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The improvement of high-temperature oxidation of α_2-Ti_3Al by anodic coating in the phosphoric acid with sodium silicate

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Abstract

The 800 °C cyclic oxidation resistance of α_2-Ti_3Al can be improved by anodic coating in 4 wt% phosphoric acid with 2.9 wt% Na_2SiO_3 at 18 °C. Cyclic oxidation test indicates that, at 350 V anodizing voltage, the parabolic oxidation rate constant can be reduced to about 1/160 of that for as-homogenized α_2-Ti_3Al.

Keywords: A. Titanium aluminides, based on Ti_3Al; B. Oxidation; C. Coatings, intermetallic and otherwise; F. Electron microscopy, scanning; G. Environmental applications

1. Introduction

The major concerns for structural applications of Ti_3Al-based alloys are the insufficient oxidation resistance and oxygen embrittlement at high temperature [1,2]. The 800 °C cyclic oxidation resistance of γ-TiAl can be substantially improved by an aqueous phosphoric acid treatment [3] and the anodic coating in phosphoric acid solution [4]. However, the anodic coatings formed in phosphoric acid exhibit limited resistance against high-temperature oxidation for α_2-Ti_3Al. It was reported that the Si addition can promote the formation of a compact TiO_2 and SiO_2 in the oxide scale acted as a barrier against the oxidation [5]. Therefore, Si and P are beneficial elements for the high-temperature oxidation resistance of α_2-Ti_3Al alloy. In this study, we aim to modify the surface of α_2-Ti_3Al by anodic coating in an aqueous phosphoric acid solution with sodium silicate (Na_2SiO_3).

2. Experimental

The α_2-Ti_3Al was prepared by a vacuum arc remelter and homogenized at 1000 °C. Specimen surfaces were polished to a final polishing of 0.3-μm alumina, then ultrasonically cleaned with acetone and ethanol, and then rinsed with deionized water. The polished specimens were anodized with various constant direct current (DC) voltages in the stirred electrolytic solution. The exposed area for anodization was delineated by 3-M tape and measured to an accuracy of 0.1 mm. The separation between the specimen and the counter-electrode was 5 cm. After anodization, the specimens were rinsed in running water for at least 30 min.

The intermittent cyclic oxidation behaviors of anodized specimens were carried out in a muffle furnace with hot air (800 °C). The weight gains per exposed area (mg/cm^2),

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weighted on an analytical balance to an accuracy of $\pm 10^{-3}$ mg, were used to evaluate the oxidation resistance.

3. Results and discussion

3.1. Anodizing process of α_2-Ti_3Al specimen

At the early stage of anodization at constant voltage, the current density of anodization of α_2-Ti_3Al falls rapidly and then decreases monotonically. If the applied voltage is over 250 V, sparking breakdown occurs and then both the sporadic sparks and oxygen evolution happen less intensively for the later period of anodization. For a higher anodizing voltage, such as 350 V, the sparks occur very violently and oxygen evolution aggressively bursts into bubbles during anodization.

The weight gain per unit area after anodizing in binary mixing solution of phosphoric acid and Na_2SiO_3 is shown in Fig. 1. The weight gain per unit area increases with the increase in applied voltage and tends to level off when the applied voltage is above 300 V. The weight gain of anodizing oxidation may counterbalance the electrical field-assisted dissolution and the existence of sparks on the surface during anodization, which may locally raise the temperature and increase the dissolution effect of phosphoric acid.

3.2. Microstructure of the anodic coatings

The higher the voltage applied, the more the rugged surface formed. The thicknesses of the anodic film prepared at 160 V, 300 V and 400 V in solution with Na_2SiO_3 for 45 min are evaluated as 1, 4 and 9 μm, respectively. The anodization in mixing solution containing P and Si species can bring into a significant concentration of phosphorous (~4 wt%) and silicon (~4.5 wt%) in the anodic film, determined from EDX. The depletion of titanium in the anodic film of α_2-Ti_3Al implies that the preferred solvent action may occur. The anodic films are mainly amorphous with a little crystallized phase. As the applied voltage increases, the amorphous background becomes more pronounced due to the increase in the thickness of anodic coating.

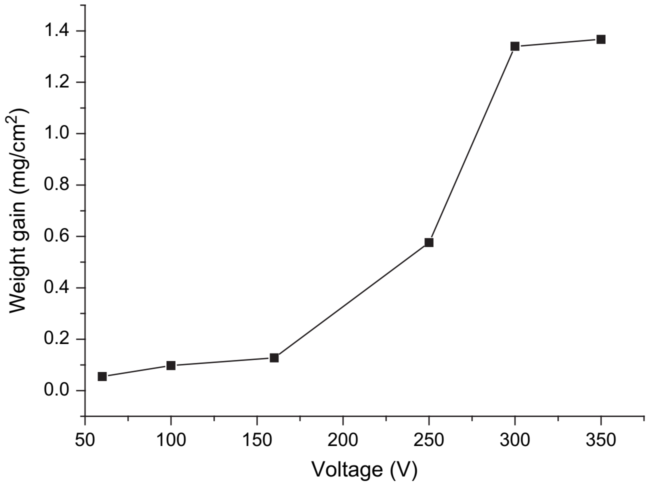

Fig. 1. Effect of anodizing voltage on the weight gains after anodization in 4 wt% phosphoric acid with 2.9 wt% Na_2SiO_3 at 18 °C for 45 min.

