Microstructure and Oxidation Behavior of Cr/Mo Modified TiAl Alloy Containing High Nb

To cite this article: Zhu-Hang Jiang et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 205 012003

View the article online for updates and enhancements.

Related content
- Effect of Cooling Rate on Microstructure of Two Kinds of High Nb Containing TiAl Alloys
  L H Chai, Z Y Feng, Z L Xiang et al.
- A study on the oxidation behavior of nickel alloys at elevated temperatures
  Jung-Yeul Yun, Dahee Park and Jei-Pil Wang
- Oxidation Behavior of Ta Thin Films as a Passivation Layer Deposited on Cu
  Takaaki Ichikawa, Mayumi Takeyama and Atsushi Noya
Microstructure and Oxidation Behavior of Cr/Mo Modified TiAl Alloy Containing High Nb

Zhu-Hang Jiang¹, Cheng-Zhi Zhao¹*, Wen-di Li¹, He-Xin Zhang ¹*

Institute for metallic materials, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, P.R.China

This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation

Email: zhaochengzhi@hrbeu.edu.cn

Abstract. In this paper, the microstructure and oxidation behaviour of Ti-45Al-8Nb-0.2Si-0.5W-0.8B, Ti-45Al-8Nb-2Cr-0.2Si-0.5W-0.8B, Ti-45Al-8 Nb-2Mo-0.2Si-0.5W-0.8B, Ti-45Al-8Nb-2Cr-2Mo-0.2Si-0.5W-0.8B were studied. The alloys were designed and fabricated via vacuum arc melting in the protection of argon shield. The oxidation experiments were carried out at 1073K for 200h in laboratory air. Microstructure evolution, elemental analysis as well as the composition distribution of the oxide scale were performed using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) technique, respectively. The results showed that the microstructure could be refined by adding of Cr and Mo to a smaller grain size. The heat treatment has a good impact on composition homogenization as well as the generation of γ-TiAl phase. The oxidation test shows that Cr and Mo modified alloy cannot improve the oxidation resistance of the alloy. The 0Cr2Mo alloy shows the poorest oxidation resistance in the three, while the Cr modified alloy can apparently slows down the oxidation rate after 50h, which owing to the formation of a compact oxidation scale.

1. Introduction

Lightweight superalloys are attracting attention worldwide in the manufacturing fields of aerospace, aircraft and high-speed transportation as high temperature structural material. Owing to the low density, excellent specific strength, high specific stiffness, good high temperature oxidation and good creep resistance, TiAl-based alloys are becoming a potential candidate of high temperature structural material that services as low-level turbine and exhaust valve. The high Nb containing TiAl based alloy exhibits superior creep properties and high temperature oxidation resistance compared to normal TiAl based alloy over 973K[1-8]. TiAl-based alloys have high mechanical strength both at room and high temperatures because of their ordered structure. Single phase TiAl-based alloy is poor in room temperature ductility. But with the presence of the second α₂ phase, it changes to near gamma phase which shows a better ductility and optimizes the microstructure. Alloying elements Cr, B, Si and W are added into the TiAl alloy for solid solution strengthening. It’s found out that over 5 atom percentage of Nb can significantly improve the high temperature oxidation resistance[9]. The effect of trace alloying element like Cr, Mo and V on oxidation resistance of these elements have not been figured out clearly yet[10-13].

Our work meant to figure out the microstructure evolution and oxidation resistance of the alloys with the addition of Cr and Mo. To this end, four high Nb containing TiAl alloy was designed and fabricated with different atomic fractions of Cr and Mo via vacuum arc melting in the protection of...
argon, and then the samples were post heat-treated in order to find out the microstructure refinement effect. The ingots then past an isothermal oxidation test. The as-cast and heat-treated microstructure, oxidation scale morphology, oxidation section composition are characterized employing scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) technique.

