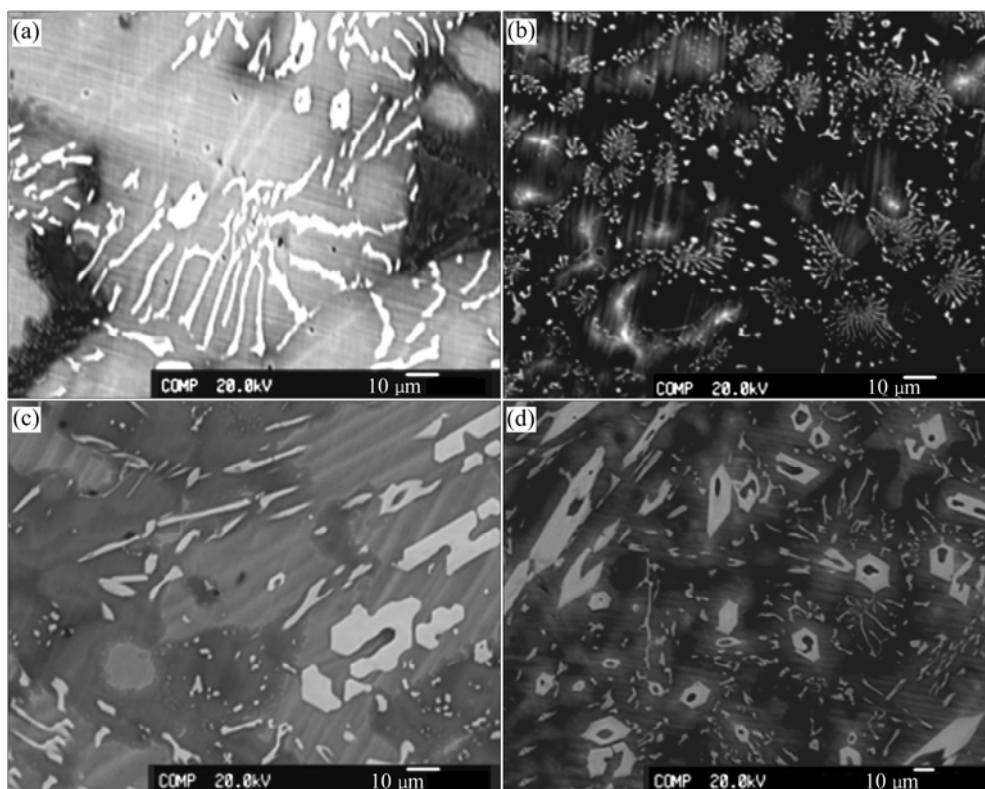
Fig.3 BEM photographs of alloys before oxidation: (a) TiAl-5Nb-3Si; (b) TiAl-10Nb-3Si; (c) TiAl-5Nb-5Si; (d) TiAl-10Nb-5Si
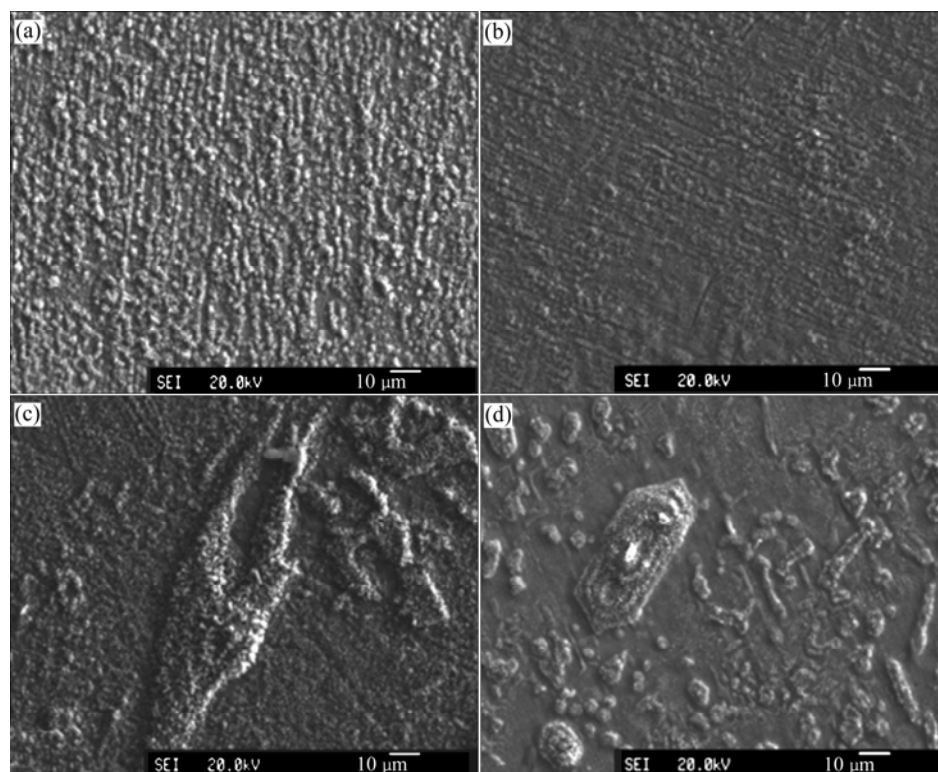

