Surface & Coatings Technology 298 (2016) 15–23

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

# Conditions for formation of MAX phase $Cr_2AlC$ in electrospark coatings deposited onto titanium alloy

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ARTICLE INFO

*Article history:*
Received 5 February 2016
Revised 19 April 2016
Accepted in revised form 25 April 2016
Available online 27 April 2016

*Keywords:*
Pulsed electrospark deposition
MAX phase
$Cr_2AlC$-based coating
TiC sublayer
Annealing
Phase composition

ABSTRACT

The technique of low-energy pulsed electrospark deposition (PED) with $Cr_2AlC$ electrodes was used to apply a protective layer onto the surface of Ti substrate. This was done in two ways: (a) thermal treatment of as-deposited coating and (b) preliminary creation of a TiC sublayer followed by PED. Upon annealing at 700 °C for 1 h in air, the coating was found to largely consist of MAX phase $Cr_2AlC$. A TiC sublayer preliminary created onto the Ti surface was found to suppress the Ti diffusion into the coating and thus to hamper the reaction of $Cr_2AlC$ with Ti. The coatings were characterized by SEM/EDS, XRD, and XPS. After thermal treatment, the coatings showed high wear resistance and friction coefficients of 0.6 and 0.4 at 25 and 700 °C, respectively.

## 1. Introduction

As is known [1,2], titanium alloys find wide application in aerospace engineering, shipbuilding, and automobile industry due to unique combination of their density, strength, impact resistance, crack growth resistance, and corrosion resistance. At the same time, these materials exhibit some drawbacks such as low hardness, wear resistance, proneness to scuffing during friction under load, and loss of service parameters at temperatures above 500 °C.

In the class of MAX compounds (general formula $M_{n+1}AX_n$, where M is an early transition metal; A some Group IIIA or IVA element; and $X = C$ and/or N), most promising for use in protective coatings onto titanium is the $Cr_2AlC$ phase because thermal expansion of this compound ($13.3 \times 10^{-6}\ K^{-1}$ [3]) is close to that of Ti ($10.5 \times 10^{-6}\ K^{-1}$ [4]) over a wide temperature range of 30–1200 °C. This circumstance not only favors the adhesion but also minimizes the probability of cracking in conditions of cyclic thermal loading. Good electroconductivity [$(1.4–2.3) \times 10^{-6}\ \Omega^{-1}\ m^{-1}$] and thermal conductivity [(17.5–22.5 W/m K)] [3,5,6] make this material attractive for use in the technology of pulsed electrospark deposition (PED). In addition, this MAX phase is known for its mechanical strength and oxidation resistance at temperatures up to 1300°C [5,7–9]. A distinctive feature of these compounds is their layered structure with alternating atomic layers of chromium carbide and aluminum monolayers. High reactivity and diffusivity of Al at high temperature favor the formation of a continuous protective layer on the surface of coated material.

However, in deposition of $Cr_2AlC$ coatings one encounters a serious problem concerning the phase purity. For instance, the magnetron deposition of thin coatings requires a high temperature of substrate [10–12] while film sputtering from a three-element target (Cr, Al, C), subsequent annealing [13,14]. PED from MAX electrodes is not a simpler technological process. In conditions of pulsed thermal loading, it involves some micro metallurgical events on the processed surface (cathode), intermixing of cathode and anode materials, and interaction with gaseous environment [15], and each affecting phase composition of coating.

Recently [16] we explored the structure and phase composition of PED coatings deposited from $Cr_2AlC$ electrodes in various conditions and analyzed in detail those deposited in energy-intensive modes. It has been found that a layer of titanium carbide is formed during the initial stage of deposition at the interface as a result of chemical reaction between $Cr_2AlC$ electrode and Ti substrate.

In case of energy-intensive processing in Ar flow, a rapidly formed TiC layer plays a positive role of diffusion barrier. In case low-energy deposition, chemical reaction between $Cr_2AlC$ electrode and Ti becomes incomplete and the MAX phase is almost entirely consumed in this reaction.

