ARTICLE IN PRESS

Corrosion Science xxx (xxxx) xxx-xxx



Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci



Synergistic effect of B and Y on the isothermal oxidation behavior of TiAl-Nb-Cr-V alloy

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ARTICLE INFO

Keywords: Intermetallics SEM XRD Oxidation Selective oxidation

ABSTRACT

Isothermal oxidation was conducted at 900 $^{\circ}$ C to investigate the synergistic effect of B and Y on the oxidation behavior of Ti44Al6Nb1Cr2V alloy. The results indicated that Ti44Al6Nb1Cr2V0.15Y0.1 B possessed superior oxidation resistance. B and Y refined the crystalline particles size and reduced the oxygen activity. As a results, the formation of TiO₂ and vanadium oxides was suppressed. The reduction of dissolved oxygen in the alloy promoted the selective oxidation of Al. Meanwhile, oxide pegs were formed at the interface of oxide scale and Ti44Al6Nb1Cr2V0.15Y0.1 B alloy. Therefore, the spalling resistance of the oxide scale was enhanced by adding B and Y.

1. Introduction

In the past decades, a large number of manpower and material resources have been spent on the research of TiAl alloys. TiAl-based alloys are considered as a promising structural material to partly replace the heavy Ni-based alloys. It is because that their low density, high specific strength and good creep resistance [1-3]. However, the application of TiAl alloys was limited by their low ductility at ambient temperatures and insufficient oxidation resistance at high temperatures (above 800 °C). Many methods have been proposed to over these obstacles which can be divided to alloying and surface modification [4-7]. Compared with surface modification, adding alloying elements is more extensive and basic. The previous research has found the mechanical properties and oxidation resistance of alloys can be improved by adding ternary and quaternary elements [8-10]. The alloying elements, such as V, Cr, Mn, Nb, B and so on, have been used to improve the properties of TiAl alloys. Among these elements, Nb can not only improve the oxidation resistance, but also enhance the strength [11,12]. However, not all the elements can balance the mechanical properties and oxidation resistance. For example, the presence of alloyed V is beneficial to mechanical properties, but is harmful to the oxidation resistance [13–15]. Y is a rare earth element which has a big atomic radius and a high valence. Many studies have indicated rare elements are beneficial to improve the oxide scale adhesion [16–18]. Zhao et al. [19] found 0.3 at. % Y addition can improve the isothermal and cyclic oxidation resistance of Ti-45Al-8Nb alloys. However, excessive Y addition is detrimental to the oxidation resistance due to the increase of lattice defects. B addition can reduce the grain size, thereby improving creep strength,

rupture strength and ductility. Klein et al. [20] investigated the effect of B on the oxidation resistance of Co-based alloys. They indicated that boron accumulates in the inner oxide layer can enhance oxide scale adhesion effectively.

In our previous work, we have found that Y or B addition can enhance the tensile and compression properties at room temperature of Ti44Al6Nb1Cr2 V alloy [21,22]. B is a special element because it is neither β -stability nor α -stability element. B improves the mechanical properties of the TiAl alloy by refining the microstructure. Y addition was based on the reactive element effects. Rare earth elements have a high affinity to oxygen, which results in the formation of yttrium oxide. Yttrium compounds are preferred to segregate at the grain boundaries due to its large atomic radius. Therefore, the movement of grain boundaries is hindered, thereby reducing the grain size. It is interesting that the Ti44Al6Nb1Cr2V alloy possessed the most excellent tensile and compression properties at room temperature when B and Y were added simultaneously. And the optimized contents of B and Y are 0.1 at. % and 0.15 at.%, respectively. This indicated B and Y have a synergistic effect on the mechanical properties of Ti44Al6Nb1Cr2V alloy. Although some studies have reported B or Y addition is beneficial to improve the oxidation resistance of TiAl alloys, no research is on the coeffect of B and Y until now. Therefore, it is necessary to investigate the synergistic effect of B and Y on the oxidation resistance of TiAl alloy.

In this work, Ti44Al6Nb1Cr2 V (hereinafter referred to as 0Y0B) and Ti44Al6Nb1Cr2V0.15Y0.1 B (hereinafter referred to as 0.15Y0.1B) alloys were prepared. Isothermal oxidation experiments of the alloys were carried out at 900 $^{\circ}$ C for 100 h. The synergistic effect of B and Y on morphology of oxide scale, microstructure and oxidation behavior of

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https://doi.org/10.1016/j.corsci.2017.12.013

Received 11 July 2017; Received in revised form 10 December 2017; Accepted 13 December 2017 0010-938X/ © 2017 Elsevier Ltd. All rights reserved.

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Table 1
Nominal and measured compositions of the alloys (at.%).

Nominal composition	Measured composition						
	Ti	Al	Nb	Cr	V	В	Y
Ti44Al6Nb1Cr2V Ti44Al6Nb1Cr2V0.15Y0.1B	Bal. Bal.	43.98 43.94	5.83 5.89	1.04 1.11	2.05 1.98	- 0.10	- 0.136

0Y0 B alloy was systematically investigated.

