

# Structures and properties of ceramic films on TiAl intermetallic compound fabricated by microarc oxidation

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## Abstract

The ceramic oxide films with a thickness of 120  $\mu\text{m}$  were prepared on  $\gamma$ -TiAl intermetallic compound by alternating-current microarc oxidation in silicate electrolyte. Isothermal oxidation of TiAl alloy coated with the ceramic oxide film was carried out in air at 1100 °C. Result showed that the dense layers in the oxide film were mainly composed of  $\text{Al}_2\text{TiO}_5$  and  $\text{TiO}_2$  rutile phase, while the loose layer contained a large amount of amorphous  $\text{SiO}_2$  besides  $\text{Al}_2\text{TiO}_5$  and  $\text{TiO}_2$  rutile phase. Thermal shock tests revealed a good adhesion between the films and TiAl substrate, and the oxidation resistance of the TiAl alloy was improved.

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## 1. Introduction

TiAl metallic compounds are one of the most attractive materials nowadays due to their excellent properties: high melting point, low density and high specific strength. However, it can only be used at a temperature of less than 800 °C due to its tendency of high temperature oxidation [1]. In order to improve its anti-oxidation property under high temperature, some surface modification techniques, such as low-pressure plasma spraying [2], aluminizing [3], MCrAlY overlay film [4], silicide and silicon carbide ceramics [5,6] and ion implantation [7], have been studied.

Microarc oxidation (MAO) is a novel technology to fabricate a ceramic film on valve metals. The film exhibited good adhesion to the substrate due to the in-situ growth of film. The metallic ions of the film can be formed from the substrate while the  $\text{O}^{2-}$  comes from the electrolyte solution. The qualities of MAO films are easily controlled by technique parameters such as the composition of the substrate, the nature of the electrolyte,

and the parameters of the electrical source etc. [8,9]. Many researches and significant progress have been made on the preparation of the MAO films on Ti, Al and Mg alloys [10–14]. However, the research about microarc oxidation on TiAl intermetallic compounds was rarely reported. In this work, we tentatively applied the microarc oxidation method to TiAl alloy to avoid high temperature oxidation. The structure and composition of the MAO films on TiAl alloy were analyzed. Thermal shock and high-temperature oxidation properties were evaluated.

## 2. Experimental procedure

A  $\gamma$ -TiAl alloy with the nominal composition of (at.%) 48Al, 2Cr, 2Nb was used as the raw material. The original samples with a size of 36 mm  $\times$  12 mm  $\times$  2 mm were polished up to 600<sup>#</sup> emery paper. A 30 kW alternating-current pulse power supply was employed to fabricate the film on the TiAl alloy surface. The electrolyte consists of sodium silicate (6 g/l) with KOH (1 g/l) additive. During the MAO processing, the solution temperature was kept below 50 °C. The samples and container walls were used as anode and cathode electrodes, respectively. The samples

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were sequentially taken out of the electrolyte bath at the oxidation time of 7, 30, 90 and 120 min. The film thicknesses were 5, 30, 110 and 120  $\mu\text{m}$ , respectively, measured by eddy-current thickness gauge.

The surface morphology of the films was investigated using a Siron 200 scanning electron microscopy (SEM). The composition profiles across the films were analyzed by the energy dispersive X-ray spectrum (EDX). X-ray diffraction (XRD) was performed using an X'PERT PRO MPD X-ray diffractometer to identify the phase constituents in the films.

The adhesion performance between the film and the alloy was evaluated by cyclic thermal shock test, in which the coated samples were quenched from 900  $^{\circ}\text{C}$  into the 25  $^{\circ}\text{C}$  water. The maximum crack length was examined using an optical microscope. The anti-oxidation performance of the film was carried out using isothermal oxidation method at 1100  $^{\circ}\text{C}$ . The samples were put into an electrical furnace at 1100  $^{\circ}\text{C}$ . After isothermal oxidation in air for 10, 20, 40, 60, 80 and 100 h respectively, they were taken out of the furnace. The samples were cooled down to room temperature, and the weight was measured using an analytical balance with the accuracy of  $10^{-4}$  g.

