

Oxidation Behavior of NiTi-Al Based Alloy with Nb and Mo Additions

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Abstract. Oxidation behavior of a Ni-45Ti-5Al-2Nb-1Mo (composition in at %) alloy was studied in comparison with the Ni-45Ti-5Al alloy by X-ray diffraction (XRD), scanning electron microscopy (SEM) and cyclic oxidation tests. The results show that the microstructure of Ni-45Ti-5Al-2Nb-1Mo alloy is composed of NiTi matrix, Ti₂Ni and (Nb, Ti) solid solution phases. By 2 at% Nb and 1 at% Mo addition, the Ni-45Ti-5Al-2Nb-1Mo alloy shows excellent oxidation resistance. The mass gain of Ni-45Ti-5Al-2Nb-1Mo alloy after 100 h exposure at 800 °C is 2.29 mg/cm², which is much lower than that of Ni-45Ti-5Al alloy. This is mainly resulted from the doping effect of Nb and Mo in TiO₂ and the formation of a continuous Al₂O₃ layer by Nb and Mo addition. The oxide scale of the present alloy is with multi-layer structure in order of TiO₂ layer/ Al₂O₃ + NiAl₂O₄ mixture layer/ TiO₂ layer/ Nb-rich TiO₂ layer/ Ni₃Ti layer from outside.

1. Introduction

Order intermetallic alloys based on aluminides have been developed as high temperature structural materials for decades [1]. Recent investigations indicate that NiTi-Al based intermetallic alloys have the potential to use as high temperature structural materials for aerospace applications because of their low density, high strength at high temperature and good corrosion resistance. The addition of small amount of Al (no more than 8 at%) into NiTi alloy can dramatically improve the strength especially at high temperature [2-3]. Alloying is an effective method to improve the mechanical properties of NiTi-Al based alloys. Many elements, such as Mo, Nb, Hf, Zr, B and RE, have been added to strengthen the NiTi-Al alloys [4-7]. It has been reported that a Nb- and Mo modified Ni-45Ti-5Al-2Nb-1Mo (at%) alloy is expected to become a potential high-temperature structural material with strength of 650 MPa at 650 °C and 350 MPa at 800 °C [8-9].

Actual applications in the aerospace industry require the alloys to be considered in a variety of high-temperature environments. The oxidation behaviors of ternary NiTi-Al alloys at temperatures between 600 °C and 800 °C have been systemically studied, which found that NiTi-Al alloys shows poor oxidation resistance with the mass gain more than 20 mg/cm² after exposure in air at 800 °C for 100h. By adding little quaternary element Nb (3 at%), the oxidation resistance of NiTi-Al alloys can be notably improved [10-11].

However, so far the studies on the oxidation behavior of NiTi-Al based alloys are limited, especially the knowledge of NiTi-Al based alloy simultaneously modified by two or more alloying elements are still lack. Therefore, in this paper, the isothermal oxidation behavior of Nb- and Mo-containing Ni-45Ti-5Al-2Nb-1Mo alloy is studied and discussed in detail.



2. Experimental Procedure

A 10 kg ingot with nominal composition of Ni-45Ti-5Al-2Nb-1Mo (at%) alloy was prepared by vacuum induction furnace using high purity Ni, Ti, Al, Nb and Mo as raw materials. To minimize the segregation of composition the ingot was repeatedly melted four times. The ingot was homogenized at 1000 °C for 24 h, and then isothermal forged at 900 °C into plates.

The specimens with dimensions of 10 mm × 10 mm × 8 mm for the oxidation tests were cut using an electro-discharge machine and then the surface was mechanically polished with 1000 grit SiC paper. The cyclic oxidation experiments were carried out at 800 °C in air for 100 h. Three samples were employed in order to obtain an average mass change. The mass gain was weighed by an electronic balance with the precision of 0.1 mg. The morphology on the surface and cross-sections of the oxide scales were observed by a JSM-5600 scanning electron microscopy (SEM) equipped with a Link ISIS energy-dispersive X-ray spectroscopy (EDS). The phase structure of the oxide scales was identified by a Regaku D/max 2200PC X-ray diffractometer (XRD) using Cu K α radiation ($\lambda=0.154$ nm).

3. Results and Discussion

3.1. Microstructure

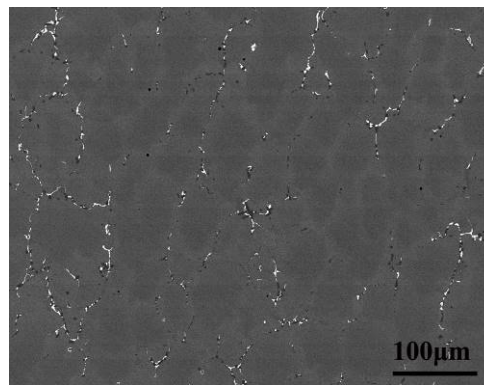


Figure 1. Microstructure for Ni-45Ti-5Al-2Nb-1Mo alloy before oxidation

Figure 1 shows the SEM micrograph of Ni-45Ti-5Al-2Nb-1Mo alloy before oxidation. According to the EDS and XRD results, the microstructure of Ni-45Ti-5Al-2Nb-1Mo alloy consists of NiTi matrix, black Ti₂Ni phase and white (Nb, Ti) solid solution phase. The latter two phases are precipitated along the grain boundaries. It is noted that Nb and Mo are dissolved within these three phases, and Nb is enriched in the grain boundaries.