Fig.4 Surface morphologies of oxidation scale: (a) TiAl-5Nb-1Si; (b) TiAl-10Nb-1Si; (c) TiAl-5Nb-5Si; (d) TiAl-10Nb-5Si

3.4 Cross-section morphology

Fig.5 shows the back scattered electron micrographs of cross-sections of the oxidation layer. For TiAl-5Nb-3Si (Fig.5(a)), the oxidation layer adheres to the matrix incompactly and there are several voids and pores in the oxidation scale and at the layer interfaces.
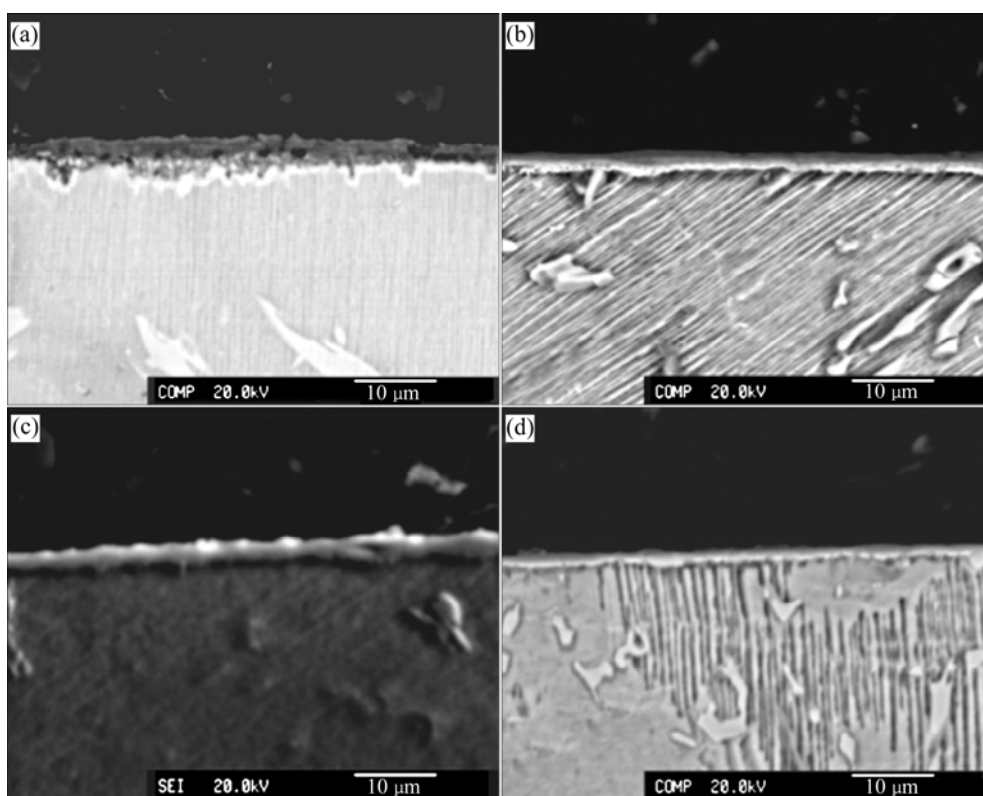
Fig.5 Cross-sectional micrographs of alloys: (a) TiAl-5Nb-3Si; (b) TiAl-10Nb-3Si; (c) TiAl-5Nb-5Si; (d) TiAl-10Nb-5Si

