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Electrochemical corrosion behavior of the carburized porous TiAl alloy

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ABSTRACT

Carburization was carried out to improve corrosion resistance of porous Ti–46.5 Al (at.%) intermetallic compound. X-ray diffractometry (XRD) and scanning electron microscopy (SEM) were applied to analyze the carburized layers. Electrochemical corrosion behavior of the untreated and the carburized samples were investigated using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and open circuit potential. The results reveal that the continuous and thick carburized layers form after carburization treatment at 1203 K for 10 h, whose main phase is a functional complex ceramic phase, Ti_2AlC. Carburization can improve corrosion resistance of the porous TiAl alloy. Among the carburized samples, the carburized one at 1203 K for 10 h presents the highest corrosion resistance and has the most stable oxide film.

1. Introduction

TiAl alloy has been considered as structure materials owning to its low density, high strength at elevated temperatures, good oxidation resistance, good corrosion resistance [1–7], etc. He et al. [8] developed a novel technique to fabricate a porous TiAl alloy using elemental powders by reactive synthesis process and opened a new application for TiAl alloy. In recent years, the group did a lot of research on anti-corrosion property of the porous TiAl alloy [9,10]. They found that the porous TiAl alloy exhibited high corrosion resistance, used it as microporous membranes [11], and successfully applied it to filtration of titanium tetrachloride and hydrometallurgy area. However, the corrosion resistance of the porous TiAl alloy is not good enough under rugged conditions owing to the intrinsic activity of metals and the enormous surface area. Therefore, the investigation on improvement of the corrosion resistance of the porous TiAl alloys is very important.

Many studies have been reported that chemical thermal treatment can improve corrosion resistance of materials [12–14]. However, little related research has been devoted to surface modification of porous metal materials by the same treatment, although it is widely applied to compacted TiAl alloys [15–18] and titanium alloys [19,20]. Brady and Tortorelli [21] once putted forward that the synthesis of functional complex ceramic phase can be obtained by a gas–metal reaction on the surface of alloys. Moreover, the functional complex ceramic phases exhibit good corrosion resistance [22].

The paper of primary goal was to synthesize a functional complex ceramic phase on the surface and around the pores of the porous TiAl alloy by a gas–metal reaction in a carburizing atmosphere and improve the corrosion resistance of the porous TiAl alloy. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were used to evaluate the corrosion resistance of the untreated and the carburized porous TiAl alloy. Open circuit potential was also measured after static polarization at 2 V for 1 h to estimate the stability of the passive film.

2. Material and methods

2.1. Preparation of the porous TiAl alloy

The preparation of the porous Ti–46.5 Al (at.%) was started with elemental powders. Al powders and dehydrided Ti powders were used in experiments having 99.8% purities and the particle sizes of the powders varying between 200 and 300 mesh. The powders were dry-mixed in a tumbler ball mill for 12 h with the rolling rate of 75 rpm, followed by cold pressing into compacts with a dimension of 5 mm × 45 mm × 2 mm and $\varnothing$32 mm × 2 mm at 200 MPa. Finally, the specimens were sintered in a vacuum furnace with a pressure of 10^{-3} Pa at 1573 K. The sintering temperature as a function of the sintering time was described the details in other work [8].

2.2. Carburization of the porous TiAl alloy

Carburization tests were carried out in a tube furnace at 1203 K for 8 h, 10 h and 12 h. The carbon resource was supplied by solid carburizer (which is composed of barium carbonate (7–12 wt.%), sodium carbonate (1–3 wt.%), and the remained

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charcoal) with equal in mass and a size of 3–5 mm at every test and the specimens were placed on hardware cloth. The ultra-high-purity nitrogen gas with a flow rate of 0.8 L/min was used to deoxygenate before reaching the carburization temperature, and then the gas flow rate decreased to 0.2 L/min for maintaining carbon potential. The specimens were ultrasonically cleaned in de-ionized water for 30 min, rinsed in acetone and dried at 333 K for an hour before and after carburization.

The open porosity and the pore size of the samples were measured by the Archimedes method in water [23] and the bubble point method [24] using the sample with a dimension of ∅32 mm × 2 mm, respectively.

2.3. Electrochemical measurements

Electrochemical measurements were performed on CHI-660D electrochemical workstation with a three-electrode system. The reference electrode was a saturated calomel electrode (SCE) separated from the main compartment by a bridge with a Luggin cupinary tube, and all potentials quoted were based on this reference system in this paper. The auxiliary electrode was a large piece of Pt foil, and the electrolyte was 0.5 mol/L H_2SO_4 solution.

Insulated copper wires were connected to the specimens with conducting resin to avoid undesirable ohmic effects. All specimens were sealed with epoxy resin exposing the whole geometric area of 1 cm^2 with both sides exposed to the solution and allowed to cure for 24 h at room temperature.

For a fresh working electrode, it was immersed for ten hours in the supporting electrolyte solution in order for the fully infiltration. Anodic polarization measurement or electrochemical impedance spectroscopy (EIS) was recorded when open circuit potential (E_{OCP}) achieved stability, every measurement was performed three times with a fresh specimen and a fresh solution in air at 298 K. Potentiodynamic polarization curves were recorded at a scan rate of 1 mV/s ranging from open circuit potential (E_{OCP}) to 2 V. Electrochemical impedance spectroscopy (EIS) was obtained at open circuit potential (E_{OCP}) in the frequency ranging from 100 kHz to 0.01 Hz and 12 points measuring per decade, with a perturbation amplitude of 5 mV.