### 3. Results and discussion

#### 3.1. Morphology and microstructures of the MAO film on TiAl intermetallic compound

Fig. 1 illustrates the surface feature and the cross-sectional microstructure of the 120 min MAO films. In the initial stage of microarc discharge, the spark distribution on the alloy surface was not uniform. With increasing oxidation time, the sparks became brighter and more uniform. After 30 min, the bright micro-discharge sparks gradually disappeared. Many weak sparks, however, could still be observed on the sample's surface. For the 120 min coated samples, small residual pores of less than 1  $\mu\text{m}$  still kept on the film surface (see Fig. 1a and b).

Fig. 1c shows the cross-sectional microstructure of the MAO films. It was obvious that the films contained three layers: a

dense layer, an intermediate layer and a loose layer. The total thickness for the 120 min MAO treatment was up to 120  $\mu\text{m}$ , which was consistent with the result of the eddy current measurement.

The Al, Ti and Si distributions in the films of 120 min MAO treatment time are shown by EDX line analysis in Fig. 1c. The Al and Ti contents increased from the film surface to the substrate, while the Si profile had been measured to be reverse to the Al element. In the loose layer, the Al content was higher than that of the Ti, and the Ti content was hardly detected on the film surface. This might be attributed to the different diffusion rates of the Ti and Al in the film. The measured Si distribution also revealed the three-layer structures. The Si content in the loose layer was higher than that in the intermediate layer and dense layer. With increasing time, the Si content in the dense layer was reduced as shown in Fig. 1c and no silicon element be detected in the films near the interface.

#### 3.2. Phase composition of the ceramic films

XRD results for samples at different MAO treatment times are shown in Fig. 2. After the loose layer of the 120 min coated sample was polished, a dense layer of 35  $\mu\text{m}$  was left and its phase composition was given in Fig. 2d.

Both in the dense layer and loose layer of the samples treated for different MAO time, the films mainly consisted of  $\text{TiO}_2$  and  $\text{Al}_2\text{TiO}_5$ . EDX analysis in Fig. 1c identified a high Si content in the loose layer of the film. However, crystalline silica could not be observed in Fig. 2. Therefore, it was assumed that there was a certain amount of amorphous  $\text{SiO}_2$  in the films. Actually, a broad amorphous peak was observed in the XRD patterns as shown in Fig. 2b and c. Furthermore, the amorphous peak was not observed in the dense layer (see Fig. 2d). The Si content in the film coming from the solution is combined with O and penetrated into the film through the plasma discharge channel and thermal diffusion due to the local elevated temperature during MAO treatment. The Al and Ti are oxidized to form  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  phases, respectively. At temperature above

