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Fabrication and mechanical properties of high purity of Cr_2AlC coatings by adjustable Al contents

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ABSTRACT

The effect of Al content on phase structure and mechanical properties of vacuum annealed Cr-Al-C coatings was investigated. Cr-Al-C coatings were deposited by co-sputtering of Cr_2Al and Al targets in optimized CH_4/Ar atmosphere. The atomic content of Al was adjusted through the control of Al target current from 0.5 A to 3.0 A, thus Cr-Al-C coatings with different stoichiometric ratios were obtained. After 1.5 h thermal annealing at 750 °C in vacuum, Cr_2AlC MAX phase was observed from the XRD measurements. The Rietveld refinement of XRD spectra results indicated that the annealed coatings were composed of Cr_2AlC, Al_8Cr_5 and Cr_7C_3 phases with different amounts. With the increase of Al content, the hardness and modulus of the Cr_2AlC MAX phase coatings varied from 10.17 to 19.00 GPa and 198.43 to 267.62 GPa, respectively, while the toughness suffered an obvious decline. HRTEM analysis demonstrated that the excess of Al content resulted in the formation of Al_8Cr_5 and Al segregation at grain boundaries, which led to the deterioration of mechanical properties.

1. Introduction

MAX phases are ternary nanolayered metal carbides or nitrides with the general formula $M_{n+1}AX_n$, where M refers to early transition metal, A on behalf of IIIA or IVA elements, X represents C or N, n = 1, 2 or 3. The crystal structures of metallic (M-A) and covalent/ionic (M-X) bonding nature enable them to combine the properties of both metals and ceramics [1,2] such as high strength, outstanding oxidation resistance, good thermal shock resistance and damage tolerance, *etc* [3–6]. Benefiting from the formation of a protective Al_2O_3 layer well adhered to the surface, Cr_2AlC MAX phase attracts many attentions for the potential applications in high temperature oxidation and hot corrosion resistance [5,7–9]. Meanwhile, it exhibits excellent mechanical properties, including relative high hardness and Young's modulus, intermediate fracture toughness, good flexural strength, compression strength [10,11], electrical and thermal conductors [12]. Various methods have been applied to fabricate Cr_2AlC MAX phase coatings in recent years, including pulsed electro spark deposition [13], cathodic arc deposition [14], pulsed laser deposition [15], plasma spraying [16] and magnetron sputtering. Particularly, direct current magnetron sputtering (DCMS) takes the advantages of depositing dense and uniform coatings. Therefore, it is widely utilized to synthesize MAX phase coatings.

It has been reported that the purity of MAX phase in the coatings is the pre-requisite for achieving the excellent performances [17]. Usually, the fabricated MAX phase coatings contain a certain amount of impurities, such as binary carbides/nitrides and intermetallic compounds. In magnetron sputtering processes, composition deviation between coatings and targets will lead to the non-stoichiometric coatings, where impurity phases exist. Stanislav et al. [18] reported that the sputtering yields and transport efficiency of sputtered species were distinct for different target elements, which led to composition deviation between the deposited Cr-Al-C coatings and the Cr_2AlC compound targets. These differences always presented as the loss of C and Al in deposited coatings. Meanwhile, it has been reported that a certain excess Al in the as-deposited coating is benefit for the formation of Cr_2AlC MAX phase in the following post-heat treatment process [19–21]. For the

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purpose of synthesizing dense and high-purity Cr_2AlC MAX phase coatings, we applied an additional Al target to adjust Al contents of the coatings, which co-sputtered with Cr_2Al target in optimized CH_4/Ar atmosphere. Then a process of post-heat treatment at 750 °C in vacuum environment was followed. The aim of this work is to investigate phase compositions and mechanical properties of Cr-Al-C coatings with different Al contents after annealing processes. The phase compositions are analyzed by Rietveld refinement method from the XRD spectra. The structural and mechanical properties are also characterized by SEM, TEM, XRD and nanoindentation. The relationship between phase composition and mechanical properties is discussed in terms of microstructure evolution in the coatings.

2. Experimental setup

2.1. Sample fabrication

Cr-Al-C coatings with different Al contents were deposited on Ti-6Al-4V (TC4) substrates by a DC magnetron sputtering system, where the hybrid CH_4/Ar mixture was used as the precursor gas with an optimized flow ratio of CH_4:Ar = 1:4. The size of TC4 substrates which were polished to 3000-grit (Ra≤22 nm) by SiC paper was 15 mm × 10 mm × 2 mm. The nominal composition of TC4 is list in Table 1. A stoichiometric Cr_2Al compound target (produced by powder metallurgical process) and an additional Al target with the purity of 99.9% were co-sputtered to adjust the Al content in the coatings. The size of both targets was 400 mm × 100 mm × 7 mm. Before the deposition process, TC4 substrates were ultrasonically cleaned in acetone for 15 min, and quickly dried in warm air. Then they were fixed on a rotational substrate holder in front of Cr_2Al target with a distance of about 12 cm. A schematic diagram of the deposition experiment arrangement is shown in Fig. 1. When the base pressure of the vacuum chamber was around 2.6×10^{-3} Pa, the chamber was filled with Ar gas to reach a pressure of 1.1 Pa, which was followed the glow discharge process with −300 V pulsed DC bias (100 kHz, duty cycle: 90%) on the substrates for 40 min to remove the surface contaminations and achieve better coating adhesion.