2. Materials and methods

2.1. Specimen preparation

Four novel designed alloys Ti-45Al-8Nb-0.2Si-0.5W-0.8B, Ti-45Al-8Nb-2Cr-0.2Si-0.5W-0.8B, Ti-45Al-8Nb-2Mo-0.2Si-0.5W-0.8B and Ti-45Al-8Nb-2Cr-2Mo-0.2Si-0.5W-0.8B are namely 0Cr0Mo, 2Cr0Mo, 0Cr2Mo and 2Cr2Mo alloy respectively. Pure Al(≥99.9%), titanium sponge(≥99.7%), pure niobium(≥99.8%), Cr(≥99.98%), Mo(≥99.7%), W(≥99.95%), and AlB alloy(2.5%~3.5% mt of B) are adopted as raw materials and get cleaned up before melting. Vacuum melting was applied to cast the materials into button ingots in a non-self-consumed tungsten electrode argon environment furnace. Before melting, the furnace was firstly vacuumized to 0.005Pa, then argon was used as a protective gas and pressure in furnace finally stabilized at 0.03Pa. The melting process was repeated four times for material homogenization through the overturning platform. After the melting process, materials were cooled down in water cold copper crucible into button ingots of around 40g. The ingots were cut into small specimen with the dimension of 10mm×10mm×1mm after homogenization treatment in α-phase region(1473K) for 24h. Then specimen experienced a cyclic heat treatment, which is a three-time heat treatment in 1423K for 4h with air cooling. After the heat treatment, the ingots were polished up using 1500 SiC water proof abrasive papers before cleaned in acetone.

2.2. Isothermal oxidation test and microstructure observation

The specimens went through an isothermal oxidation test which was carried out at 1073K for 200h at atmospheric pressure using a chamber electric furnace. The specimens were moved out of the furnace after every certain fixed period of time. Everytime after cooled down, the increased weights would be measured by electric balance (error range ±0.01mg) after cooling down to room temperature. In order to minimize data error, two specimens at least were tested at a time.

The microstructure evolution were observed by back-scattered scanning electron microscope (SEM) before and after the mentioned heat treatment in 2.1. The oxidation samples were cut perpendicular to the surface of oxide and were polished by SiC papers up using 2000 and polished examined by SEM in purpose of observing oxidation section. And for oxidation surface observation, no special treatment are needed except keeping it clean.In order to find out the structure of oxidation scales, line scanning is used, as well as energy dispersive spectroscopy (EDS) analysis for oxide layer composition analysis. A PANalytical X'Pert diffractometer was applied to identify the phase, conditioning Cu Kα radiation under 40 kV and 40 mA, the scanning range (2θ) was from 10°-90°, and step size was 0.017°/step.

3. Results and discussion

Fig. 1 shows the microstructure of four alloys both in as-cast and heat-treated condition. A homogenization treatment(1473K for 24h) and cyclic heat treatment(three-time 4h 1423K air cooling) is applied on every alloy. It is noted that there are two typical microstructures, which are fully lamellar microstructure in Fig. 1(a) and near fully lamellar microstructure in others. Fully lamellar microstructure is composed of alternating lamellae of α2-Ti3Al and γ-TiAl and is beneficial to the fracture toughness and high-temperature strength properties of TiAl-based alloys, but the grain size and the inhomogeneous distribution in as-cast condition caused poor ductility in room temperature. Appropriate heat treatments can refine the phase distribution and grain size[14-16]. Fig. 1(a) and Fig. 1(b) shows that heat treatment leads to the appearance of single γ phase due to a transformation from high-temperature α to highly faulted γ phase which commonly occurs in rapid cooling process that suppresses diffusion or a result of adding of alloying elements. The microstructure that single γ phase appear in grain boundary of α2-γ phase is what is called near fully lamellar microstructure. The near fully lamellar microstructure with more γ phase in the grain boundry can can lead to more Al2O3

2
The protective oxidation scale during oxidation process because $\gamma$-TiAl phase has more Al volume fraction and better oxidation resistance than $\alpha_2$-Ti$_3$Al phase. Adding of Cr and Mo helps the rising of single $\gamma$ phase of the alloys, but as can be seen in Fig. 1 that single $\gamma$ phase takes up more volume fraction in Fig. 1(d) than Fig. 1(f), heat-treatment is more effective on Cr modified alloy than Mo modified alloy since more single $\gamma$ phase means a better transformation from $\alpha_2$ to $\gamma$ phase. Furthermore, Cr and Mo both have very good grain refining effect that lead to smaller grain size and thinner interlamellar spacing. The three alloys went through the isothermal oxidation.