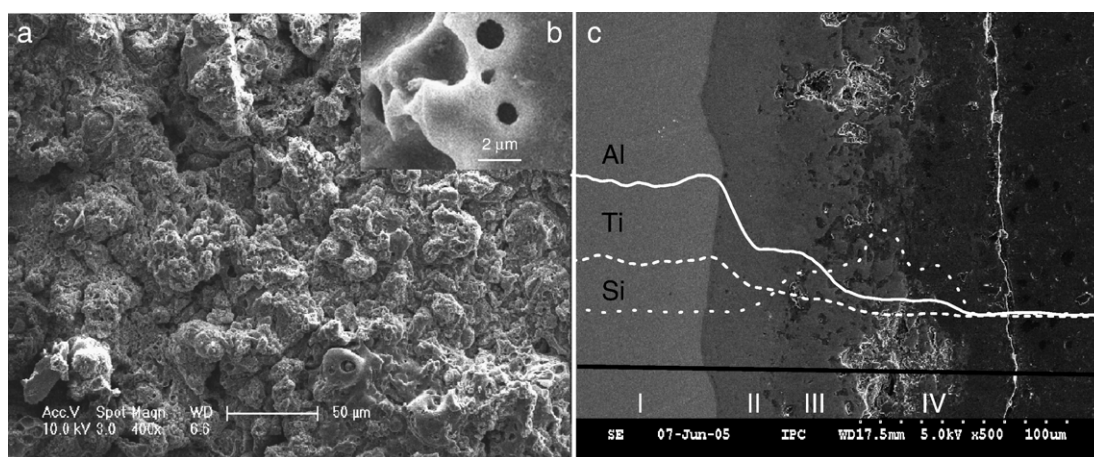


Fig. 1. Surface morphology of the film (a), microstructure and composition distribution of MAO coatings (c) for 120 min; (b) is a magnification image of (a); (I) TiAl substrate; (II) dense layer; (III) intermediate layer and (IV) loose layer.

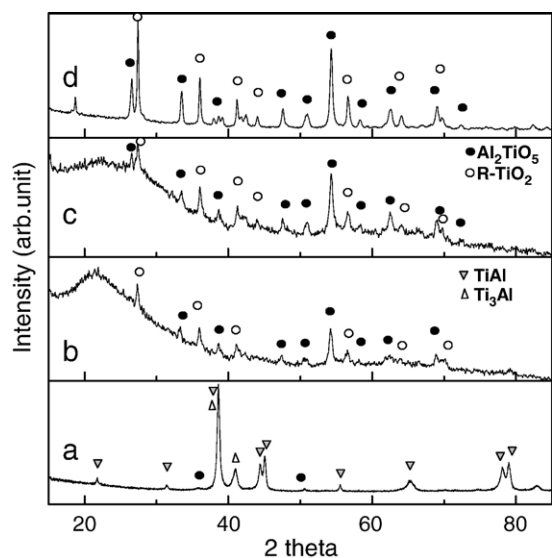


Fig. 2. XRD patterns of MAO films processed for (a) 7, (b) 30, (c) 120 min and (d) dense layer of (c) after polishing.

1570 °C, they reacted to form  $\text{Al}_2\text{TiO}_5$ . The formation of  $\text{Al}_2\text{TiO}_5$  and  $\text{TiO}_2$  implies the presence of high temperatures during the discharge process. When the treating time was more than 30 min, the phase composition of the films hardly changed as shown in Fig. 2c and d.

### 3.3. Thermal shock test

Fig. 3 depicts the dependence of the maximum crack length of the film surface on the thermal shock times. After 7 times thermal shock cycles; one crack was observed on the film surface of TiAl alloy treated by MAO for 120 min (see curve a). If the loose layer was removed by polishing and only the dense layer was remained, the first crack on the polished film surface began to appear when the thermal shock cycle reached 16 times (see curve b). Both curves a and b showed that the crack length increased with number of the thermal shock cycles. The propagating rate of crack length reduced when the thermal

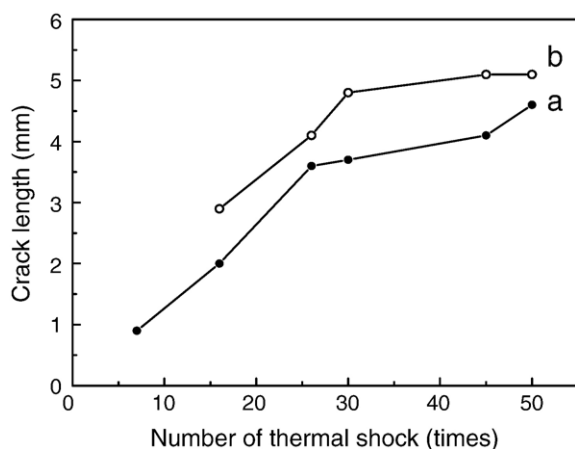


Fig. 3. The crack length on film surface changed with times of the thermal shock. (a) The unpolished MAO samples; (b) the polished MAO samples.

