Improving the oxidation resistance of AlCrN coatings by tailoring chromium out-diffusion

R. Escobar Galindo [a,*], J.L. Endrino [a], R. Martínez [b], J.M. Albella [a]

[a] Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, E-28049 Madrid, Spain
[b] AIN-Centro de Ingeniería Avanzada de Superficies, Cordovilla, E-31191 Pamplona, Spain

ARTICLE INFO

ABSTRACT

In this work, we have studied the improvement on the oxidation resistance of AlCrN-based coatings by adding a subsurface titanium nitride barrier layer. Since oxidation is interrelated with the inward diffusion of oxygen into the surface of $Al_xCr_{1-x}N$ ($x = 0.70$) coatings and the outward diffusion of Cr to the surface, the oxidation behaviour of the aluminium-rich AlCrN coatings can be tuned by designing the coating in an appropriate layered structure. The buried depth of the embedded layer and the oxidation time were varied, and the changes in the AlCrN/TiN depth composition profiles and surface oxidation stoichiometry were analysed by means of Glow Discharge Optical Emission Spectroscopy (GDOES) and Cross Sectional SEM (X-SEM) maps. It was observed that when a TiN diffusion barrier of 300 nm was deposited near the top surface (500 nm from the surface) the inhibition of the inward diffusion of oxygen and formation of beneficial alumina surface layers was promoted and consequently an increase of the oxidation resistance is achieved. This is explained in terms of a limited surplus of chromium from the coating to the surface. This was corroborated after performing experiments using CrN as embedded barrier layer which resulted in a continuous surplus of chromium to the surface and the formation of Cr-rich oxides. GDOES, in combination with X-SEM elemental maps, was proved to be a fast and accurate technique to monitor composition in-depth changes during oxidation, providing unique information regarding the oxide structure formation.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Recently, Al–Cr–N based coatings have received increasingly attention of researchers and coating designers due to their excellent mechanical properties and superior oxidation resistance compared with Al–Ti–N based coatings [1–6]. It has been predicted by the band parameters method that the critical content of Al in Al–Cr–N from B1 (NaCl-type) to B4 (wurtzitic) is 77.2% in comparison to only 65.3% solubility in Al–Ti–N [7]. This higher aluminium content in a B1 cubic phase allows for increased formation of alumina-like tribofilms without sacrificing mechanical properties such as hardness. Alumina based tribofilms have been shown to protect forming and machining tools by redirecting more heat towards the workpiece [8,9]. Nevertheless, increasing aluminium content in the protective coating does not always guarantee the formation of alumina tribofilms since the enthalpy of formation of Cr_2O_3 is lower than that of Al_2O_3.

The oxidation mechanism of AlCrN thin films have been extensively studied in the literature. In the early 90's Hofmann [10] described this process in terms of metal inter-diffusion, originating a typical oxide multilayer structure. This multilayer is explained due to the different diffusivity of the metal species. Although Al_2O_3 is the more stable compound, chromium is the more mobile species and preferentially forms a surface oxide. This chromium oxide inhibits the diffusivity of aluminium, leading to a build-up of aluminium oxide beneath this layer. In turn, the aluminium-rich layer reduces the further out-diffusion of chromium and leads to a slightly increased chromium concentration underneath. Therefore, a structure with a mixed, Cr-rich, Cr/Al oxide layer at the film surface and an Al-rich, Cr/Al oxynitride in the bulk is formed. Lately, Banakh et al. [3] corroborated this model, suggesting the de-nitridation of the film and the formation of a Cr/Al mixed oxide as the oxidation mechanism. More recently, Lin et al. studied the oxidation process of AlCrN films by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) [11]. They concluded that, for the oxidation temperature ranging from 700 to 1050 °C, thermal energy is sufficient to facilitate outward diffusion of nitrogen atoms/ions towards the film surface (de-nitridation). At the same time they proposed that the diffusion of Cr and Al ions outwards and atomic oxygen inwards will promote the formation of a $(Cr, Al)_2O_3$ layer on the film surface, acting as a effective diffusion barrier slowing down the inward diffusion of oxygen.

Therefore, it is well documented that AlCrN coatings show high short-term oxidation resistance up to 1100 °C due to the formation of Cr–Al oxides that are lubricious and have strong diffusion barrier properties against further inward diffusion of oxygen into the films. In

particular Al-rich $Al_{70}Cr_{30}N$ coatings present excellent oxidation resistance due to the formation of alumina at the surface. However, more demanding applications such as gas turbine engines, die casting and moulding industries also require of long-term oxidation resistant coatings that can withstand exposure to oxygen and water vapour containing environments for their entire service lives. Under longer exposure times in air AlCrN coatings suffer a partial depletion of aluminium at the surface and a high diffusion of chromium is promoted. In this case, the formation of surface alumina is inhibited and chromium-rich complex $(Al, Cr)_2O_3$ oxide films are formed due to the solubility of Cr_2O_3 in alumina matrix [12].

In this work we have studied the incorporation of a subsurface TiN layer in the AlCrN coatings. This layer has been shown to act as a diffusion barrier in microelectronics [13–15] and can act as an excellent diffusion barrier of chromium ions. Here, we demonstrate that the TiN barrier promotes the formation of aluminium-rich oxides at the surface of the coating, improving the long-time oxidation resistance of the films. To achieve this goal, we have used Glow Discharge Optical Emission Spectroscopy (GDOES) as a depth profiling technique [16] due to its excellent potential to accurately monitoring composition surface and in-depth changes during oxidation. GDOES has been previously applied with success to study the internal oxidation of carburized steels [17], oxide scale formation in Fe–Cr alloys [18], and oxidation resistance of AlN/CrN superlattices [19] and complex TiAlCrSiYN coatings [20]. In addition, we have compared GDOES results on selected samples with Cross Sectional Scanning emission micrographs (X-SEM).

