Surface & Coatings Technology 237 (2013) 164–169

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

# High temperature wettability of ion implanted multicomponent CrAlSiN films by molten glass

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ARTICLE INFO

Available online 30 August 2013

*Keywords:*
Ion implantation
Coating
Glass
Wettability
CrAlSiN
Arc evaporation

ABSTRACT

The phenomenon of glass-to-mold sticking is a major problem for industrial glass forming processes. Recently, multicomponent CrAlSiN films attracted considerable industrial interest because of their excellent tribological performance and high oxidation resistance at high temperatures exceeding 800 °C. Metal plasma ion implantation has being successfully developed for further improving wear, corrosion and physical properties of engineering materials. In this study, Mo and carbon ions were implanted into the multicomponent CrAlSiN film by using a metal-plasma ion implantation apparatus. The accelerating voltage of metal ions was set at 40 kV with implantation doses of $1 \times 10^{17}$ ions/cm$^2$ for Mo and $2 \times 10^{17}$ ions/cm$^2$ for carbon. After Mo and carbon ion implantation, molybdenum carbides were found in the implanted layer of CrAlSiN. The wettability of the ion implanted CrAlSiN films by molten glass at 500 °C in controlled air under 1.7 Pa was measured by using a sessile drop method. Mo and carbon ion implanted CrAlSiN films showed the lowest wettability of all tested samples, which is attributed to a reduced adhesion of molten glass at high temperature. The ion implanted CrAlSiN films showed an anti-sticking characteristic superior to the as-deposited CrAlSiN films. Results of this study demonstrate the potential of metal plasma ion implantation in improving the anti-sticking behavior of the CrAlSiN films by molten glass.



## 1. Introduction

Glass thermal forming processes are emerging industrial techniques that can be adopted for high volume manufacturing of spherical and aspherical glass optics, as well as micro glass optical components. This results in remarkably higher production efficiency in comparison to conventional material removal processes. The glass forming tools operate in air at high temperature above 300 °C, and the working surfaces of these tools are exposed to the chemically active molten glass and also subjected to mechanical and thermal cyclic operations. These severe process conditions require critical problems, such as wear, oxidation, and sticking adhesion by molten glass, to be solved which are crucial to the performance and reliability of glass molding dies and the quality of glass products [1–3]. This sticking may result in adhesive wear and damage to either the glass product or the die surface, or both. In practice, non-sticking of glass to the die surface is the key property requirement for glass molding dies. TiN and TiAlN have been applied as hard coatings for molding applications because of their high hardness, wear resistance, and chemical stability [4,5]. However, the degradation of these coatings is known because of the formation of $TiO_2$ on their surfaces [6,7]. Recently, multicomponent coatings based on different metallic and non-metallic elements showed further improvement of coating properties, including hardness and high temperature oxidation resistance [8–16]. Our previous study [17] showed that CrAlSiN films had a low oxidation rate and an anti-sticking characteristic to optical glass at high temperature superior to TiAlSiN and TiAlN coatings.

The non-equilibrium ion implantation technique as a post-deposition surface treatment has been used to enhance physical and chemical performances of thin films. In this study, the metal plasma ion implantation (MPII) process [18,19] was selected for surface modification. Generally, the MPII technique can increase the wear resistance and corrosion resistance of metals and alloys due to carbide and intermetallic compounds formed in the surface layer. The most innovative feature of the MPII process is the implantation of carbon and most metal ions into solid surfaces [20,21]. The surface integrity is usually attainable. R.K.Y. Fu et al. [22] depicted that the mechanical properties of cemented carbides can be improved by the implantation of Mo or W ions. Implantation of nitrogen and carbon ions also improves the tribological performance of nitride coatings by introduction of dense dislocation networks and high residual compressive stresses in the implanted zone [23–26].