When x(Nb) increases from 5% to 10%, the oxidation layer becomes continuous and adheres to the matrix compactly. This indicates that the addition of Nb can improve the adherence of oxidation layer to the matrix. Since the thickness of oxidation scale becomes thinner with the increase of x(Si) and x(Nb), as demonstrated in Fig.1, the oxidation scale on TiAl-10Nb-5Si is the thinnest. Furthermore, it adheres to the matrix compactly.

3.5 Elements distribution

Fig.6 shows the TEM photograph and EDS analyses of a cross-section of the oxidation layer on TiAl-10Nb-5Si after exposure at 900 ℃ for 24 h. The distribution of elements in the oxidation scale is shown clearly in this photo. According to the intensity of O K_α, the location of oxidation scale can be defined. It can be seen that the oxidation scale is divided into two layers, i.e. the coarse grain region closed to the surface and the fine grain region near the scale/substrate interface. Nb is found to be enriched in the fine grain region but not the coarse grains region, which means that the fine zone grows by inward diffusion of oxygen ions and the coarse zone grows by outward diffusion of metal ions. From the peak of Al K_α, it can be seen that Al_2O_3 mainly distributes in the substrate side near the fine region. In the left side of oxidation scale, there is an area, in which the intensity of Al K_α is weak compared with that in the substrate. It is believed that this area is the diffusion zone. In this zone,

the peak of N K_α coincides with that of Ti K_α, which implies the existence of TiN. And the peak of Si K_α coincides with that of Nb K_α, which is an indication of probable NbSi compound formation. In addition to the above findings, the distribution of Nb K_α and Si K_α suggests that a certain amount of Nb is dissolved in the scale, while Si is depleted in this region.
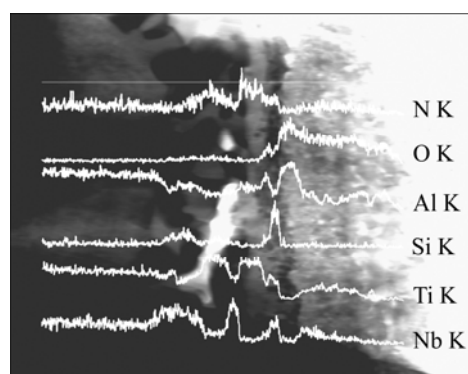

Fig.6 TEM photograph of cross-sectional morphology of TiAl-10Nb-5Si and corresponding EDS patterns

4 Discussion

The Si addition can change the typical microstructure of oxidation scale on TiAl based alloys, which is composed of the inner layer formed by inward diffusion of oxygen ions and the outer layer formed by

outward diffusion of metal ions[15]. The oxidation scale is basically composed of two layers, i.e. a surface layer of coarse crystal TiO_2, followed by a Al_2O_3-rich area in the interior of surface and then a mixed layer of TiO_2+Al_2O_3[16−17]. However, in our present study, it can be seen from Fig.6 that the microstructure of oxidation scale on alloys with 5% Si is different from the typical microstructure. For TiAl-10Nb-5Si alloy, the outer layer of oxidation scale is TiO_2, and the Al_2O_3-rich area is not in the interior side of the outer layer, but in the interior side of the inner layer(Fig.6). This structure is considered as a transitional structure of a uniformly condensed Al_2O_3 layer. From the distribution of elements in Fig.6, the content of Al is lower than that of other elements in the diffusion zone, indicating that Al content increases correspondingly in oxidation scale. It can be explained by the fact that Si promotes the diffusion of Al in oxidation scale or Si stabilizes Ti and then enhances the thermodynamic activity of Al. Due to the low solid solution of Si in the oxidation scale, as the growth of oxidation scale, Si gathers in the diffusion zone, which enhances the activity of Al further, and thus the Al_2O_3-rich layer always locates in the interior side of oxidation scale. When Si content exceeds a certain value, a uniformly condensed Al_2O_3 layer will form in the interior side of oxidation scale. XIAO et al[13] showed that, when x(Si)=15%, the dense and protective Al_2O_3 layer forms at the early stage of the oxidation process. It can thus be summarized that Si addition changes the typical structure of oxidation scale and promotes the formation of a compact Al_2O_3 layer and hence improves the oxidation resistance.

