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High temperature wettability of multicomponent CrAlSiN and TiAlSiN coatings by molten glass

Yin-Yu Chang [a,*], Chih-Ming Cheng [b], Yau-Yi Liou [b], Wolfgang Tillmann [c], Fabian Hoffmann [c], Tobias Sprute [c]

[a] Department of Mechanical and Computer-Aided Engineering, National Formosa University, Yunlin 632, Taiwan
[b] Department of Materials Science and Engineering, Mingdao University, Changhua 52345, Taiwan
[c] Department of Mechanical Engineering, Technische Universität Dortmund, Germany

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ABSTRACT

The phenomenon of glass-to-mold sticking is a major problem for industrial glass forming processes. Ternary TiAlN coatings attracted considerable industrial interest because of their excellent tribological performance and high oxidation resistance at high temperatures. Recently, multicomponent CrAlSiN and TiAlSiN coatings have been developed in order to gain high hardness and good thermal stability at temperatures exceeding 800 °C. In this study, CrAlSiN, TiAlSiN and AlTiN coatings were deposited on tungsten carbide substrates by using a cathodic-arc deposition system with lateral rotating arc cathodes. Titanium, chromium and AlSi (12 at.% of Si) cathodes were used for the deposition of CrAlSiN and TiAlSiN coatings. All the deposited CrAlSiN, TiAlSiN and AlTiN coatings showed a B1-NaCl crystal structure. The deposited CrAlSiN and TiAlSiN coatings exhibited nanocrystalline structure and possessed hardness as high as 35–37 GPa after annealing at 700 °C in air. The wettability of the CrAlSiN, TiAlSiN and AlTiN coated tungsten carbides by molten glass at temperatures between 300 °C and 700 °C in controlled air under 1.6 Pa was measured by using an improved sessile drop method. The CrAlSiN showed a low oxidation rate and a non-wetting characteristic superior to TiAlSiN and AlTiN coatings.

1. Introduction

Glass molding dies and forming tools operate in air at high temperature above 300 °C, 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]. 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. In the past decades, TiN, CrN, CrAlN and TiAlN have been applied as hard coatings because of their high hardness, wear resistance, and chemical stability [2–5]. The oxidation behavior of these hard coatings plays an important role in tool applications because they are frequently exposed to oxidative atmospheres at high temperature during their service as wear and corrosion resistant films. In addition, the degradation of TiN and TiAlN coatings is known because of the formation of TiO_2 on their surfaces [6–9]. Addition of Si to either TiN or $Ti_xAl_{1-x}N$ can increase their oxidation resistance compared to $Ti_xAl_{1-x}N$ [10,11]. An amorphous silicon nitride matrix could provide a higher stability against oxidation than that of crystalline metallic nitride. The oxidation behavior of these films depends sensitively on the deposition method and parameters that affect the crystallinity, composition, stoichiometry, and orientation. Recently, multicomponent coatings based on different metallic and non-metallic elements provide the benefit of individual components leading to a further improvement of coating properties. Multicomponent TiAlSiN coatings consisting of nanocrystalline TiAlN and amorphous silicon nitride have been developed to provide good thermal stability at temperatures exceeding 800 °C [12–17]. Several research groups have focused on CrSiN and CrAlSiN coatings for their high hardness and high temperature oxidation resistance [17,18].

In the present study, a cathodic arc ion plating system with lateral rotating arc cathodes was used for the deposition of CrAlSiN, TiAlSiN and AlTiN coatings on tungsten carbide substrates. The purpose of this study is to investigate the microstructure, oxidation behavior and wettability of the CrAlSiN, TiAlSiN and AlTiN coatings by molten glass at high temperature.

2. Experimental details

CrAlSiN, TiAlSiN and AlTiN coatings were deposited on polished tungsten carbide samples by using a cathodic arc evaporation system with lateral rotating arc cathodes. Chromium, titanium and AlSi (12 at.% of Si) alloy targets were arranged on the chamber wall to

* Corresponding author. Tel.: +886 5 6315315; fax: +886 5 6315310.
E-mail address: yinyu@mail2000.com.tw (Y-Y. Chang).