2. Experimental procedure

The alloys used in this work were produced by vacuum consumable melting furnace. In order to make the composition homogenization, the ingot was melted two times. The compositions of the alloys were measured by spectrofluorometry method. The nominal compositions of the investigated alloys are listed in Table 1. The size of the cast ingots is $\Phi225\,\text{mm}\times320\,\text{mm}$. The big ingot was cut into oxidation specimens with a dimension of $\Phi20\,\text{mm}\times6\,\text{mm}$ by electrode discharge machine. Then the surfaces of the specimens were polished with SiC papers to 800-grit, ultrasonically washed with acetone and finally dried in air.

Isothermal oxidation tests were conducted at $900\,^{\circ}\text{C}$ for $100\,\text{h}$ in a muffle furnace. During oxidation, each specimen was put into a corundum crucible with a corundum cover plate. Any spallation of the oxide scale was retained in the crucible. The weight of the specimen and crucible was measured at appointed intervals by using an electronic balance (0.1 mg precision). After each measure, the specimen with the crucible and plate was put in the muffle furnace to heat again. Two parallel specimens for each composition were prepared to show the reproducibility and scatter of the tests. A specimen was removed after exposed different time (10 h and 100 h) for subsequent analysis.

The surface and cross-sectional microstructure of the alloys were observed using Quanta 200FEG scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). The elemental distribution of the oxide scale was analyzed by the EDS. The phases of the oxide scales were identified by X-ray diffraction analysis (XRD, Model D/max-B, Japan) with Cu K_{α} radiation. The specimens were scanned in a 2θ range of $10{\text -}90^{\circ}$ with a speed of $4^{\circ}/\text{min}$.

3. Results and discussion

3.1. Microstructure of as-cast alloys

Fig. 1 shows the microstructure of the alloys before oxidation. It can

be seen that the microstructure of the 0Y0B and 0.15Y0.1B alloys is similar. Both them are composed of mainly γ phase, some α_2 and B2 phases. The different is Y-contained precipitations and TiB can be detected in the latter. The Y-contained precipitations are Y2O3 or YAl2. Y is easily to react with oxygen to form the Y2O3 due to its high affinity to oxygen. The oxidation of YAl_2 follows the reaction of $4YAl_2 + 9O_2 \rightarrow$ $4Y_2O_3 + 2Al_2O_3$. Therefore, the existence of YAl_2 will not only reduce the activity of oxygen, but also promote the formation of Al₂O₃. Lamellar colonies are in the two alloys which are composed of α_2 and γ phases. Lamellar structure of TiAl alloys is generally considered as beneficial to mechanical properties. It is should noted that the sizes of the lamellar colonies decrease after adding B and Y. Fig. 2 displays the WDS patterns of the as-cast alloy. It can be seen that TiB and vttrium compounds segregate at the grain boundaries. Therefore, the movement of the grain boundaries was blocked, which decreased the sizes of the grains. The research has reported that fine lamellar structure is conductive to high temperature performance of TiAl alloy [23]. The grain refinement will decrease the critical elemental concentration of the forming protective film. According to the Wagner theory,

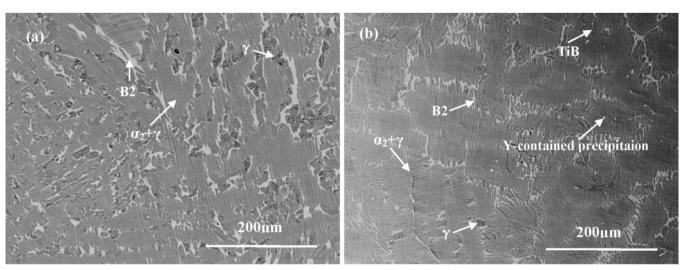
$$N_B^{(C)} > \left[\frac{\pi g^*}{2b} N_O^{(S)} \frac{D_O V_m}{D_B V_{OX}} \right]^{1/2}$$

where $N_B^{(C)}$ is the critical concentration of B in the alloy, g^* is the critical volume of oxides, $N_O^{(S)}$ is the concentration of oxygen at the gas-solid interface, D_O is the diffusion coefficient of oxygen in internal oxidation zone, D_B is the diffusion coefficient of B in the alloy, V_m is the molar volume of the alloy, V_{OX} is the molar volume of the oxides of B. The grain refinement will lead to the increase of elemental diffusion coefficient, thereby decreasing the critical elemental concentration of the forming protective film. Therefore, the selective oxidation of Al is promoted.

The XRD patterns of the 0Y0B and 0.15Y0.1B alloys before oxidation are presented in Fig. 3. The results of the XRD are consistent with that of SEM micrographs. It can be seen γ , α_2 and B2 phases are observed in the two alloys. The intensity of γ peaks are the strongest, which indicates the amount of γ phases is the most. The peaks of Y-contained precipitations and TiB were not detected because the amount of them is too little.

3.2. Isothermal oxidation kinetics

The isothermal oxidation behavior of the alloys is evaluated by the mass gain per unit area. Fig. 4 displays the oxidation kinetic curves of the 0Y0 B and 0.15Y0.1 B alloys at 900 °C for 100 h. In Fig. 4(a), it can



 $\textbf{Fig. 1.} \ \textbf{SEM} \ \textbf{micrographs} \ \textbf{showing} \ \textbf{the microstructure} \ \textbf{of the as-cast alloys:} \ \textbf{(a)} \ \textbf{0Y0} \ \textbf{B} \ \textbf{and} \ \textbf{(b)} \ \textbf{0.15Y0.1B}.$

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