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ARTICLE

Isothermal Oxidation Behavior of TiAl-Nb-W-B-Y Alloys with Different Lamellar Colony Sizes

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Abstract: The oxidation behavior of full-lamellar Ti-42.5Al-8Nb-0.2W-0.2B-0.1Y alloys with different colony sizes was investigated by a thermogravimetric method at 900 ℃ for 100 h in air. The microstructure and composition of the alloy as well as the oxide scales were analyzed by OM, SEM, EDS and XRD. It is found that the oxidation kinetic of the present TiAl alloys accords with the parabolic law, and the alloy with larger lamellar colony has a better oxidation resistance than the one with smaller lamellar colony. The mass gain of the two samples with large and small lamellar colony after 100 h oxidation is 6.45 and 7.62 g/cm^2, respectively. And correspondingly the thickness of oxide scale is about 5 and 7 μm, respectively. Based on the analysis of oxidation kinetic and microstructure characterization, we conclude that the structural differences between the two samples which affect the diffusion rate of O element into the matrix result in different oxidation behavior.

Key words: TiAl alloys; full lamellar structure; lamellar colony; oxidation behavior

TiAl-based alloys have been used in aerospace, automotive and gas turbine industries due to their exceptional combination of light weight and mechanical properties and creep resistance at elevated temperatures[1-3]. However, the oxidation resistance of TiAl-based alloys is inadequate at high temperatures up to 600~900 ℃ [4]. The competitive oxidations of Ti and Al in the TiAl alloys made it difficult for the formation of a dense and continuous Al_2O_3 layer protecting the matrix from further oxidation[5,6].

Numerous researches on oxidation resistance of TiAl alloys have been made, but the published oxidation data show a large scatter[5, 7-10]. A great deal of research work has been undertaken to improve the oxidation behavior of TiAl alloys by adding ternary and quaternary elements. In view of the third element addition, niobium and several other elements have been reported to be effective in improving the oxidation resistance of TiAl in Ref. [11-13]. And the microstructure of TiAl alloy castings has a significant influence on the oxidation behavior[14-17]. In conclusion, the variation of oxidation resistance for TiAl alloys may be attributed to the alloy purity, alloying elements, differences in surface preparation, alloy microstructure and so on[11-16]. All of these reasons affected the oxidation resistance of the TiAl alloy but the mechanisms are not clearly elucidated. The generally accepted concept was that the continuous Al_2O_3 layer protected the alloys from further oxidation and efficiently improved oxidation resistance.

In the present paper, we have studied the oxidation behavior of the full-lamellar Ti-42.5Al-8Nb-0.2W-0.2B-0.1Y alloy at 900 ℃ in air to examine the effect of colony size on oxidation resistance. The oxidation kinetics has been analyzed, and the microstructure has been characterized in detail. The obtained experimental results are useful for understanding the oxidation mechanisms of TiAl-based alloys.

1 Experiment

The TiAl alloy for this study was prepared by vacuum arc remelting (VAR) with a nominal composition of Ti-42.5Al-8Nb-0.2W-0.2B-0.1Y (at%). The ingot was cut into 10 mm×10 mm×5 mm samples used for oxidation tests. In order to obtain full-lamellar structure and adjust the colony size, two different heat treatment processes were carried out, as shown in Table 1. The samples for oxidation tests were first polished using

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Table 1 Heat treatments of the present alloy

Alloy composition/at%	Alloy	Heat treatment
Ti-42.5Al-8Nb-0.2W-0.2B-0.1Y	1#	1320 ℃/15 min
	2#	1320 ℃/5 h

SiC paper and then cleaned in acetone solution. Isothermal oxidation tests were performed at 900 ℃ in a static air atmosphere in an electric furnace for oxidation. The total oxidation time was 100 h and each oxidized specimen was weighted using an electronic balance with 0.1 mg precision. Various techniques have been used to characterize the structure and thickness of the matrix and the oxide scale. X-ray diffraction (XRD) with Cu Kα radiation was applied for phase identification, and the SEM analysis was performed for the layer morphology examination as well as the thickness measurements of the oxidation layer.