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deposit the CrAlSiN and TiAlSiN coatings. The rotational speed of the substrate holder was fixed at 5 rpm for all samples. A base pressure prior to deposition was less than 1×10^{-3} Pa. TiN and CrN were deposited as interlayers of TiAlSiN and CrAlSiN, respectively, at N_2 pressure of 2.0 Pa and bias voltage of −120 V. The cathode current (70–150 A) of Ti, Cr and AlSi cathodes was used to control the composition of the deposited CrAlSiN and TiAlSiN coatings. The chemical content ratios of Ti/(Ti + Al + Si) and Cr/(Cr + Al + Si) were controlled to be 0.4–0.6 in order to obtain optimal mechanical properties. Substrate bias voltage of −80 V and N_2 pressure of 3.0 Pa were used. For the deposition of CrAlSiN, the cathode currents of Cr and AlSi were 90 A and 120 A, respectively. An AlSi-rich CrAlSiN coating was obtained. For the deposition of TiAlSiN coating, the cathode current of Ti and AlSi was 100 A. For the deposition of AlTiN coating using an AlTi (67 at.% of Al) alloy target, a substrate bias voltage of −80 V and N_2 pressure of 3.0 Pa were used. The temperature of the sample during the deposition was measured by a thermocouple located near the sample and controlled within the range of 400–430 °C. The thickness of the deposited coatings was controlled at 1.4 ± 0.2 μm.

For the high temperature oxidation experiment, the deposited CrAlSiN, TiAlSiN and AlTiN samples were annealed at 800 °C in air for 2 h. The heating rate was 5 °C/min and the samples were subsequently furnace-cooled. An empty pure alumina crucible served as a reference. The wettability test of the CrAlSiN, TiAlSiN and AlTiN coated tungsten carbides by molten glass (K-PG325, glass transition temperature(T_g) = 288 °C, Sumita Optical Glass, Inc.) was conducted at temperatures between 300 °C and 700 °C in controlled air under 1.6 Pa by using a sessile drop method in a vacuum furnace. A CCD camera coupled to a microscope was used to acquire images of the molten glass drop during the contact angle measurement.

The chemical composition of the deposited coatings was determined by using a high resolution electron probe microanalyzer (FE-EPMA, JEOL JXA-8500F). In order to show the depth profile of the sub-surface in the oxidized layer, the samples were identified by using an X-ray photoelectron spectroscope (XPS) and sputtered with Ar ions at a voltage of 3 kV. The texture of the CrAlSiN, TiAlSiN and AlTiN films was examined by X-ray diffraction (PANalytical X'pert Pro MRD) for phase identification. The coating morphology and microstructure were investigated by using a JEOL JSM-7000F high resolution field emission scanning electron microscope (FESEM) and a field emission gun high resolution transmission electron microscope (FEG-HRTEM, FEI Tecnai G^2 20 S-Twin) equipped with an energy-dispersive X-ray analysis spectrometer (EDS). Hardness 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 140 nm, therefore, the influence of substrate on the measured hardness is negligible.

3. Results and discussion

3.1. Microstructure characterization of the as-deposited CrAlSiN, TiAlSiN and AlTiN coatings

From the chemical composition measurement, it showed atomic stoichiometries of $Cr_{0.46}Al_{0.48}Si_{0.06}N$, $Ti_{0.55}Al_{0.40}Si_{0.05}N$ and $Al_{0.64}Ti_{0.36}N$ for the deposited CrAlSiN, TiAlSiN and AlTiN coatings, respectively. The nitrogen content of all the deposited coatings was 50.7–54.2 at.%. As shown in Fig. 1, the XRD results showed that all the deposited coatings possess B1-NaCl crystal structure and have multiple orientations of (111), (200), (220) and (311). It corresponded with the results of Rafaja et al. [19], which showed that the cubic structure remained with (Al + Si)/(Ti + Al + Si) content ratio lower than 0.6. For the CrTiAlSiN deposited on Si substrates, K. Ichijo et al. [20] showed that the cubic structure changed to a hexagonal structure with increasing (Al + Si)/(Cr + Ti + Al + Si) content ratio higher than 0.7. The hardness