Specific surface area of each specimen was measured by small amplitude cyclic voltammetry in order to obtain a current density before anodic polarization measurement. In addition, open circuit potential was recorded for the untreated and the carburized porous TiAl alloy at 1203 K for 10 h after potentiostatic anodization at 2 V for 1 h.

2.4. XRD and SEM characterization

X-ray diffraction (XRD: D/MAX-255) with Cu Kα radiation (wavelength $k = 1.5406$ Å) was used to identify the phases in the carburized porous TiAl alloy. The pore structure of samples and the carburized layer of cross-section were analyzed by scanning electron microscopy (NOVA NANOSEM 230).

3. Results and discussion

3.1. XRD and SEM analysis

The X-ray diffraction patterns of the untreated and the carburized porous TiAl alloy at 1203 K for 10 h is shown in Fig. 1. The main phase is Ti_2AlC rather than TiAl after carburization, which proves the functional complex ceramic phase formed by gas–metal reactions. Ti_2AlC is the most stable layered ternary-phase in the Ti–Al–C system [25], belongs to a class of ternary ceramics called MAX phases [26] and exhibits good corrosion resistance in H_2SO_4 solution [27].

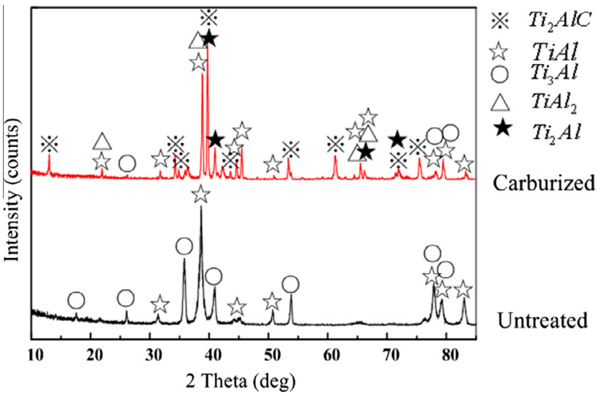

Fig. 1. X-ray diffraction patterns of the carburized sample at 1203 K for 10 h.

The sintered and the carburized samples have a same pore size distribution of 20–30 μm, and the same open porosity of 28–30%. The pore formation mechanism during the elemental powder synthesis has been documented in other works [8] and the pore structure of the porous TiAl alloy is presented in Fig. 2. As can be clearly seen from these SEM images, the general pore size of the samples do not change after carburization, the carburized samples exhibits layered microstructure on the surface. The EDX analysis of the carburized sample at 1203 K for 10 h shows the significant carbon peak (Fig. 2c). From the above analysis, it is believed that the layered microstructure is Ti_2AlC phase.

SEM backscattered electron images of the carburized porous TiAl alloy are exhibited in Fig. 3. As can be seen from backscattered electron images, there are significant backscattered electron contrasts in cross-sectional microstructure. The ash black presents the carburized layers and the gray stands for the no-carburized layer or the diffusion layers. From the backscattered electron contrasts perspective, the carburized layers observed on the cross section of the carburized porous TiAl alloy at 1203 K for 8 h is continuous on the border of the sample (Fig. 3a), and the thickness of the thin layer around the pores at the centre of the sample is no more than 2 μm (marked with arrows and the dotted oval in Fig. 3b). The carburized layers formed at 1203 K for 12 h exhibit apparent multilayer structures and porous layers at the outer side of the sample (indicated with arrows and the dotted oval marked as Fig. 3e) and coarse microstructures at the centre of the sample (Fig. 3f) with full coverage of the carburized layers. By contrast, the well-distributed carburized layers appear on the cross section of the carburized porous TiAl alloy at 1203 K for 10 h even if around the narrow pores at the centre of the sample with the thickness of more than 7 μm (indicated with arrows and the dotted oval marked as Fig. 3d).

The carburized mechanism of the identical composition TiAl alloy has been reported in other work [28]. The thickness and microstructure of the carburized layer strongly depend on the carburization time under the other same conditions. For the carburized porous TiAl alloy at 1203 K for 8 h, the carburization time is enough to form continuous and thick carburized layers at the outer side, by comparison, it is not enough for formation of the thick carburized layers around the pores at the centre of the sample owing to the low carbon potential in the pores. As carburization time extends to ten hours, the well-distributed carburized layers form on the border and at the centre of the sample even if around the narrow pores at the centre. However, the too long carburization time can result in many drawbacks [29,30], such as multilayer structures, porous layers and coarser microstructures. The drawbacks have negative direct impacts on corrosion resistance.

3.2. Anodic polarization study

The anodic polarization curves recorded for the untreated and the carburized samples from open-circuit potential to 2 V are given in Fig. 4. The untreated sample has a negative corrosion potential (−0.63 V) and a higher passive current density (3.396e−4 A cm^{-2}) compared with all the carburized samples and presents passive behavior between 0–2 V. Among the carburized samples at 1203 K for 8 h, 10 h and 12 h, they have the similar corrosion potential value and current densities before 1.2 V. Then the difference in the current density occurs, the carburized samples at 1203 K for 8 h show a higher passive current density than the other two carburized samples with a same passive current density.

The corrosion behavior is closely related with the composition and microstructure of materials. As a whole, the untreated porous TiAl alloy has the same corrosion behavior as the compacted TiAl