The isothermal oxidation kinetics curves of the four alloys at 1073K in laboratory air are showed in Fig.1. The gained weights of 0Cr0Mo, 2Cr0Mo, 0Cr2Mo and 2Cr2Mo alloys are 0.52684 mg/cm$^2$, 0.63218 mg/cm$^2$, 0.76357 mg/cm$^2$ and 0.64298 mg/cm$^2$ respectively, after the 200-hour oxidation test. The mass gain results of the alloys are much lower than that of normal TiAl binary alloy, which is about 1 mg/cm$^2$ or more at similar oxidation condition$^{[13]}$. It’s clear that all the three alloys have superior oxidation resistance compared to normal TiAl based alloy. It can be draw from the kinetics curves that Cr and Mo both raised the final oxidation weight. The 0Cr0Mo alloy exhibits superior oxidation resistance than the other three alloys. The weight of 2Cr0Mo alloy increased fast in the first 50 hours($5.27 \times 10^{-3}$ mg/(cm$^2$.h)) and slowed down afterwards($1.05 \times 10^{-3}$ mg/(cm$^2$.h)) in the last 100h, the oxidizing rate even less than that of 0Cr2Mo alloy’s($1.31 \times 10^{-3}$ mg/(cm$^2$.h)), which transformation means a formation of good oxidation scale that can prevent oxygen from coming in. The situation of 2Cr2Mo alloy is almost the same with 0Cr2Mo alloy, which means Mo barely has good effects in the oxidation resistance of the alloys.
**Fig. 3** shows the morphology of the oxidation scales of the four alloys after 200h oxidation test. **Fig. 5** shows that the main oxides of the oxidation surface are $\text{Al}_2\text{O}_3$, $\text{TiO}_2$, $\text{Ti}_3\text{O}_4$, $\text{TiN}$, $(\text{Al}_{0.9}\text{Cr}_{0.1})_2\text{O}_3$ and $\text{SiO}_2$. There are only a very small amount of Mo oxide in the 0Cr2Mo and 2Cr2Mo alloy. **Fig. 3(a)** shows that 0Cr0Mo alloy has the weeniest structure in the three samples.There are barely any oxidation structure that sticks out, which surface morphology can keep steady oxidation resistance without any desquamating of the oxides. With the 2% at addition of Cr shown in **Fig 3(b)**, some sparse and scatter structure began to form on the surface, which differs from 0Cr0Mo alloy and grows clearly with Cr addition. **Fig. 4 (a)** and **Fig. 4 (b)** shows that the oxidation scale of 2Cr0Mo alloy is mainly two layers, in which the outer layer is much thicker than the inner. We can figure out from **Fig. 6** that the inner layer are composed of titanic oxides and aluminium oxides which is an incompact oxidation structure, while the outer layer is almost titanic oxides which is poorer in oxidation resistance than $\text{Al}_2\text{O}_3$.

![Figure 3. SEM scanning of the oxidized surface of (a)0Cr0Mo, (b)2Cr0Mo, (c)0Cr2Mo and (d)2Cr2Mo](image)

![Figure 4. SEM scanning of oxidized section of (a)0Cr0Mo, (b)2Cr0Mo, (c)0Cr2Mo and (d)2Cr2Mo](image)

The 0Cr0Mo alloy is mainly composed of three layers, in which the inner layer is the thickest in the three. We can find out in **Fig. 6** that inner layer is titanic oxides and aluminium oxide mixture, middle layer is mostly titanic oxides, while outer layer is almost aluminium oxide. This kind of oxidation scale can keep most oxygen off the matrix from further oxidation. **Fig. 3(c)** shows the oxidation surface of 0Cr2Mo alloy consists of tiny oxides with may gaps, which structure fails to hold back oxygen from the matrix of the ingot according to the oxidation kinetics curves. As can be learnt from the **Fig. 4**, the thickness of the oxidation scale is of no responsible for the oxidation resistance. **Fig. 6** indicates that the oxides of 0Cr2Mo alloy are mostly titanic oxides, while Mo barely have any positive effects on the oxidation resistance. As there are little $\text{Al}_2\text{O}_3$ in the oxidation scale, the increase weight of oxidation
keeps increasing at an almost fixed rate. When Cr and Mo are added at the same time, the oxidation process of the 2Cr2Mo alloy is similar to the 2Cr0Mo alloy on the basis of the kinetics curves. However, the Fig.3(b) and Fig.3(d) show that the oxidation structure of 2Cr2Mo alloy has more scattered structures that protruded out than that of the 2Cr0Mo alloy. The structure may have more chances of peeling off and thus leads to further oxidation. The oxides in 2Cr2Mo alloy conclude more

![Figure 5. SEM scanning of the oxidized surface of (a)0Cr0Mo, (b)2Cr0Mo, (c)0Cr2Mo and (d)2Cr2Mo](image)

![Figure 6. EDS analysis of main oxides in oxidation section of 0Cr0Mo, 2Cr0Mo, 0Cr2Mo and 2Cr2Mo](image)

Cr and Al oxides that formed a (Al0.9Cr0.1)2O3 oxide combination which is compact and can serve as a stopper of oxygen entrance. The adding of Cr may have caused the increase of the mass gain of the alloy, while it can really produce a compact oxidation structure that protect the matrix alloy from further oxidation. The adding of Mo alloy is not good for the alloy’s oxidation resistance. The adding of both Cr and Mo has a similar oxidation rate with 2Cr0Mo alloy, but the adding of Mo still hinders the improvement of oxidation.

