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Oxidation behaviour of Ti–Al–C films composed mainly of a Ti_2AlC phase

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This paper addresses the oxidation behaviour of Ti–Al–C films composed mainly of a Ti_2AlC phase. The films exhibited rather low oxidation rates at 600 and 700 °C, with an oxygen-rich zone or a thin oxide layer appearing on the film surfaces. Much faster oxidation rates were observed at 800 and 900 °C. The Ti_2AlC phase was quickly consumed by oxidation. From the film surface to the inner zone, TiO_2-rich layer, Al_2O_3-rich layer, and $TiO_2 + Al_2O_3$ mixed layer was observed, respectively. The oxidation mechanism of the Ti–Al–C film is discussed based on the experimental results.

1. Introduction

$M_{n+1}AX_n$ (abbreviated as MAX, where M is an early transition metal, A is an IIIA- or IVA-group element, X is C or N, and $n = 1$, 2, or 3) phases are a family of nanolaminated compounds with $M_{n+1}X_n$ layers being interleaved with single layers of A-atoms [1–3]. Due to the mixed metallic-covalent nature of the M–X bonds which are exceptionally strong, together with the weaker M–A bonds, the MAX phases possess unique combination of typical ceramic properties (e.g., high melting point, good oxidation and corrosion resistance) and typical metallic properties (e.g., good thermal and electrical conductivity, easy machinability, excellent thermal shock resistance and damage tolerance). This unique combination of properties makes MAX phases fascinating for potential applications, e.g., high temperature components, protective coatings, and electrical contacts. So far, approximately 60 different MAX phases and their solid solutions have been synthesised, either as bulk material or as films [3].

As one example of nanolaminated MAX phases, Ti_2AlC was paid significant attentions in recent years. Several techniques, such as hot isostatic pressing (HIP) [4], spark plasma sintering (SPS) [5], and combustion synthesis [6] have been investigated for synthesising bulk Ti_2AlC materials. Ti_2AlC thin films and coatings have been synthesised by using magnetron sputtering [7,8], pulsed cathodic arc deposition [9], and high velocity oxy-fuel spraying [10] techniques. Over the last 10 years, the crystalline and electronic structure of Ti_2AlC phase and properties of bulk Ti_2AlC materials have been extensively investigated [2,11,12]. However, oxidation properties of Ti_2AlC films remain less explored. The main problems might lie in the difficulty in low-temperature synthesis of Ti_2AlC films [13].

In this work, Ti–Al–C films consisting mainly of MAX phase were synthesised on polycrystalline Al_2O_3 substrates in an industrial coater and their oxidation properties were investigated in the temperature range between 600 and 900 °C. The oxidation mechanisms were discussed based on the experimental results.

2. Experimental details

The substrates used here were disk-shaped polycrystalline Al_2O_3 specimens (96 wt.%, 20 mm diameter and 1 mm thickness, produced by the KERAFOL Keramische Folien GmbH). Their surfaces were in polished status with surface roughness of about 0.5 μm. The films were deposited by unbalanced magnetron sputtering using a CC 800/9 industrial-size coater from CemeCon AG, Germany. Prior to deposition, the coating chamber was evacuated to a background vacuum of 8 mPa. The specimens constantly rotated during the coating process, in order to obtain a fully covered surface deposition. Three elemental targets [Ti (99.9 wt.%), Al (99.9 wt.%), C (99.9 wt.%)] with same dimension of $500 \times 88 \times 10\ mm^3$ were co-sputtered in an Ar atmosphere. The deposition temperature and applied bias voltage was 540 °C and

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−90 V, respectively. The film composition was controlled by adjusting the sputtering power of the targets. Film thickness was controlled to be 8–10 μm by adjusting deposition time. To obtain the Ti_2AlC MAX phase, the Ti–Al–C films were vacuum-annealed at 800 °C for 1 h after deposition process, based on earlier results [13].

Intermittent isothermal oxidation tests were conducted in static air at 600–900 °C in alumina crucibles placed in a muffle furnace. The specimens were taken out of the furnace and cooled to room temperature at various intervals for mass measurement. The total mass of a specimen including the crucible was recorded. The sensitivity of the balance was 10^{-5} g. The Al_2O_3 substrates do not oxidise at 600–900 °C. Therefore, the oxidation of coated specimens on Al_2O_3 substrates can be taken as oxidation of Ti–Al–C films exclusively.

The phase compositions of vacuum annealed and oxidised films were identified by X-ray diffraction (XRD). Two kinds of scanning modes were used: (1) two-dimensional XRD (XRD^2) analyses with incidence angle at 10° using a Bruker D8 General Area Detector Diffraction System (GADDS); (2) grazing angle XRD (GAXRD) analyses with incidence angle at 2° using a Bruker D8 conventional XRD instrument. To avoid the influence of preferred orientation, in the XRD^2 analyses, 2θ and chi scans were conducted simultaneously. The morphologies and chemical compositions of films and oxide scales were observed and determined using a scanning electron microscope (SEM, Mira 20 kV or Hitachi S4800 15 kV) equipped with an energy dispersive X-ray spectrometer (EDX, Oxford).