2. Experimental

2.1. Coating deposition

A front-loading Balzers' rapid coating system (RCS) machine has been employed for the deposition of the coatings in this study. The RCS machine is equipped with 6 cathode arc sources positioned at two different heights. Two of the six sources contained Ti targets and were used to deposit a 0.3 μm thick titanium nitride adhesion layer as well as to deposit a TiN subsurface diffusion barrier. The remaining four sources contained AlCr (70:30) targets which were employed to deposit the main AlCrN layer with a thickness of 3 μm in all the samples. In this study, 20 mm-diameter cold work tool steel coupons were used as substrates. During the deposition, the chamber was back-filled with pure reactive nitrogen to a pressure of 3.5 Pa and the temperature of the substrates was held at approximately 450 °C. Also, a substrate bias voltage of − 100 V was applied to the substrates.

2.2. Multilayer characterisation

GDOES depth profile analysis of the coatings was completed using a Horiba Jobin Yvon RF GD Profiler equipped with a 4 mm diameter copper anode and operating in argon gas [21–23]. In previous works [24,25] Escobar Galindo et al. performed a complete optimization of the operating conditions for the analysis using this GDOES system. By applying a radio frequency discharge pressure of 650 Pa and a forward power of 40 W multilayers in the nanometre range were able to be analyzed. Therefore in this study we have kept fixed these operation settings. The emission responses from the excited sputtered elements were detected with a polychromator of focal length of 500 mm. The optical path of the spectrometer is nitrogen purged. The emission lines used were 130.21 nm for oxygen, 149.262 nm for nitrogen, 156.14 nm for carbon, 371.99 nm for iron, 396.15 nm for aluminium and 425.43 nm for chromium. The chamber was cleaned by sputtering a silicon (100) sample for 20 min prior to the measurements. This procedure minimises the surface contamination of the samples and allows a faster stabilisation of the plasma [26]. No memory effects were observed after this pre-sputtering procedure. Before every

experiment, the samples were flushed with argon during 60 s. This is a typical procedure to remove the contaminants (carbon, oxygen, hydrogen) from the inner walls of the anode prior to the analysis of the sample and has been extensively applied by GDOES users. Molchan et al. have recently proposed [27] that this procedure can be improved by using a low-energy plasma (<5 W) to gently remove contaminant from the surface of the sample. The high etching rates obtained during GDOES analysis resulted in very short experimental times (below 1 min of operation). A collection rate of 200 points/second was used to measure all the samples. Quantified profiles were obtained automatically using the standard Jobin Yvon QUANTUM Intelligent Quantification (IQ) software. The setup was calibrated
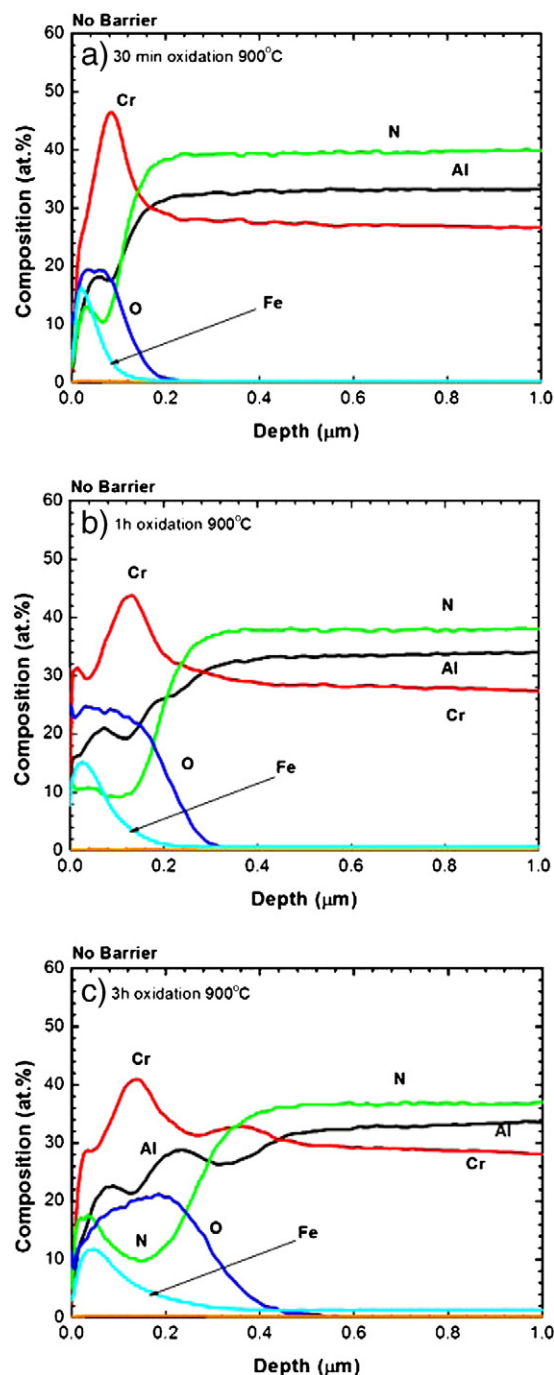

Fig. 1. GDOES profiles of AlCrN coatings without TiN barrier after oxidation in air at 900 °C for a) 30 min, b) 1 h and c) 3 h.