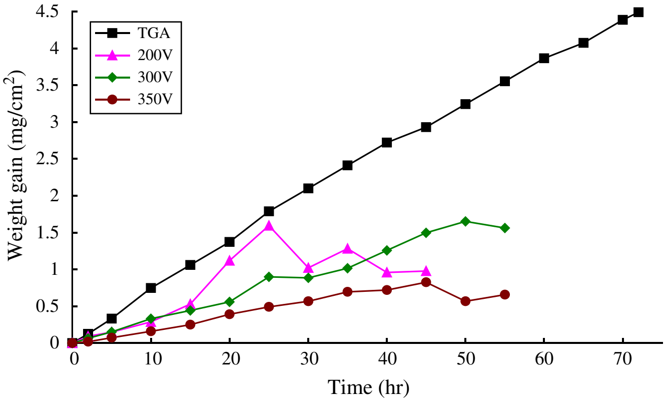

Fig. 2. The cyclic oxidation kinetics in static air at 800 °C for α_2-Ti_3Al anodized in the electrolyte of 4 wt% phosphoric acid at 18 °C under various voltages for 45 min. Note that there is no Na_2SiO_3 added in the electrolyte of this figure.

3.3. The cyclic oxidation kinetics of α_2-Ti_3Al with the anodic coatings

Since the intermittent cyclic oxidation curve for as-homogenized α_2-Ti_3Al is so scattered due to the serious scale spallation even after 24 h static air exposure at 800 °C, TGA was used instead. The TGA curve for α_2-Ti_3Al, as shown in Fig. 2, indicates that the oxidation rate does not completely obey the parabolic law in all periods of oxidation.

Fig. 2 also shows the cyclic oxidation kinetics in static air at 800 °C for α_2-Ti_3Al anodized in the electrolyte of 4 wt% phosphoric acid without Na_2SiO_3. The pitting-like spallation of the surface oxide layer begins at 10–20 h oxidation time, and then large area spallation occurs for the further oxidation. Therefore, the weight gain curve exhibits a zigzag fluctuation. This means that the 800 °C cyclic oxidation resistance of α_2-Ti_3Al cannot substantially be improved by anodic coating in solutions without Na_2SiO_3 at 18 °C.

Fig. 3 shows the cyclic oxidation kinetics at 800 °C for α_2-Ti_3Al with anodic coatings prepared in the electrolytic solution containing 4.7 wt% phosphoric acid and 2.9 wt% Na_2SiO_3 under various anodizing voltages. When the specimens are anodized at the applied voltage below 200 V, the

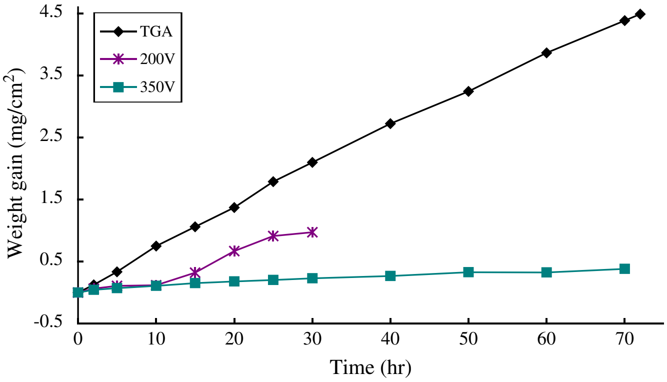

Fig. 3. The cyclic oxidation kinetics in static air at 800 °C for α_2-Ti_3Al anodized in the electrolyte of 4 wt% phosphoric acid with 2.9 wt% Na_2SiO_3 at 18 °C under various voltages for 45 min.

scale spallation still appears severely during cyclic oxidation and therefore the test was terminated after 30 h of oxidation. However, if the specimen is anodized at the voltage above 300 V, no scale spallation occurs during cyclic oxidation. It implies that the thicker anodic film on α_2-Ti_3Al exhibits good barrier against oxidation and adheres very well to the substrate. After about 10 h of oxidation, the oxidation behavior of the anodized specimen has shifted from quasi-linear to the parabolic law. For specimen anodized at 350 V, the parabolic oxidation rate constant is calculated as 0.00175 mg^2/cm^4h, which is about 1/160 of as-homogenized α_2-Ti_3Al, say, 0.2798 mg^2/cm^4h.

4. Conclusion

The 800 °C cyclic oxidation resistance of α_2-Ti_3Al can be improved by anodic coating in 4 wt% phosphoric acid with 2.9 wt% Na_2SiO_3 at 18 °C. The test results indicate that the anodized α_2-Ti_3Al can remarkably reduce the 800 °C oxidation rate and the improvement increases with the increasing anodizing voltage up to 350 V, at which the parabolic constant can be reduced to about 1/160 of that for as-homogenized α_2-Ti_3Al.

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