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Effects of silicon and multilayer structure of TiAl(Si)N coatings on the oxidation resistance of Ti6Al4V

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ABSTRACT

For improvement of the oxidation resistance of the titanium alloy, multi-layered $Ti_{0.5}Al_{0.5}N/Ti_{0.7}Al_{0.3}N$ and monolayer $Ti_{0.5}Al_{0.5}N$, $Ti_{0.5}Al_{0.45}Si_{0.05}N$, $Ti_{0.6}Al_{0.3}Si_{0.1}N$ were deposited on Ti6Al4V alloy by arc ion plating. The isothermal and cyclic oxidation behaviors of the coated alloy were investigated at 650 °C and 750 °C in air. At 650 °C the oxidation resistance of the substrate was significantly improved by all the coatings. At 750 °C, the beneficial effects were maintained by $Ti_{0.6}Al_{0.3}Si_{0.1}N$ and $Ti_{0.5}Al_{0.45}Si_{0.05}N$ but not by $Ti_{0.5}Al_{0.5}N$ and $Ti_{0.5}Al_{0.5}N/Ti_{0.7}Al_{0.3}N$ coatings. The TiAlSiN coating exhibited better oxidation resistance than the TiAlN coating could be attributed to Si addition eliminating defect formation in the TiAlN coating during the oxidation process.

1. Introduction

Titanium and its alloys, such as Ti6Al4V, are widely used in many industries due to their superior combination of mechanical properties with low density, excellent strength and good corrosion resistance. However, the high affinity of titanium towards oxygen at elevated temperature, which led to accelerated oxidation and embrittlement by dissolved oxygen, is one of the main factors that limit the application of titanium alloys at high temperatures. In order to improve their oxidation resistance, coatings can be applied to titanium and titanium alloys.

Several coatings have been applied to titanium alloys to improve their oxidation resistance, such as aluminide and Pt-modified aluminide [1,2], silicides [3], MCrAlY [4,5], TiAl(Cr) [4,6,7], TiAlCrYN [8], Cr_2AlC [9] and enamel coatings [10,11]. Among them, the TiAlCrYN coatings exhibited good oxidation resistance by effectively preventing oxygen dissolution and diffusion into the titanium substrate, and are a promising candidate for oxidation protection of titanium alloys [8]. However, during extended exposure, defects in the nitride coatings led to substrate oxidation and formation of rapidly growing titania [8]. Minimisation of the coating defects and improvement of the oxidation resistance of the coating so as to block the diffusion of Ti and oxygen through the defects by the rapid development of a protective oxide may be the solution to the problem. Recently, it was reported that the addition of silicon can improve oxidation performance of TiAlN [12,13]. A. Vennemann et al. [12] studied oxidation performance of $Ti_{0.2}Al_{0.3}Si_{0.1}N$ and $Ti_{0.3}Al_{0.2}Si_{0.03}N$ coatings at 800 °C and 1000 °C in a vacuum chamber with a base pressure of $P \leq 0.1$ mPa and found that the addition of silicon to titanium–aluminum nitride favored the formation of an aluminum oxide top layer. Y. S. Li et al. [13] investigated oxidation the behavior of $Ti_{0.25}Si_{0.75}N$, $Al_{0.25}Si_{0.75}N$ and $Ti_{0.3}Al_{0.3}Si_{0.3}N$ coatings at 900 °C and found that any enrichment of Si or Al on the surface was absent and the structures of the films remained basically unaffected. The authors [13] attributed the superior oxidation resistance of the Si-rich nanocomposite nitride films to the chemically high inertness of amorphous SiNx interfacial phase. The effects of Si improving the oxidation performance of TiAlN coating are remarkable, however, the relevant studies are few and the fundamental mechanism needs to be further distinguished. In addition, as widely used hard and wear resistant coatings for cutting tools, the oxidation and corrosion properties of nitride coatings are usually studied deposited on stainless steel. As a possible oxidation protective coating of titanium alloy, oxidation performance of nitride coatings deposited on titanium alloy needs to be studied. Up to now, only one paper has been reported [8] to conduct such investigation.