From Fig.1 and Fig.4, as x(Si) increases, the thickness of oxidation scale becomes thinner and the oxides formed on the alloys become finer and smother. When x(Si)＞3%, the rod-like grains of Ti_5Si_3 phase are formed in the alloys, on which the oxides are coarse crystal TiO_2. Since TiO_2 grows much faster than Al_2O_3, and the brittleness of Ti_5Si_3 phase may initiate cracking in oxidation layers and spallation of the oxides, the formation of Ti_5Si_3 phase is harmful to the oxidation resistance of alloys.

Nb improves the oxidation resistance of the TiAl based alloys with Si addition, firstly due to the impeding effect on the formation of the rod-like Ti_5Si_3 phase. From Fig.3, as Nb content increases, the amount of Ti_5Si_3 phase decreases and Ti_5Si_3 phase becomes finer and smoother. Furthermore, Ti_5Si_3 phase distributes more symmetrically in the alloys. It is believed that Nb increases the solid solution of Si in γ-TiAl, which is related to the decrease of amount of Ti_5Si_3 phase. The distribution of elements in diffusion zone indicates that the Ti-rich portion coincides with the N-rich portion, and the Si-rich portion coincides with the Nb-rich portion.

Therefore, after the recombination of elements by diffusion in the diffusion zone, the element Ti is likely to form TiN, and the element Si tends to form a NbSi compound. This implies that the increase of Nb content strengthens the tendency of decomposition of Ti_5Si_3 phase. Second, the Nb addition improves the adherence of oxidation scale to the substrate. The adherence mainly lies on the nature of elements in diffusion zone. Actually, the elements recombine in diffusion zone based upon their thermodynamic characteristics. It should be stated that in the diffusion zone, the phases balanced with oxidation scale are TiN and NbSi compounds, but not Ti_5Si_3 phase. This suggests that there is a barrier layer between oxidation scale and Ti_5Si_3 phase, which impedes the direct contact of oxides with Ti_5Si_3 phase, and then improves the adherence. Third, the Nb addition impedes mass transfer in TiO_2. As Nb content increases, the growth of TiO_2 on surface and on Ti_5Si_3 phase are impeded noticeably, resulting in the improvement of oxidation resistance. Nb not only impedes the diffusion of Ti and oxygen ions, but also impedes that of Al ions[14]. This indicates that Nb eliminates the amount of Al in oxidation scale and then weakens the effect of Al_2O_3 on improving oxidation resistance. However, according to the analysis of Fig.6, the elements Nb and Si tend to form NbSi compounds, which means the effect of Nb on impeding the diffusion of Al ions is weakened.

Based on the above analyses, the element Si can enhance the thermodynamic activity of Al in alloys and then strengthen the tendency to form protective Al_2O_3 layer to improve the oxidation resistance, and the element Nb can improve the oxidation resistance of the alloys by impeding mass transfer in TiO_2. Moreover, Si can weaken the deficiency of Nb in impeding Al ions and Nb can weaken the deficiency of Si in forming coarse Ti_5Si_3 phase. It is concluded that the combination of Nb and Si not only improves the oxidation resistance of alloys by different mechanism, but also weakens the mutual defects.

5 Conclusions

1) The typical structure of oxidation scale of TiAl based alloys is changed by Si addition. In alloys with Si addition, the compact Al_2O_3 forms in the interior side of oxidation scale.

2) The Ti_5Si_3 phase forms in TiAl based alloys with x(Si)＞3%, and the coarse crystal TiO_2 forms on Ti_5Si_3 phase after oxidation.

3) The increase of Nb content in the TiAl based alloys can impede the growth of Ti_5Si_3 phase, and the formation of the coarse crystal TiO_2 formed on surface and on the Ti_5Si_3 phase is also impeded.

4) The oxidation resistance of the TiAl based alloys

is improved by the combination of Nb and Si.