3. Results and discussion

3.1. Ti–Al–C films before oxidation

As shown in Fig. 1a and b, the Ti–Al–C films after vacuum annealing at 800 °C for 1 h were composed mainly of Ti_2AlC MAX phase. Especially in Fig. 1a, the diffraction peak of (0 0 0 2) planes at ∼13° was observed, which is the characteristic peak of the Ti_2AlC MAX phase [7–9]. Diffraction peaks from other phases, such as Ti_3AlC and TiC, were also detected in the XRD spectra. Similar phenomena have been reported by Garkas et al. [13]. Fig. 1c and d show surface and fractured cross-section SEM images of the Ti–Al–C films on polycrystalline Al_2O_3 substrates. From the surface observations, the film seems to have a columnar structure. However, the fractured cross-section observations revealed that the film was very dense and actually composed of fine sub-micro-equiaxed crystals. From the EDX analyses on the cross-sections, the chemical composition of the coating was rather uniform, close to the stoichiometric Ti_2AlC: Ti 48–52 at.%, Al 25–28 at.%, and C 21–25 at.%.

3.2. Oxidation of Ti–Al–C films at 600 and 700 °C

Fig. 2a shows the interrupted isothermal oxidation results of the Ti–Al–C films at 600 and 700 °C. The mass gain was very low at 600 °C, less than 0.2 mg/cm^2 after 300 h of oxidation. Oxidation curve was greater at 700 °C, reaching about 0.7 mg/cm^2 after 200 h of oxidation. The oxidation kinetics exhibited a two-segment logarithmic curve at 600 °C (Fig. 2b) while the oxidation obeyed a parabolic rate law at 700 °C (Fig. 2c).

Fig. 3a and b show the XRD results of Ti–Al–C films after oxidation at 600 °C for 300 h in air. Ti_2AlC MAX phase remained as the main phase in the oxidised films, both on the surface (Fig. 3a) and in the bulk of the films (Fig. 3b). Very weak peaks of titanium oxide (rutile) as oxidation products were detected. In addition, the intensity of other phases, such as Ti_3AlC and TiC decreased or disappeared. It is speculated that the thermal activation during oxidation leads to a continuous solid state reaction to form the Ti_2AlC phase. The reaction was obviously not completed during 1 h annealing at 800 °C (Fig. 1a and b).

The SEM micrographs of Ti–Al–C film surface and cross-section oxidised at 600 °C for 300 h are shown in Fig. 3c and d, respectively. Fine needle-like oxide crystals nucleated on the surface at

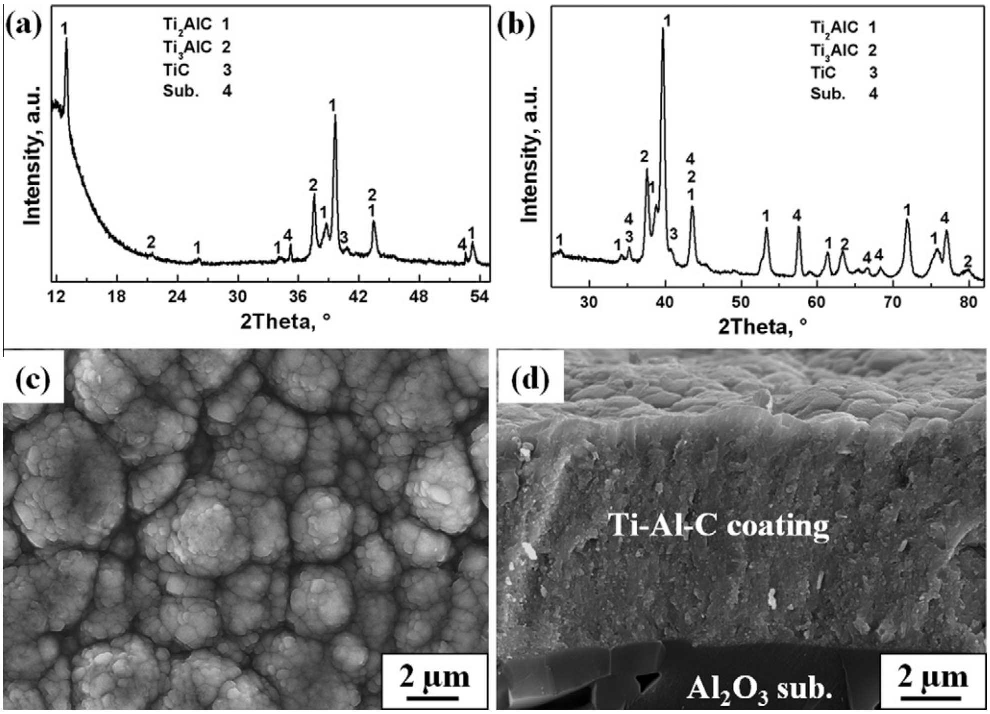

Fig. 1. (a) GAXRD and (b) XRD^2 patterns of vacuum-annealed Ti–Al–C films; (c) surface and (d) cross-sectional SEM images of vacuum-annealed Ti–Al–C films.