2 Results and Discussion

2.1 Initial microstructure

The microstructures of the Ti-42.5Al-8Nb-0.2W-0.2B-0.1Y alloy with different lamellar colony sizes before oxidation are shown in Fig.1. From the OM images in Fig.1a and Fig.1b, one can note that both the alloys have fully lamellar microstructure. However, the colony size in the two alloys is quite different due to the different heat treatment processes. When the alloy is treated for 15 min at 1320 ℃ (labeled as 1#), the colony size is much smaller, whereas the colony size in the 2# alloy (heat treated at 1320 ℃ for 5 h) is much larger. Fig.1c and Fig.1d show the SEM images of the alloys at higher magnification, and it is found that the lamellar spacing in the 2# alloy is comparable with that of the 1# alloy.

It was reported that the TiAl alloys with fine fully lamellar microstructure possesses the best high temperature performance[18]. High Nb containing TiAl alloys without B and Y element generally produce coarse microstructure. B and Y addition can not only improve the high temperature oxidation of alloys but also enhance the mechanical properties by refining the microstructure.

The histogram of the colony sizes of the present TiAl alloys are shown in Fig.2. One can observe that the colony size in 1# alloy is in the range of 20~160 μm, and yields an average value of about 85 μm. In contrast, the colony size is 50~350 μm for 2# alloy with an average value of about 195 μm. In addition, one can notice that the colony size is increased with the holding time in α phase, which is in accordance with the Baker equation[19].

2.2 Oxidation kinetics

Fig.3 shows the mass gain curves. The results indicate that the two microstructures show similar oxidation kinetics at 900 ℃. A review of earlier investigations on oxidation kinetics of the TiAl based alloys revealed that the parabolic rate law was considered as the basis of data processing and interpretation of the mass gain vs. time data[20]. In order to understand whether a simple kinetics law can apply, the curves can be fitted by an equation model as:

$$\Delta M_n = k_n t \quad (1)$$

where ΔM is mass grain per unit surface area of specimen, t is exposure time and k_n is the rate constant. The rate constant k_n and exponent n were evaluated from the linear regression fitting of $\ln(\Delta M)$ vs. $\ln t$ data. And the relationship of the two data is as follows:

$$\ln(\Delta M) = \frac{1}{n}\ln t + \frac{1}{n}\ln k_n \quad (2)$$

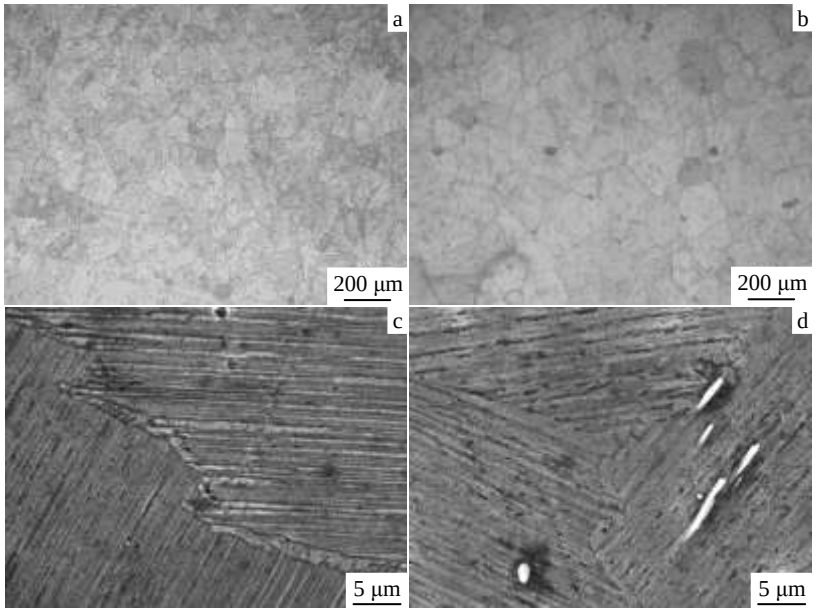

Fig.1 OM (a, b) and SEM (c, d) of microstructures of TiAl alloys: (a, c) small lamellar colony and (b, d) large lamellar colony