3.2. Oxidation Kinetics

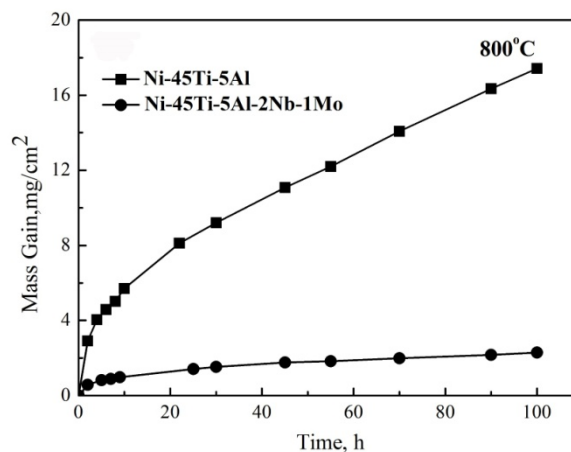


Figure 2. Isothermal oxidation kinetics of Ni-45Ti-5Al-2Nb-1Mo alloy exposed at 800 °C for 100 h

The oxidation kinetic of Ni-45Ti-5Al-2Nb-1Mo alloy at 800 °C is shown in Figure 2. The result of Ni-45Ti-5Al alloy is also illustrated for comparison [11]. It can be found that the mass gain after 100 h exposure at 800 °C is 2.29 mg/cm² for Ni-45Ti-5Al-2Nb-1Mo alloy, which is much lower than that for Ni-45Ti-5Al alloy of 17.42 mg/cm², indicating that the former alloy exhibits much better oxidation resistance than the latter. Thus, the oxidation resistance of NiTi-Al based alloy is remarkably improved by Nb and Mo addition.

3.3. Morphology and Microstructure of Oxide Scale

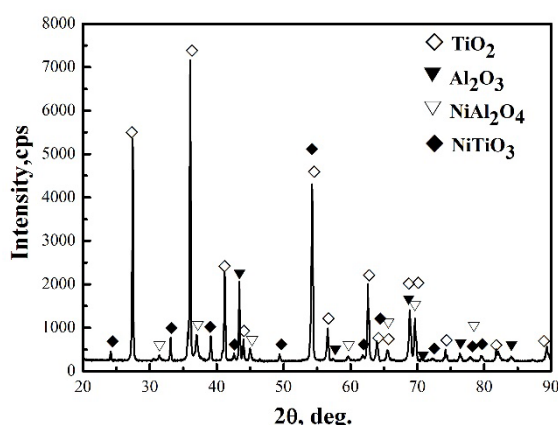


Figure 3. XRD spectra of the oxide scale on the Ni-45Ti-5Al-2Nb-1Mo alloy after 100 h isothermal oxidation at 800 °C

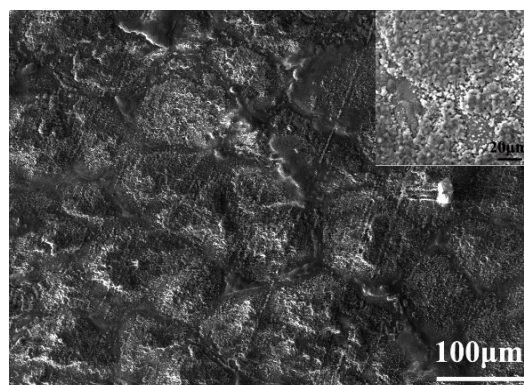


Figure 4. SEM micrograph of the surface morphology of the oxide scale in Ni-45Ti-5Al-2Nb-1Mo alloy after oxidation at 800 °C for 100 h

Figure 3 shows the XRD spectra of the oxide scale on the sample of the Ni-45Ti-5Al-2Nb-1Mo alloy after oxidation for 100 h at 800 °C. It is indicated that the external oxide scale in the Ni-45Ti-5Al-2Nb-1Mo alloy mainly consists of TiO₂ and Al₂O₃ with a trace of NiAl₂O₄ and NiTiO₃. Figure 4 shows the surface morphology of the oxide scale in the Ni-45Ti-5Al-2Nb-1Mo alloy after oxidation for 100 h at 800 °C. Compared with ternary NiTi-Al alloy, the oxides on the sample are dense and fine, namely the addition of Nb and Mo improves the adherence of oxide scale to the substrate. It is notable that a rugged morphology is observed on the oxide surface, which is similar to the results reported in NiTiNb and NiTi-Al-Nb alloys [10, 12]. This is suggested to be associated with the inhomogeneous distribution of Nb elements, i.e. the NiTi matrix containing less Nb is much easier to be oxidized than the grain boundaries with more Nb content.