In PED, one faces with the dilemma of choice of such a relationship between the low- and high-energy deposition modes that would provide best simultaneous combination of the desired properties of deposited coating (surface roughness, composition, structure, uniformity, thickness, etc.) On one hand, high-energy (HE) deposition modes afford

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http://dx.doi.org/10.1016/j.surfcoat.2016.04.058
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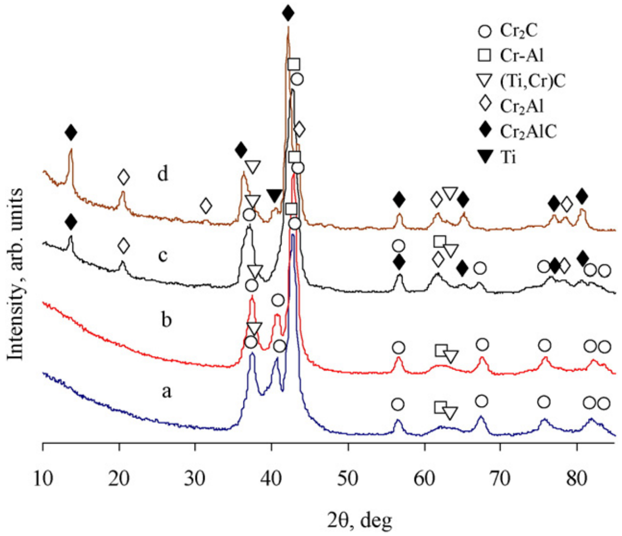

**Fig. 1.** Diffraction patterns for coatings subjected to thermal treatment for 1 h at indicated temperatures: a — as-prepared (without annealing); b — 500 °C; c — 600 °C; d — 700 °C.

to get relatively thick (70–80 μm) coatings containing marked amounts of MAX phase $Cr_2AlC$ but at this the surface is too rough. On the other hand, low-energy (LE) deposition modes ensure low surface roughness but the phase composition turns to be far from a desired one.

In this work, we checked out the applicability of low-energy PED to preparation of MAX phase based coatings by using $Cr_2AlC$ electrodes. At this, we used two approaches: (1) annealing of as-deposited coating; and (2) two-stage treatment of Ti substrate first with graphite electrodes and then with $Cr_2AlC$ electrodes.

## 2. Materials and methods

Low-energy PED of coatings was performed on an Alier-Metal 2002 stand. An analog-to digital converter L-CARD (Russia) and multichannel plotter LGraph2 (Russia) were used to monitor current $I$ and duration of current pulse packet $\tau$. In our experimental conditions ($I = 70$ A, $\tau = 110$ μs), voltage drop $U$ in the discharge gap was 20 V, so that the discharge energy ($P = IU\tau$) had a value of 0.16 J. Electrospark processing was performed in several local passes over the same area of the cathode surface.

Depositions were carried out in a 0.25-L box under argon. The flow rate of argon gas was 1 L/min. Anodes were fabricated by self-propagating high-temperature synthesis (SHS) using the technique of forced SHS pressing [17]. They had a shape of rectangular rods (40 × 2.5 × 2.5 mm). The electrodes for creation of TiC sublayer were made from graphite (SGL Carbon AG, Germany) [18].

The 10 × 10 × 5 mm substrate plates (cathodes) were made of titanium alloy VT-20.

PED with the graphite electrodes was performed in three stages: (*i*) for 3 min followed by ultrasound surface cleansing in water, (*ii*) drying in air, and (*iii*) repeated PED for 2 min followed by removal of free graphite in an ultrasound bath. The electrospark deposition from $Cr_2AlC$ electrodes lasted for 10 min.

**Table 2**
Elemental composition of as-prepared and etched coatings (at. %).

| Coating | C | O | N | Cr | Al | Ti |
|---|---|---|---|---|---|---|
| As-prepared | 23.5 | 9.5 | 2.0 | 40.0 | 16.5 | 8.5 |
| After etching with Ar ions | 22.4 | 2.8 | 2.2 | 44.7 | 18.4 | 9.5 |

X-ray diffraction (XRD) measurements (Cu-$K_\alpha$ radiation) were carried out in two different modes: symmetrical (Bragg–Brentano) and asymmetrical (grazing incidence diffraction [19]) geometries (incidence angle 5°). The diffraction patterns were processed by using program package [20].