In the present study, a cathodic arc ion plating system with lateral rotating arc cathodes was used for the deposition of CrAlSiN coatings on cemented carbide substrates. Mo and carbon ions were implanted into the CrAlSiN coatings by using a MPII system. Wettability is a macroscopic representation of microscopic characteristics for solid surface structure and properties, dependent of surface properties and chemical composition. When a refractory metal nitride is oxidized to form

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0257-8972/$ – see front matter 
http://dx.doi.org/10.1016/j.surfcoat.2013.08.037

a non-reactive oxide, such as molybdenum oxide, adhesion energy decreases, and hydrophobic behavior is observed. Molybdenum oxides and carbides possess some excellent physical and chemical properties, and they are widely applied in the fields of metallurgy, machinery, electronic devices etc. However, few studies focus on the surface wettability of Mo and C ion implanted CrAlSiN coatings. The purpose of this study is to investigate the microstructure and wettability of the Mo and C ion implanted CrAlSiN coatings by molten glass at high temperature.

## 2. Experimental details

Mo and carbon ion implanted CrAlSiN coatings were synthesized on polished cemented carbide samples (K10 with 6 wt.% Co, surface roughness Ra = 0.5 ± 0.2 μm) by using a cathodic arc evaporation system with lateral rotating arc cathodes and an MPII system. The experimental parameters of the deposition and ion implantation process are shown in Table 1. The cathodic arc evaporation system is equipped with lateral rotating arc cathodes. Cr and AlSi (12 at.% of Si) alloy targets were arranged on opposite sides of the chamber wall to deposit the CrAlSiN coating (denoted as sample A). The rotational speed of the substrate holder was fixed at 5 rpm for the sample deposition. In order to improve the adhesion strength, CrN was deposited as interlayer of CrAlSiN at $N_2$ pressure of 2.0 Pa and bias voltage of −150 V. The thickness of the CrN interlayer was 0.2 μm. For the deposition of CrAlSiN layer, the cathode currents of the Cr and AlSi targets were 90 A and 120 A, respectively. By alternating evaporation of chromium and AlSi targets during the rotation of samples, the CrAlSiN coating contained a laminate structure with stacking of Cr-rich and AlSi-rich CrAlSiN layers. The chemical content ratio of Cr/(Cr + Al + Si) was controlled to be 0.4–0.5 in order to obtain optimal mechanical properties [27]. The thickness of the deposited coatings was controlled at 2.2 ± 0.3 μm. After the deposition, Mo ions were implanted into the CrAlSiN films for the Mo implanted sample (denoted as sample B). For the Mo and carbon implanted CrAlSiN films (denoted as sample C), Mo and carbon ions were sequentially implanted into the CrAlSiN films.

The chemical composition of the as-deposited and implanted CrAlSiN coatings was measured by using an Auger electron spectroscope (AES, Ulvac-PHI 700) after 1 min Ar ion etching. A grazing-incidence X-ray diffractometer (XRD, PANalytical X'pert Pro MRD) with Cu radiation at a glancing angle of 0.5° was employed for phase identification. The diffractometer was operated at 40 kV and 1 mA. The residual stresses of the as-deposited and ion implanted coatings were calculated from the $\sin^2\psi$ method by using the grazing-incidence X-ray diffraction [28]. The (220) diffraction peak and 9 ψ tilt angles (0°, 23°, 33°, 42°, 50°, −23°, −33°, −42° and −50°) were used to calculate the residual stresses. The center of each Bragg peak was identified using the Gaussian curve-fitting method. The microstructural characterization of the ion implanted CrAlSiN coatings was performed using a high-resolution transmission electron microscope (FEG-HRTEM, FEI Tecnai $G^2$ 20S-Twin) and a high angle annular dark field (HAADF) scanning transmission electron microscope (STEM, JEOL TEM-3010) equipped with an energy-dispersive X-ray analysis spectrometer (EDS). The surface roughness was measured by a surface profilometer to obtain average roughness heights (Ra). Hardness values of the films were obtained using XP-MTS nano-indentation with a Berkovich indenter, under load–unloading condition, and measured as a function of indenter displacement using continuous stiffness measurement method. The maximum penetration depth was controlled at 150 nm, therefore, the influence of substrate on the measured hardness is negligible.