To clarify the mechanism for the formation of such oxide structure, cross-sectional morphology of the oxide scale of Ni-45Ti-5Al-2Nb-1Mo alloy is observed on SEM, as shown in Figure 5. It can be found that the oxide scale consists of a multi-layer with a total thickness of about 30 μm. The compositions of each layer detected by EDS are listed in Table 1. The outer oxide scale is composed of two fold TiO₂ layers (marked as A and C) with a thin dark Al-rich oxide layer (marked as B) embedded. The XRD result suggests that the Al-rich oxide layer is a mixture of Al₂O₃ and NiAl₂O₄ (NiO·Al₂O₃). Beneath the sandwich oxide structure, a layer with discontinuous white particles dispersed (marked as D) is observed. The white particle is too small to analyze its composition, so the result shown in Table 1 is the average composition of layer D. It is supposed that layer D is also TiO₂ containing more Nb and Mo content than layer C, which is due to the outward diffusion of Nb and Mo in the substrate. And then a Ti-depleted area in light-grey colour (marked as E) next to the substrate can be observed due to the net Ti-consumption during the course of oxidation. The EDS analysis indicates that it is stoichiometric close to Ni₃Ti phase. Thus, the formed oxide scale of the Ni-45Ti-

5Al-2Nb-1Mo alloy is in order of TiO_2 layer/ $\text{Al}_2\text{O}_3 + \text{NiAl}_2\text{O}_4$ mixture layer/ TiO_2 layer/ Nb-rich TiO_2 layer/ Ni_3Ti layer from outside.

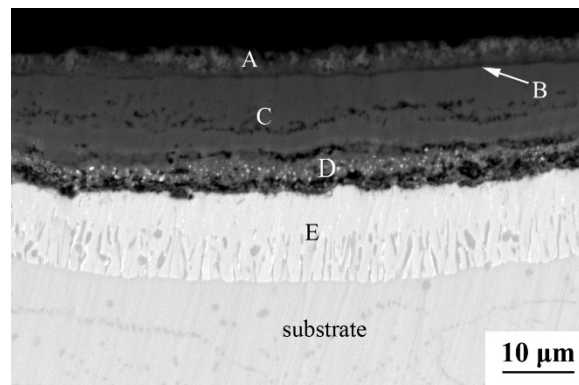


Figure 5. Cross-sectional SEM morphology of Ni-45Ti-5Al-2Nb-1Mo alloy after oxidation at 800°C for 100 h

Table 1. Compositions of oxide layer for Ni-45Ti-5Al-2Nb-1Mo alloy after oxidation in Figure 5.

Layer	Composition (at %)					
	Ni	Ti	Al	Nb	Mo	O
A	0.18	26.97	2.3	0.24	-	70.31
C	3.08	21.01	4.2	0.87		70.84
D	4.09	29.23	-	3.07	1.40	62.21
E	68.63	25.36	4.43	0.82	0.76	-

In the present alloy, the oxidation resistance for Ni-45Ti-5Al-2Nb-1Mo alloy at 800 ° C is dramatically improved compared with ternary Ni-45Ti-5Al alloy. This is mainly attributed to the beneficial effect of 2 at% Nb and 1 at% Mo addition on the oxidation behavior. Firstly, the growth of TiO_2 is primary by oxygen diffusion through oxide scales via a vacancy mechanism [13]. In the studied alloy, 3.07 at% Nb and 1.4 at% Mo is detected in the TiO_2 layer by EDS. This will lead to a decrease of the oxygen vacancies, and thus slow the diffusion of oxygen. Secondly, the addition of Nb and Mo can increase the thermodynamic activity of Al, and accelerate the formation of a stable and continuous alumina scale, which can provide an oxidation barrier and prevent the diffusion of oxygen. Similar phenomenon has been found in Ni-50Ti-9Al-1Mo alloy, in which 1 at% Mo addition promotes to form a continuous dense Al-rich layer beneath the outmost TiO_2 layer.

4. Conclusions

In this study, the oxidation behavior of Nb- and Mo- modified NiTi-Al based alloy at 800 ° C was investigated. By 2 at% Nb and 1 at% Mo addition, the Ni-45Ti-5Al-2Nb-1Mo alloy shows an excellent oxidation resistance. Nb and Mo additions dramatically lower the oxidation rate and improve the adherence of oxide scale to the substrate. The mass gain is 2.29 mg/cm^2 after 100 h exposure at 800 ° C, which is much lower than that for ternary Ni-45Ti-5Al alloy. The oxide scale of the present alloy is about 30 μm in thickness with multi-layer structure in order of TiO_2 layer/ $\text{Al}_2\text{O}_3 + \text{NiAl}_2\text{O}_4$ mixture layer/ TiO_2 layer/ Nb-rich TiO_2 layer/ Ni_3Ti layer from outside. The improvement of oxidation resistance for Ni-45Ti-5Al-2Nb-1Mo alloy is mainly attributed to the doping effect of Nb and Mo in TiO_2 which can decrease the oxygen vacancy concentration and slow the diffusion of oxygen. Moreover, Nb and Mo elements enhance the formation of a dense and continuous Al_2O_3 layer to provide an oxidation barrier.

5. Acknowledgments

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6. References

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