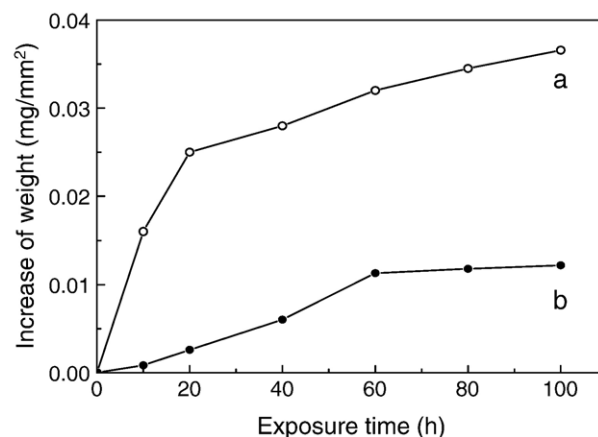


Fig. 4. Dynamics of isothermal oxidation on TiAl alloy and MAO film at 1100 °C: (a) TiAl substrate, (b) MAO treatment of 90 min.

shock reached 26 times for curve a and 30 times for curve b, respectively. However, even after 50 thermal shock cycles, the films still adhered well to the substrate showing a good adhesion between the film and the TiAl substrate. Moreover, the unpolished sample with loose layer exhibited better adhesion to the TiAl substrate than that of the polished sample.

With the increase of the crack length and number on the film surface, the thermal stress in the films was gradually released. Thus the crack propagation rate decreased after a certain amount of thermal shock cycles. While the loose layer of films was polished away, the film became thin. So the generation of cracks in the polished film was delayed, and the obvious cracks were observed after 16 thermal shock cycles. On the other hand, the porous loose layer was beneficial in restraining the crack propagation, which the maximum crack length of the unpolished samples was shorter than that of the polished samples under the same thermal shock cycle. However, further reasonable mechanism should be discussed in later research.

### 3.4. Isothermal oxidation test

Fig. 4 depicts the weight variation of the samples with the increase of thermal oxidation time at 1100 °C in air. It was indicated that the thermal oxidation resistance of the samples with MAO films was better than that of the substrates. Each of the two curves of the oxidation consisted of two stages. The weight of the samples in the initial oxidation stage increased quickly. In this stage, the rate of isothermal oxidation of the TiAl substrate was  $1.3 \times 10^{-4} \text{ mg/mm}^2$ . However, the oxidation rate for the coated sample was reduced almost one order of magnitude below  $1.6 \times 10^{-5} \text{ mg/mm}^2$ . After 20 h thermal oxidation, the oxidation rate of TiAl substrate was reduced to  $1.2 \times 10^{-5} \text{ mg/mm}^2$ . In comparison, the weight of the coated sample hardly increased after 60 h. It was observed that at 100 h isothermal oxidation, the total oxidation rate of the coated TiAl alloy was reduced about three times compared to the uncoated substrate. Hence, microarc oxidation was a potential technique to enhance the high-temperature oxidation resistance of TiAl alloys.

#### 4. Summary

TiAl ceramic films contained three layers: a dense layer, an intermediate layer and a loose layer. The dense layer was mainly composed of  $\text{Al}_2\text{TiO}_5$  and  $\text{TiO}_2$  rutile phase, and the Si was rarely detected. Apart from  $\text{Al}_2\text{TiO}_5$  and  $\text{TiO}_2$  rutile phase, a large amount of amorphous  $\text{SiO}_2$  was also found in the loose layer.

The MAO film on TiAl alloy displayed a good thermal shock resistance and an excellent adhesion with alloy substrate. Furthermore, the isothermal oxidation tests indicated that the oxidation resistance of the TiAl alloy was improved three times after it was subjected to microarc discharge treatment. Microarc oxidation is an available method to improve the anti-oxidation performance of the TiAl intermetallic compounds.

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