In this paper, a multilayered $Ti_{0.5}Al_{0.5}N/Ti_{0.7}Al_{0.3}N$ coating (The outer layer was $Ti_{0.5}Al_{0.5}N$ and the inner layer was $Ti_{0.7}Al_{0.3}N$), and a few monolayer coatings of $Ti_{0.5}Al_{0.5}N$ and TiAlSiN have been applied to protect a Ti6Al4V alloy. The multilayered structure is thought to be helpful to minimize through-thickness coating defects by inhibiting the inheritance of the coating defects. Furthermore, the deposition of the $Ti_{0.7}Al_{0.3}N$ interlayer can promote the adhesion of the top $Ti_{0.5}Al_{0.5}N$ coating and the substrate. The internal stress, which mainly originated from deposition growth process, and structure and thermal-expansion properties discrepancy between the coatings and the substrate [14],

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has a great effect on the adhesive strength [15]. The linear thermal expansion coefficient of the titanium alloy is around 1×10^{-5}/K, those for TiN and $Ti_{0.5}Al_{0.5}N$ are 9.4×10^{-6}/K and 7.5×10^{-6}/K respectively [16], and the linear thermal expansion coefficient of $Ti_{0.7}Al_{0.3}N$ is between TiN and $Ti_{0.5}Al_{0.5}N$. The linear thermal expansion coefficient gradient from the substrate to the coating surface in the multilayered coating will be beneficial to the decrease of the average residual stress in the coating thus increases the adhesive strength. The coatings were prepared by arc ion plating (AIP). The aim of this study is concerned with the oxidation behavior of the coated Ti6Al4V alloy at 650 °C and 750 °C.

2. Experimental procedures

A Ti6Al4V ingot was cut into specimens sized 15 × 10 × 2 mm, which were ground down to 2000# emery paper and polished to 2.5 μm diamond, and then cleaned ultrasonically in alcohol. The monolayer $Ti_{0.5}Al_{0.5}N$, $Ti_{0.6}Al_{0.3}Si_{0.1}N$, $Ti_{0.5}Al_{0.45}Si_{0.05}N$ coatings and the multilayered $Ti_{0.5}Al_{0.5}N/Ti_{0.7}Al_{0.3}N$ coating were deposited on Ti6Al4V substrates by arc-ion plating in a coating unit (DH-4, China). The substrates were mounted on a frame which revolved and rotated. Before deposition, the substrates were sputter-cleaned using Ar ions under −1000 V d.c. bias voltage to ensure good adhesion of the deposited coatings. The coating was deposited in a mixed $Ar–N_2$ atmosphere; the main deposition parameters are: N_2 partial pressure 1.5 Pa, arc current 60 A, substrate bias voltage −450 V and deposition time 60 min. In order to improve the adhesive strength of the coatings, a TiN interlayer around 0.5 μm thick was deposited. The total thickness of the coatings was 3.5–5 μm. For the multilayered coating, the thickness ratio of the outer $Ti_{0.5}Al_{0.5}N$ and the inner $Ti_{0.7}Al_{0.3}N$ is 2:1.

Quasi-isothermal oxidation tests were performed in box furnaces at 650 and 750 °C in air, where the oxidation was stopped every 20 h and the specimens placed in alumina crucibles were weighed and visually inspected. During cooling the alumina crucibles were covered with alumina lids in order to collect any spalled oxide. Cyclic oxidation tests were carried out in an automated rig in air at 650 and 750 °C up to 300 cycles. One cycle consisted of 1 h at temperature and 15 min cooling down to room temperature. The specimens were weighed to characterize the oxidation kinetics every 20 cycles.

After oxidation, the specimens were examined using X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray analysis (SEM/EDX) and electron-probe microanalysis (EPMA).

3. Results and discussion

3.1. Microstructure of as-prepared coatings

Typical surface morphology and cross-sectional microstructure of the coatings are shown in Fig. 1. The coatings are dense with droplets of different sizes on the surface (Fig. 1a). The droplets are the commonly known undesirable but inevitable macroparticles that formed in the cathodic-arc evaporation process [16]. The morphology seen in Fig. 1 is typical of nitride coatings deposited by the AIP method. From the cross-sectional microstructure (Fig. 1b), it can be seen that the coating was very dense, uniform and adherent to the substrate alloy.