References

[1] APPLE F, WAGNER R. Microstructure and deformation of two-phase γ-titanium aluminides [J]. Mater Sci Eng R, 1998, 22: 187−268.

[2] KUMPFERT J, KIM Y W, DIMIDUK D M. Effect of microstructure on fatigue and tensile properties of the gamma TiAl alloy Ti-46.5Al-3.0Nb-2.1Cr-0.2W [J]. Mater Sci Eng A, 1995, 192/193: 465.

[3] LIU Zi-cheng, WANG Yan-li, LIN Jun-pin, ZHANG Wei-jun, CHEN Guo-liang. Thermal activation approaches to deformation mechanisms for high Nb containing TiAl base alloys [J]. Journal of Materials Research, 2002, 12(6): 1081−1086.

[4] YOSHIHARA M, KIM Y W. Oxidation behavior of gamma alloys designed for high temperature applications [J]. Intermetallics, 2005, 13: 952−958.

[5] LU Wei, CHEN Chun-lin, XI Yan-jun, GUO Chang-you, WANG Fu-hui, HE Lian-long. TEM investigation of the oxide scale of Ti-46.5Al-5Nb at 900 ℃ for 50 h [J]. Intermetallics, 2007, 15: 824−831.

[6] LU Wei, CHEN Chun-lin, HE Lian-long, XI Yan-jun, WANG Fu-hui. Effect of niobium on oxidation behavior of TiAl [J]. Journal of Materials Research, 2007, 22(6): 1486−1490.

[7] DONG Zi-qiang, JIANG Hui-ren, FENG Xiao-ran, WANG Zhong-lei. Effect of Cr on high temperature oxidation of TiAl [J]. Trans Nonferrous Met Soc China, 2006, 16: S2004−S2008.

[8] WENDLER B G, KACZMAREK Ł. Oxidation resistance of nanocrystalline microalloyed γ-TiAl coatings under isothermal conditions and thermal fatigue [J]. Journal of Materials Processing Technology, 2005, 164/165: 947−953.

[9] WU Y, HWANG S K, HAGIHARA K, UMAKOSHI Y. Isothermal oxidation behavior of two-phase TiAl-Mn-Mo-C-Y alloys fabricated by different processes [J]. Intermetallics, 2006, 14: 9−23.

[10] MAKI K, SHIODA M, SAYASHI M, SHIMIZU T, ISOBE S. Effect of silicon and niobium on oxidation resistance of TiAl intermetallics [J]. Mater Sci Eng A, 1992, 153: 591−596.

[11] AI Tao-tao, WANG Fen, ZHU Jian-feng. Microstructure and mechanical properties of Al_2O_3/TiAl composite [J]. Trans Nonferrous Met Soc China, 2006, 16: S1924−S1927.

[12] NAKANO T, YOKOYAMA A, UMAKOSHI Y. Effect of Nb addition on the plastic behavior of TiAl crystals containing oriented lamellae [J]. Scripta Metall Mater, 1992, 27(10): 1253−1258.

[13] XIAO Wei-hao, ZHANG Liang, JIANG Hui-ren. Effects of Si on high temperature oxidation resistance of TiAl alloy [J]. Journal of Beijing University of Aeronautics and Astronautics, 2006, 32: 365−368. (in Chinese)

[14] JIANG H R, HIROHASI M, LU Y. Effect of Nb on the high temperature oxidation of Ti-(0−50%)Al [J]. Scripta Materialia, 2002, 46(9): 639−643.

[15] TANIGUCHI S, JUSO H, SHIBATA T. Improvement in high-temperature oxidation resistance of TiAl by addition of 0.2 mass% Zr [J]. Mater Trans, 1996, 37: 245−251.

[16] SHIDA Y, ANADA H. Oxidation behavior of binary TiAl alloys in high temperature air environment [J]. Mater Trans JIM, 1993, 34(3): 236−242.

[17] DETTENWANGER F, SCHUMANN E, RUHLE M, RAKOWSKI J, MEIER G H. Microstructural study of oxidized γ-TiAl [J]. Oxid Met, 1998, 50(3/4): 269−307.

(Edited by YUAN Sai-qian)