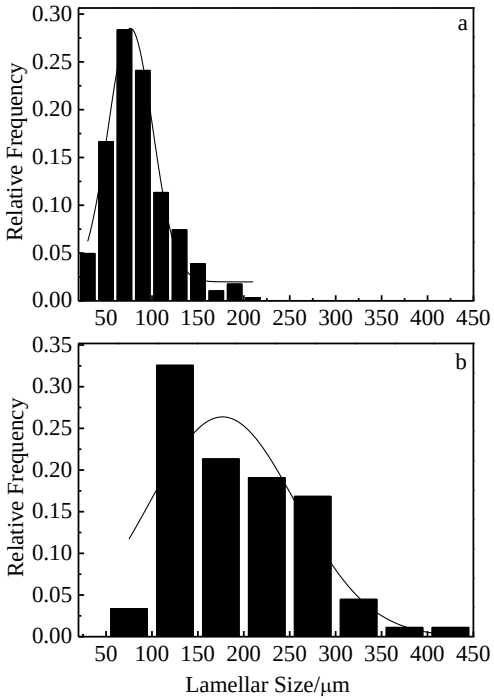

Fig.2 Lamellar sizes distributions of TiAl alloys lamellar colony: (a) small lamellar colony and (b) large lamellar colony

Table 2 Values of *n* of alloys after isothermal oxidation at 900 ℃ for 100 h

Alloys	*n*	*t*(*n*)
1#	1.95	0~100
2#	2.12	0~100

It is found that the oxidation rate is fairly fast at the initial stage of oxidation, and gradually decreases with the time, as shown in Fig.3. And after taking logarithm of mass gain and exposure time, the oxidation kinetic curves of the two alloys with different colony sizes obey a pseudo-parabolic or parabolic growth kinetics after oxidation as shown in Table 2. From Fig.3 it is also observed that the mass grain after 100 h reaches 7.62 g/m^2 for the 1# alloy with smaller colony size and 6.45 g/cm^2 for the 2# alloy with larger colony size. It is apparent that the larger colony size is beneficial for oxidation resistance. Therefore, the colony size is an important factor affecting the oxidation behavior of TiAl alloys.

2.3 Oxide scale analysis

Fig.4 shows the XRD patterns for the surfaces of the two alloys after oxidation. It can be seen that the main oxidation products include TiO_2, Al_2O_3 and Ti_3Al, which are consistent with reported in literatures [12, 21]. Fig.5 shows SEM images of the surface morphology of the two TiAl alloys after oxidation. It is found that both of the alloys show a rough surface due to the intensive formation of TiO_2 particles. One should note that the particle size for 1# alloy is somewhat larger than that of 2# alloy.