Microstructure and elemental composition of deposited coatings were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) by using an S-3400N Hitachi microscope (Japan) equipped with an EDS accessory (Ultra Dry Silicon Drift X-ray Detector, Thermo Fisher Scientific, USA).

X-ray photoelectron spectra (XPS) were taken by using a PHI 5500 ESCA spectrometer (Perkin Elmer). Photoemission was excited by monochromatic Al-$K_\alpha$ radiation ($h\nu = 1486.6$ eV, 200 W). The scale of binding energy was calibrated by using the spectrum of adsorbed C1*s* atom ($E = 285.0$ eV) as a reference. The high-resolution spectra were approximated (by Lorentz and Gauss functions) by applying non-linear least-square technique. Prior to analysis, the deposited samples were subjected to preliminary etching with Ar ions for 15 min at a rate of 2–3 nm/min.

Annealing was carried out in a SNOL 7.2/1200 electric furnace at 500, 600, and 700 °C for 1 h in air.

Resistance to high-temperature oxidation in air was estimated from weight gain of the samples oxidized in air [21].

The samples (all faces having PED coatings) were placed in crucibles and subjected to annealing at 700, 800, and 900 °C. Weight gain was determined gravimetrically at an accuracy of $10^{-5}$ g (KERN 770 balances) for the samples held for 0.25, 0.5, 1, 2, 3, 4, 5, 10, 15 20, 25, and 30 h at high temperature and then cooled down to room temperature.

The coatings deposited onto titanium alloys were annealed in air at 700–1000°C for 1 h to estimate the short-time oxidation resistance. The elemental depth profiles for the as-deposited and oxidized coatings were obtained by glow discharge optical emission spectroscopy (GDOES) [22] using a PROFILER-2 instrument (Horiba Jobin Yvon). Sputtering of samples was performed – at a frequency of 13.56 MHz, power 35 W, pressure 700 Pa – for an analysis area of 4 mm in diameter. Intensity of lines at 267.716 nm (Cr), 396.152 nm (Al), 165.701 nm (C), 365.350 nm (Ti), and 130.217 nm (O) was used in calculations. A typical set of standard samples from Horiba Jobin Yvon, CrN, and TiCNO-based coatings with well-known elemental composition obtained by XPS were used for calibration.

Friction coefficients were measured at 25 and 700 °C in air with a tribometer (CSM, Switzerland) by pin-on-disk method using an $Al_2O_3$ ball 6 mm in diameter as a counterbody (load 1.0 N, linear velocity 10 cm/s, length way 150 m).

**Table 1**
XRD results for coatings subjected to thermal treatment for 1 h at indicated temperatures.

| Phase | Structural type | As-prepared | | 500°°C | | 600°°C | | 700°°C | |
|---|---|---|---|---|---|---|---|---|---|
| | | Content, vol% | Lattice parameter, Å | Content, vol% | Lattice parameter. Å | Content, vol% | Lattice parameter, Å | Content, vol% | Lattice parameter, Å |
| $Cr_2AlC$ | | – | – | – | – | 25 | $a = 2.879$ $c = 12.968$ | 50 | $a = 2.860$ $c = 12.886$ |
| $Cr_2C$ | $L'3$ | 70 | $a = 2.771$ $c = 4.440$ | 60 | $a = 2.773$ $c = 4.436$ | 30 | $a = 2.798$ $c = 4.417$ | | |
| (TiCr)C | $B1$ | 20 | $a = 4.119$ | 35 | $a = 4.181$ | 20 | $a = 4.240$ | 15 | $a = 4.197$ |
| $Cr_2Al$ | $C11b$ | – | – | – | – | 15 | $a = 3.028$ $c = 8.783$ | 30 | $a = 3.007$ $c = 8.661$ |
| Cr-Al | $A2$ | 10 | $a = 2.999$ | 5 | $a = 3.002$ | 10 | $a = 3.050$ | – | – |
| α-Ti | $A3$ | – | – | – | – | – | – | 5 | – |