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Phase formation and microstructure evolution of arc ion deposited Cr_2AlC coating after heat treatment

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ABSTRACT

Due to the excellent oxidation and hot corrosion resistance and matched thermal expansion coefficient to normal alloys, Cr_2AlC has potential applications as high-temperature protective coating. In the present work, the preparation of Cr_2AlC coating has been achieved through cathodic arc deposition method combined with heat post-treatment. It was found that the coating, deposited from Cr_2AlC compound target in the unintentional heating condition, was amorphous. After annealing at 620 °C in Ar for 20 h, the amorphous Cr–Al–C coating happened to crystallize and transformed to crystalline Cr_2AlC as the major phase. It is obvious that the formation temperature of Cr_2AlC was decreased from about 1050 °C for sintered bulk to around 620 °C for the as-deposited coating, resulting from the homogeneous mixture of the Cr, Al and C at atomic level in the Cr–Al–C coating. Apart from crystalline Cr_2AlC, the annealed coating also contained $AlCr_2$ and little Cr_7C_3. $AlCr_2$ formed due to the loss of C during deposition, and little Cr_7C_3 always existed in the sintered Cr_2AlC compound target as impurity phase.

1. Introduction

Ternary layered carbide Cr_2AlC is a typical one of $M_{n+1}AX_n$ phases (where n is 1, 2, and 3, M is an early transition metal, A is an A-group element and X is either C or N [1–3]). This compound possesses a unique combination of the merits of both metals and ceramics [4], such as low density, high elastic modulus, easy machinability and excellent thermal shock resistance. In addition, previous investigations on the bulk Cr_2AlC [5–7] indicate that it also has excellent oxidation and hot corrosion resistance, due to the formation of a protective Al_2O_3-rich scale during the oxidation and hot corrosion [8]. Therefore, Cr_2AlC has a great potential for practical applications not only as high temperature structural ceramic but also as oxidation resistant coating. Especially, Cr_2AlC possesses matched thermal expansion coefficient (TEC) with Ni based alloys (the TEC value of Cr_2AlC is $13.3 \times 10^{-6}\ K^{-1}$ in the range of 30–1200 °C [9]), which is great beneficial for the adhesion as well as cracking and spallation resistance of Cr_2AlC coating due to reducing of the thermal stress.

With respect to the preparation of the Cr_2AlC coating, previous efforts mainly focused on the direct growth of phase-pure crystalline Cr_2AlC coating using magnetron sputtering on heated substrates, either from elemental targets or from compound target [10–12]. Nowadays, phase-pure crystalline Cr_2AlC coating has been successfully deposited using this method. Moreover, investigations on the oxidation behavior of the Cr_2AlC coating have been conducted [13–15]. It was proved that the Cr_2AlC coating could effectively improve the oxidation resistance of the Ti6242 alloy and the M38G superalloy. However, due to its limited coating thickness and the columnar structure, the Cr_2AlC coating experienced serious degradation during the oxidation process [14]. Therefore, from the perspective of industrial applications, the preparation of thicker and denser Cr_2AlC coating using low cost method is indispensable.

Cathodic arc is a low-voltage, high current plasma discharge that takes place between two electrodes in vacuum [16,17]. High degree of ionization in the target material, the easy control of the parameters and the high deposition rate make the cathodic arc ion plating technique (AIP) one of the most perspective physical vapor deposition methods. This technique has been widely used to deposit tribological, decorative, protective and functional coatings. Especially, the high degree of ionization results in the densification of growing film due to increased adatom mobility [18]. As a new comer for the preparation of MAX phase coating, cathodic arc deposition method has been successfully used to prepare Ti_2AlC [19–21] and Ti_2AlN [1] coatings. Rosén et al. [20] have synthesized epitaxial Ti_2AlC film using a cathode high-current pulsed vacuum arc deposition system from elemental Ti, Al, and C cathodes at 900 °C. Hereafter, highly orientated hexagonal Ti and Ti_2AlC thin films were deposited on α-Al_2O_3 (0 0 1) single crystal substrate

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[19]. And Ti_2AlN film was deposited by utilizing reactive cathodic arc deposition at 500 °C [1]. This deposition temperature was 200 °C lower than that in the process of sputtering deposition of Ti_2AlN. Although previous works have proved that the preparation of MAX phase films using cathodic arc deposition method is available, high deposition temperature was still needed. Especially, the report on cathodic arc deposition of Cr_2AlC coating is absent. Therefore in the present work, in order to increase deposition rate and lower deposition temperature, a combined method of cathodic arc deposition and subsequent heat treating was explored for the preparation of MAX film. Cr–Al–C coating was deposited on a Ni-based superalloy using cathodic arc deposition from a compound Cr_2AlC target in the unintentional heating condition, the phase formation and microstructure evolution of the as-deposited Cr–Al–C coating after heat treatment was investigated using XRD, SEM and TEM.

2. Experimental procedure

2.1. Coating preparation

Cr–Al–C coating was prepared using a cathodic arc deposition system (SKY Technology Development Co., Ltd, China). A piece of as-synthesized bulk Cr_2AlC was machined into a target with dimensions of Φ60 mm × 6 mm. The bulk Cr_2AlC was fabricated by an in situ reaction/hot pressing method, as has been described elsewhere [22]. Disk sample of commercial brand M38G was chosen as the substrate in the present work. The nominal compositions (wt.%) of the alloy are given as follows: Ni, bal; Cr, 15.3–16.8; Co, 8.0–9.0; W, 2.3–2.9; Mo, 1.4–2.0; Al, 3.5–4.5; Ti, 3.2–4.0; Nb, 0.4–1.0. The substrate samples were cut into dimensions of 10 mm × 10 mm × 1.5 mm by an electric discharge method, their surfaces were ground down to 800 grit SiC paper. Afterwards, the samples were degreased ultrasonically cleaned in acetone, ethanol and distilled water for 10 min and then dried in air. The dried samples were placed on the rotating substrate holder; the distance from substrate coupons to the target was in the range of 70–200 mm.