XRD patterns of the coatings are shown in Fig. 2. All the coatings had the B1–NaCl structure, which is consistent with earlier works [17–19], implying that Si and Al were incorporated in the TiN lattice as solid solution by a substitution of the Si and Al ion into Ti sites; alternatively, Si could be present in an amorphous phase and Al atoms in solid solution substituted for the Ti in TiN. Compared with (Ti, Al)N coatings, (200) peak of $Ti_{0.6}Al_{0.3}Si_{0.1}N$ shifted to low angles. Carvalho et al. [19] observed similar phenomenon for higher silicon content TiAlSiN and attributed it to the segregation of Si atoms from the Ti positions in the crystalline lattice, which enhanced the formation of TiAlN grains. Since the Al content in the $Ti_{0.6}Al_{0.3}Si_{0.1}N$ coating was the lowest among the four coatings, a lesser number of the smaller Al atoms were incorporated in the TiN lattice. Previous works [20] showed that for $(Ti_{1-x}Al_x)N$ ($x < 0.6$) XRD peaks gradually shifted to higher angles in proportion to x values and the lattice parameters decreased with the additions of Al due to the substitution of larger Ti atoms by the smaller Al atoms. The (Ti, Al) N and $Ti_{0.6}Al_{0.3}Si_{0.1}N$ coatings showed strong texture along a preferred (220) orientation, but the $Ti_{0.5}Al_{0.45}Si_{0.05}N$ coating did not.

3.2. Oxidation kinetics

The quasi-isothermal and cyclic oxidation kinetics of Ti6Al4V with and without the applied coatings at 650 and 750 °C in air are plotted in Fig. 3. The substrate, or uncoated alloy, oxidized at a high rate; serious spallation of the oxide scale occurred during the initial 20 cycles at 750 °C, so all the oxidation tests of the substrate were carried out for only 100 h. Fig. 3 only shows parts of the kinetic data of the substrate that were obtained during the oxidation tests, because the differences of the mass changes between the coatings and the substrate were so large that the mass changes of the coatings cannot be clearly shown if the whole data of the substrate were included. From the quasi-isothermal and cyclic kinetics, it can be seen that at both temperatures the slowest oxide growth rate among the coated alloys was found on the Si modified TiAlN coatings, while the fastest rate was on the multilayered coating. At 650 °C, all the coated alloys exhibited very low mass gains after oxidation for 300 h or for 300 cycles. At 750 °C, from the quasi-isothermal kinetics, it can be seen that the oxidation rates of the multilayered $Ti_{0.5}Al_{0.5}N/Ti_{0.7}Al_{0.3}N$ and the monolayer $Ti_{0.5}Al_{0.5}N$ coatings tend to accelerate after 80 h. During cyclic oxidation, the two coatings oxidized heavily in the later period, and the experiment was discontinued after 215 cycles. The $Ti_{0.6}Al_{0.3}Si_{0.1}N$ and $Ti_{0.5}Al_{0.45}Si_{0.05}N$ coatings exhibited very low mass gains under both quasi-isothermal and cyclic conditions, and the differences in mass gain of the two

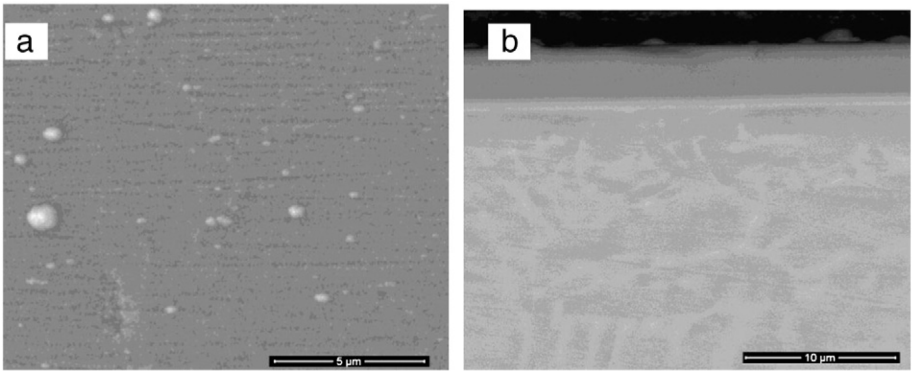

Fig. 1. (a) Surface morphology and (b) cross sectional microstructure of as-deposited $Ti_{0.6}Al_{0.3}Si_{0.1}N$ coatings on Ti6Al4V.