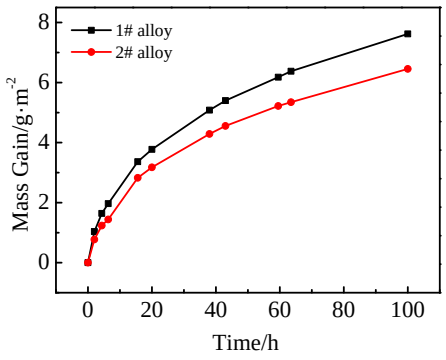

Fig.3 Oxidation kinetic curves of lamellar-TiAl alloys

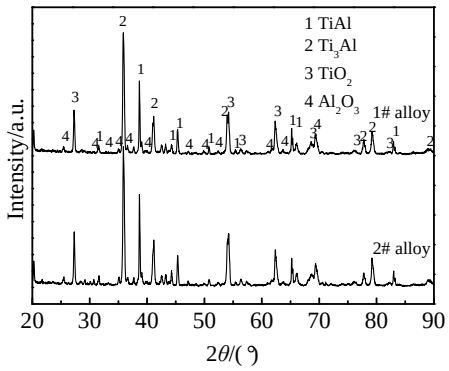

Fig.4 XRD patterns of 1# and 2# TiAl alloys after isothermal oxidation tests at 900 ℃ for 100 h in air

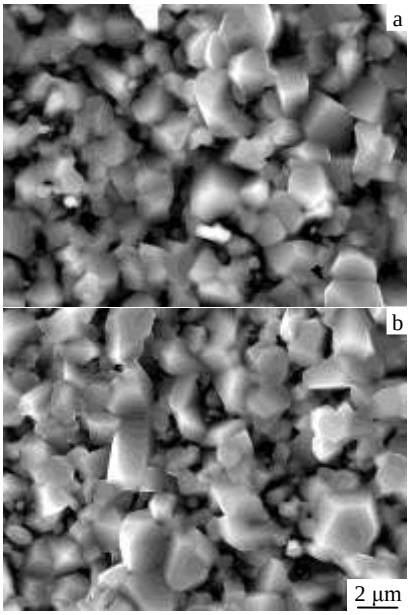

Fig.5 SEM images of oxide scales in TiAl alloys after oxidation for 60 h: (a) 1# alloy and (b) 2# alloy

Fig.6 shows the cross-section morphologies of the oxide layers. EDS analysis was performed vertical to the oxidation layer

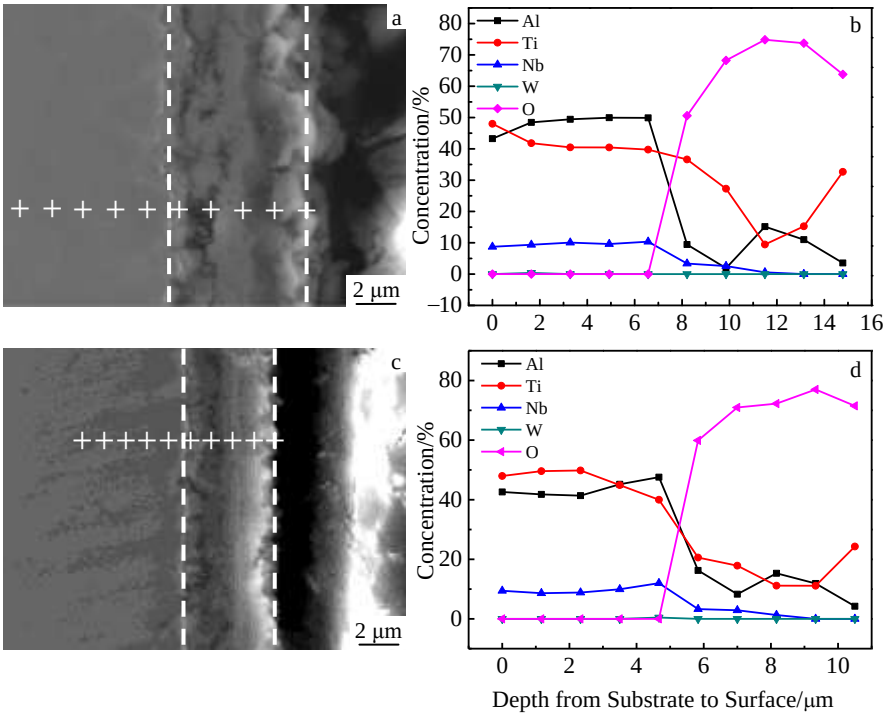

Fig.6 Back scattered SEM images (a, c) and element line scanning (b, d) of 1# (a, b), and 2# (c, d) TiAl alloys after isothermal oxidation tests at 900 ℃ for 100 h in air