Prior to deposition, ion bombardment of the substrates was carried out under 500 V pulse negative bias voltage for 5 min, after the base pressure of the vacuum chamber was pumped below 1.0×10^{-3} Pa. Then inert gas (Ar, 99.999%, 40 SCCM) was introduced into the sputtering chamber to initiate the target electrical arc. During the deposition process, the working pressure was kept at about 0.4 Pa by controlling the valve of the vacuum chamber and no intentional heating of the substrates was conducted. A 60 A current was applied on the Cr_2AlC target. The deposition time was 15 min.

2.2. Annealing treatment

Annealing treatment of the as-deposited coating was conducted at 620 °C in Ar for 20 h to fulfill the crystallization of Cr–Al–C. Before annealing treatment, the as-deposited substrates were sealed in a quartz tube, which was filled with high pure Ar to avoid oxidation during annealing. Then the quartz tube was put into the Muffle furnace and heated to the annealing temperature with a heating rate of about 10 °C/min.

2.3. Characterization of the coating

The crystal structure of the as-deposited and annealed Cr–Al–C coating was identified by XRD analysis. The XRD data was collected by a step-scanning diffractometer with Cu K_α radiation (XRD, Rigaku D/mac-2400, Tokyo, Japan). Scanning electron microscope (SEM, LEO Supra 35, Oberkochen, Germany) was used to investigate the morphology of the coating. The chemical composition of the coating was determined by employing electron-probe microanalysis (EPMA, Shimadzu EPMA-1610, Kyoto, Japan). A 300 kV Tecnai G^2 F30 high-resolution transmission electron microscope (HRTEM, FEI, Eindhoven, Netherlands), equipped with an energy dispersive spectroscopy (EDS) detector in the STEM system, was used for high-resolution TEM and selective area electron diffraction (SAED) analysis. Fast Fourier transformation (FFT) was carried out using a digital micrograph software package. Cross-sectional TEM specimens were prepared in the usual way, consisting of mechanical grinding and polishing, followed by 5 keV Ar^+ ion milling with a Gatan PIPS apparatus.

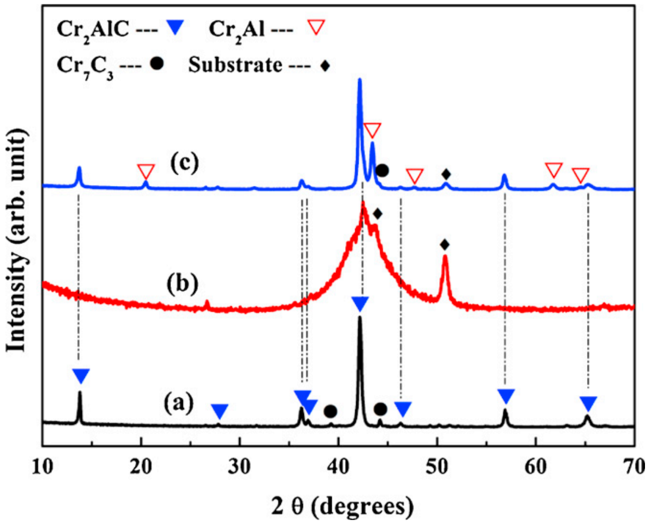

Fig. 1. XRD patterns of (a) the Cr_2AlC target, (b) as-deposited and (c) annealed Cr–Al–C coating.

3. Experimental results and discussion

3.1. Phase constituents of the Cr–Al–C coating before and after annealing

Fig. 1(a) and (b) shows the XRD patterns of the Cr_2AlC target and as-deposited coating, respectively. It can be seen that the target was on the verge of single-phase Cr_2AlC (Fig. 1(a)), with a little mount of Cr_7C_3 impurity. In Fig. 1(b), a broad diffraction peak appeared at about 43°, indicating that the as-deposited Cr–Al–C coating was amorphous. Besides, diffraction peaks from M38G substrate also appeared in the as-deposited Cr–Al–C coating (see Fig. 1(b)), indicating the coating was thin.

It has been reported that the amorphous Cr_2AlC could crystallize to crystalline Cr_2AlC at about 610 °C [23]. In the deposition process of 15 min, the maximum temperature was monitored to be around 200 °C in the vacuum chamber, due to the bombardment of the arc plasma. Hence in our deposition condition, the amorphous Cr–Al–C coating was obtained. This result is consistent with that obtained by Walter et al. [11], which shows that the coating deposited by using magnetron sputtering from Cr_2AlC target without intentional heating of the substrate was amorphous.

In order to promote the crystallization of the as-deposited amorphous Cr–Al–C coating, the heat post-treatment was conducted. The series annealing tests were carried at 610–1000 °C for 1–20 h in Ar. It was found that at higher temperature (>700 °C), the coating, mainly composed of Cr_7C_3 rather than Cr_2AlC, could be obtained after annealing (for brevity the corresponding XRD results not shown here). In fact, it has been known that in Cr_2AlC, Al possesses a high activity due to weak bonding between Al and Cr atoms [24]. Above 660 °C (the melting temperature of Al), the volatility of Al might become serious, so Cr_7C_3 formed more easily due to Al loss. Finally, an optimization annealing condition has been achieved,