The wettability test of the ion implanted CrAlSiN coatings by molten glass (K-PG325, glass transition temperature ($T_g$) = 288 °C, Sumita Optical Glass, Inc.) was conducted at 500 °C in controlled air under 1.7 Pa by using a sessile drop method in a vacuum furnace, as shown in Fig. 1. The temperature of the sample was measured by a thermocouple attached to the sample to be within the range of 500 ± 10 °C. In general, the wettability is connected with the area covered by a liquid drop put on a solid surface. It depends on the liquid and surface and it is measured by the contact angle, defined as the angle between the liquid drop and the solid surface. The apparatus essentially consisted of a graphite heater, which was located in a water-cooled vacuum chamber. The chamber was fitted with windows to allow a digital video camera to record the shape of the droplet. The CCD camera coupled to a microscope was used to acquire images of the molten glass drop during the contact angle measurement. The static contact angle was measured (CAM110, Creating Nano Tech. Co.), and the obtained images were analyzed to calculate the contact angle for each sample. 10 measurements were conducted for each sample, and each reported contact angle was the mean value with accuracy less than 1.5°. The diameter of the molten glass droplet was 2.5 mm to make sure that no size effect is influencing the measured contact angle. For the high temperature oxidation experiment, the ion implanted CrAlSiN coatings were annealed at 500 °C in controlled air under 1.7 Pa for 1 h. The heating rate was 5 °C/min and the samples were subsequently furnace-cooled. An empty pure alumina crucible served as a reference.

**Table 1**
Operating parameters of the molybdenum and carbon ion implanted CrAlSiN coatings.

| Parameters | Values |
|---|---|
| Base pressure (Pa) | $5 \times 10^{-3}$ |
| CrAlSiN coating (sample A) | |
| Reactive gas pressure (Pa) | 3.0 ($N_2$) |
| Deposition time (min) | 50 |
| Distance of cathode to substrate (mm) | 150 |
| CAE targets | Cr and $Al_{0.88}Si_{0.12}$ |
| Arc currents (A) | Cr: 90; $Al_{0.88}Si_{0.12}$:120 |
| Bias voltage at ion cleaning stage (V) | −1000 |
| Bias voltage at coating stage (V) | −80 |
| Substrate temperature (°C) | 380–420 |
| Ion implantation | |
| MPII targets | Mo, C |
| Ion implantation doses (ions/cm$^2$) | Mo ion implantation (sample B): Mo: $1 \times 10^{17}$<br>(Mo + C) ion implantation (sample C):Mo: $1 \times 10^{17}$; C: $2 \times 10^{17}$ |
| Acceleration voltage (kV) | 40 |

## 3. Results and discussion

### 3.1. Chemical and microstructure analyses

Table 2 shows the chemical composition of the as-deposited and ion implanted CrAlSiN coatings. From the AES chemical composition measurement, the as-deposited CrAlSiN coatings had 50.8 ± 0.7 at.% of N, 21.9 ± 0.5 at.% of Cr, 18.7 ± 0.8 at.% of Al, and 8.6 ± 0.4 at.% of Si. By applying a higher cathode current on the AlSi target (120 A) than on the Cr target (90 A), the (Al + Si)/(Cr + Al + Si) concentration ratio was higher than 0.5, which is pre-requisite to obtain a dense structure and high hardness [27]. The Mo-implanted CrAlSiN films (sample B) contained 12.5 ± 0.6 at.% of Mo and 34.2 ± 0.5 at.% of N. A lower content of nitrogen was observed due to ion sputtering. After Mo and C ion implantation, the sample C had 13.6 ± 0.5 at.% of Mo, 28.2 ± 0.4 at.% of N and 26.1 ± 0.7 at.% of C. After carbon ion implantation, the Mo content did not change a lot as compared to the Mo ion implanted CrAlSiN film at the same ion dosage of Mo ($1 \times 10^{17}$ ions/cm$^2$). The carbon ion implantation did not sputter Mo in the implanted layer seriously. The sample C had an over-stoichiometry in non-metals (C + N = 54.3 at.%). It would change the microstructure in the ion implanted layer and even influence the wettability of the sample by molten glass.

As shown in Fig. 2(a), the XRD results show that the as-deposited CrAlSiN coatings possess B1-NaCl crystal structure and have multiple orientations of (111), (200), (220) and (311). Fig. 2(b)–(d) show the (111), (200), and (311) diffraction peaks, respectively. After Mo implantation, the primary reflexes of the Mo ion implanted films include (111),