4. Conclusions
Four high Nb-TiAl alloys containing different percentages of Cr and Mo, i.e. 0Cr0Mo, 2Cr0Mo, 0Cr2Mo and 2Cr2Mo alloy were prepared. The conclusions can be drawn as follows:

(1) Cr and Mo modified alloy can both refine the microstructure by decreasing the grain size of the alloy and a transformation from fully lamellar structure to near fully lamellar structure.

(2) The heat treatment has a different effect on Cr and Mo modified alloys. Heat-treatment is more effective on Cr modified alloy than Mo modified alloy in driving the solid-state phase transformation from α₂ to γ.

(3) The four alloys show superior oxidation resistance over normal TiAl-based alloy. The adding of Cr increased the oxidized mass gain of the alloy, but the (Al₉₃Cr₀₇)₃O₅ oxide structure slows down the oxidation rate in the last 100h by filling the entrance of oxygen among the incompact TiO₂/Al₂O₃ oxidation structure. The adding of Mo alloy weakens the oxidation resistance of the alloy.

(4) The oxidation behavior of Cr and Mo modified alloy is similar to Cr modified alloy, the oxidation surface is different in flateness which matters a lot in long-term oxidation.

References

[1] Krause D, Lerch B, Locci I E. Development and evaluation of TiAl sheet structures for hypersonic applications[J]. Materials Science & Engineering A, 2007, 464(1):330-342.

[2] Dimiduk D M. Gamma titanium aluminide alloys—an assessment within the competition of aerospace structural materials[J]. Materials Science & Engineering A, 1999, volume 263(2):281-288(8).

[3] Shida Y, Anada H. The influence of ternary element addition on the oxidation behaviour of TiAl intermetallic compound in high temperature air[J]. Corrosion Science, 1993, (5-8):945-953.

[4] Taniguchi S, Uesaki K, Zhu Y C, et al. Influence of niobium ion implantation on the oxidation behaviour of TiAl under thermal cycle conditions[J]. Materials Science & Engineering A, 1998, 249(1):223–232.

[5] Liu Z C, Lin J P, Li S J, et al. Effects of Nb and Al on the microstructures and mechanical properties of high Nb containing TiAl base alloys[J]. Intermetallics, 2002, 10(7):653–659.

[6] He X, Yu Z, Lai X. Analysis of high temperature deformation behavior of a high Nb containing TiAl based alloy[J]. Materials Letters, 2008, 62(26):4181–4183.

[7] Bystrzanowski S, Bartels A, Clemens H, et al. Creep behaviour and related high temperature microstructural stability of Ti–46Al–9Nb sheet material[J]. Intermetallics, 2005, 13(5):515–524.

[8] Chen G, Sun Z, Zhou X. Oxidation of Intermetallic Alloys in Ti-Al-Nb Ternary System[J]. Corrosion, 1992, 48(1):939-946.

[9] ZHAO Lili, LIN Junpin, WANG Yanli, et al. Early oxidation behaviors of Ti50Al and Ti45A18Nb alloys at high temperature[J]. Acta Metallurgica Sinica, 2008.

[10] CHEN G. L, ZHANG L. C. Deformation mechanism at large strains in a high-Nb-containing TiAL at room temperature[J]. Materials Science & Engineering A Structural Materials Properties Microstructure & Processing, 2002, 329(1):163–170.

[11] Kesler M S, Goyel S, Rios O, et al. A study of phase transformation in a TiAlNb alloy and the effect of Cr addition[J]. Materials Science & Engineering A, 2010, 527(12):2857-2863.

[12] Huang S C, Hall E L. The effects of Cr additions to binary TiAl-base alloys[J]. Metallurgical & Materials Transactions A, 1991, 22(11):2619-2627.

[13] Lin J P, Xu X J, Wang Y L, et al. High temperature deformation behaviors of a high Nb containing TiAl alloy[J]. Intermetallics, 2007, 15:668–674.

[14] Cheng T T, Willis M R, Jones I P. Effects of major alloying additions on the microstructure and mechanical properties of γ-TiAl[J]. Intermetallics, 1999, 7(1):89-99.

[15] Tian W H, Nemoto M. Effect of carbon addition on the microstructures and mechanical properties of γ-TiAl alloys[J]. Intermetallics, 1997, 5(3):237-244.

[16] Niu H Z, Chen Y Y, Xiao S L, et al. Microstructure evolution and mechanical properties of a novel beta γ-TiAl alloy[J]. Intermetallics, 2012, 31:225-231.

Acknowledgement This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.