to reveal the element distribution such as Ti, Al, O, Nb and W in the oxide scale. It can be seen that the Ti concentration gradually decrease from the substrate toward the intermediate layer, and then increase slightly in the outer layer. The evolution of Al concentration seems similar to that of Ti element, but is different in the intermediate layer. Beneath the substrate, the Ti concentration exhibits an obviously higher level than the Al concentration. Then the concentration line crosses, as shown in Fig.6. Finally, the Ti concentration becomes higher than the Al concentration once more. The O concentration increases from the substrate to the outside for both alloys, and the W and Nb concentration continuously decreases from the substrate toward the outside. The evolution of the Ti, Al and O concentration indicates the formation of the titanium oxides and aluminum oxides, which is confirmed by XRD results shown in Fig. 4. In addition, it can be seen from Fig.6 that beneath the substrate, a loose TiO_2 layer forms for both alloys, and a relatively dense mixing layer consisting of TiO_2 and Al_2O_3 develops beneath the loose TiO_2 layer. Finally much more TiO_2 phase and little Al_2O_3 form on the surface of the two alloys.

Examination in cross section of specimens also reveals that the thickness of the oxide scale is different for the two TiAl alloys. The thickness of the oxidation layer reaches a value of about 7 μm for 2# TiAl alloy while it is only 5 μm for 1# alloy. In conclusion, in comparison with the 1# TiAl with smaller colony size, 2# alloy has a better oxidation resistance from all above analysis. This should be attributed to the less colony boundaries of 2# alloy, which results in the decrease of effective diffusion rate of O element into the matrix. This point, as well as the oxidation mechanisms, will be clarified in the next paper.

3 Conclusions

1) The oxidation kinetics of the Ti-42.5Al-8Nb-0.2W-0.1Y alloys with different colony size follows a parabolic or quasi-parabolic law in air at 900 ℃.

2) The alloy with larger colony size has a better corrosion resistance in comparison with the one with smaller colony size. The mass grain of 1# and 2# alloys after 100 h oxidation reaches 7.62 g/m^2 and 6.45 g/cm^2, respectively.

3) The oxide scale mainly consists of Al_2O_3 and TiO_2. The different oxidation kinetics of the two microstructures lead to the differences of the oxidation layer. The thickness of the oxidation layer reaches a value of about 7 μm for the TiAl alloy with smaller colony size while it is only 5 μm for the alloy with larger colony size.

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具有不同大小片层团的 Ti-Al-Nb-W-B-Y 合金的等温氧化行为

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摘　要：以Ti-42.5Al-8Nb-0.2W-0.2B-0.1Y (原子分数, %)合金为研究对象，通过热处理获得不同大小片层团的2种全片层显微组织，并在900 ℃空气条件下，进行了100 h的抗氧化性实验。利用OM、SEM、TEM、XRD和EDS对试样的微观结构、相组成及微区成分进行了分析。恒温氧化动力学结果表明：在900 ℃空气条件下，具有2种不同大小全片层组织的TiAl合金，其恒温氧化动力学曲线符合近抛物线规律，且大片层组织合金的抗氧化性能优于小片层组织。氧化100 h后，大片层组织的合金其氧化增重为6.45 g/m^2，小片层组织的合金的氧化增重为7.62 g/cm^2。对合金截面进行观察后发现，具有大小片层团2种合金表面氧化物的厚度分别为5和7 μm。通过对氧化动力学曲线、组织结构、氧化膜结构、氧化表面形貌进行综合分析，2种合金组织结构的不同影响了O元素在基体中的扩散，而扩散速率的不同最终导致2种TiAl合金表现出不同的氧化行为。

关键词：TiAl 合金；全片层；片层团；氧化行为

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