During the deposition process, the current applied on Cr_2Al target was fixed at 2.5 A, while the current on Al target was varied from 0.5 to 3.0 A, in order to tailor the Al content in the coatings. The working pressure was kept at 0.48 Pa by controlling the main valve of the vacuum chamber. The substrate bias was set at −200 V, no intentional heating of the substrates was conducted. The detailed deposition parameters of the Cr-Al-C coatings are listed in Table 2. After deposition, a vacuum annealing process was conducted at 1.0×10^{-2} Pa for the deposited coatings to obtain Cr_2AlC MAX phase. The heating rate was about 5 °C/min. After 1.5 h thermal insulation at 750 °C, the samples were cooled inside the furnace to room temperature.

2.2. Characterization methods

The crystal structures of the deposited and annealed coatings were characterized by X-ray diffraction (XRD), using a BrukerD8 Advance diffractometer with Cu Kα radiation, operating in θ-θ configurations and collecting data over a 2θ-range from 10° to 90°.

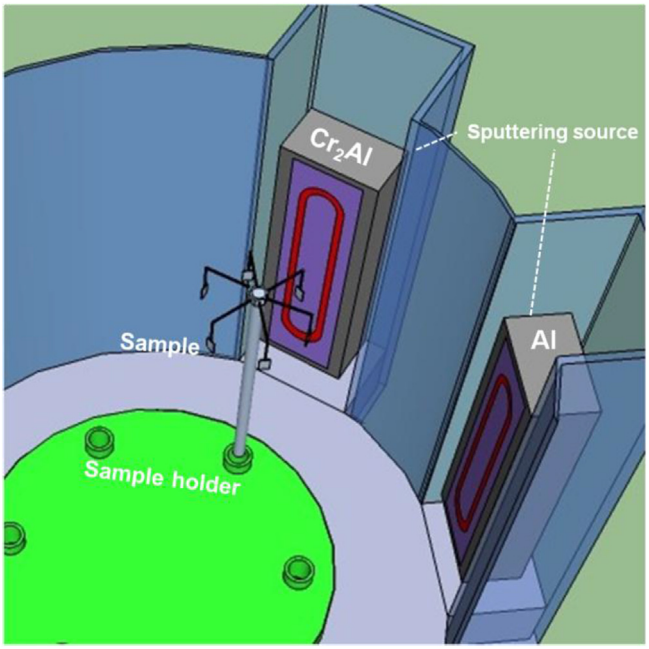

Fig. 1. Schematic diagram of the experiment arrangement.

Table 2
Deposition parameters for Cr-Al-C coatings.

Parameters	Values
Al target current (A)	0.5, 1.0, 2.0, 3.0
Cr_2Al target current (A)	2.5
Flow rates of CH_4/Ar (sccm)	20/80
Pressure (Pa)	0.48
Substrate bias voltage (V)	−200
Target to substrate distance (cm)	12

In order to quantitatively analyze the phase compositions of annealed Cr-Al-C coatings with different Al contents, all XRD patterns were processed using the Bruker TOPAS software to do Rietveld refinement. For the refinement procedure, the crystal structure files (.cif) and XRD patterns with different Al content were used. The emission profile (.lam) was represented by CuKα5.lam and the atomic positions of C (0, 0, 0), Cr (1/3, 2/3, 0.086), Al (2/3, 1/3, 0.25) in the unit cell were used in the Rietveld refinement [22]. The global parameters, such as zero error, air scattering factor and phase scale factors were refined in the initial refinement cycles. The background was fitted by using a Chebyshev function with 5 terms of the polynomial equation. The refinement was carried out for several cycles until a stable weighted reliability factors (Rwp) and satisfactory fits were obtained.

The chemical compositions were examined by scanning electron microscope (SEM, FEI Quanta FEG 250) equipped with an energy-dispersive X-ray spectrometry (EDS) using an EDAX Sapphire Si (Li) detector. The microstructure of the coatings were characterized using SEM and transmission electron microscope (TEM, Tecnai F20, US). TEM cross-sectional view images were obtained by a focused ion beam (FIB) process (Auriga, Germany), and a

Table 1
The element contents of TC4 substrate.

Element	Al	V	Fe	C	N	O	H	Ti
wt%	5.61	3.72	0.151	0.031	0.017	0.16	0.001	balance