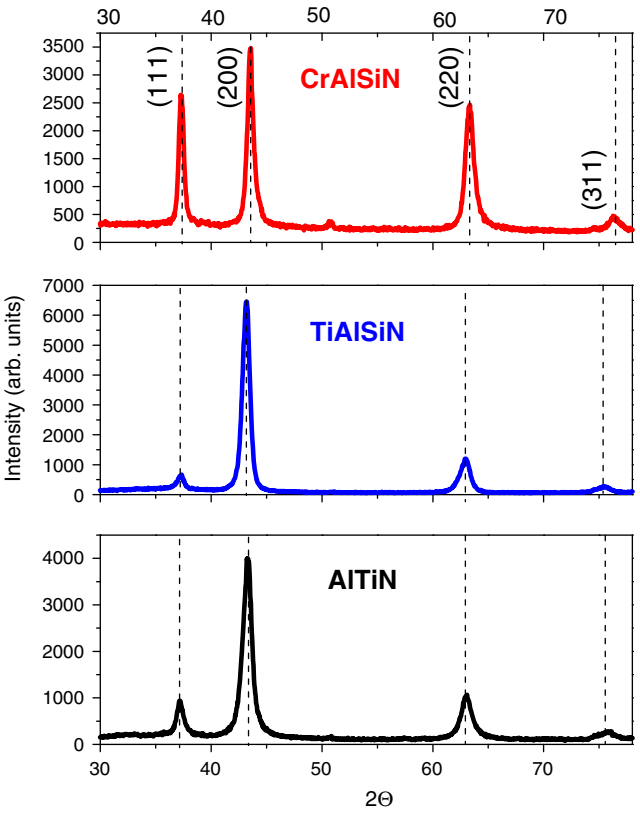

Fig. 1. Glancing angle X-ray diffraction spectra of the $Cr_{0.46}Al_{0.48}Si_{0.06}N$, $Ti_{0.55}Al_{0.40}Si_{0.05}N$ and $Al_{0.64}Ti_{0.36}N$ coatings deposited by a cathodic-arc evaporation method.

decreased lower than 30 GPa when hexagonal phases were present in the deposited coatings. In this study, the $Ti_{0.55}Al_{0.40}Si_{0.05}N$ deposited with (Al + Si)/(Ti + Al + Si) content ratio of 0.45 only showed B1-NaCl crystal phases and no hcp-AlN phase was found. The $Cr_{0.46}Al_{0.48}Si_{0.06}N$, $Ti_{0.55}Al_{0.40}Si_{0.05}N$ and $Al_{0.64}Ti_{0.36}N$ possessed high hardness of 37 ± 2 GPa, 35 ± 2 and 33 ± 2 GPa, respectively. The hardness of the $Cr_{0.46}Al_{0.48}Si_{0.06}N$ and $Ti_{0.55}Al_{0.40}Si_{0.05}N$ still remained as high as 35–37 GPa after annealing at 700 °C in air, while the hardness of $Al_{0.64}Ti_{0.36}N$ decreased to 31 GPa. It showed the $Cr_{0.46}Al_{0.48}Si_{0.06}N$ and $Ti_{0.55}Al_{0.40}Si_{0.05}N$ possessed higher thermal stability and abrasive wear performance than $Al_{0.64}Ti_{0.36}N$. The stress-free lattice parameters of the $Cr_{0.46}Al_{0.48}Si_{0.06}N$, $Ti_{0.55}Al_{0.40}Si_{0.05}N$ and $Al_{0.64}Ti_{0.36}N$ calculated from XRD pattern were 0.414 nm, 0.420 nm and 0.421 nm, respectively. In comparison with intrinsic lattice parameters of TiN (0.424 nm) and CrN (0.417 nm), the lattice parameters of the deposited coatings indicated the existence of solid solution in these coatings.

The cross-sectional TEM micrograph showed a weakly columnar structure of the deposited $Cr_{0.46}Al_{0.48}Si_{0.06}N$ and $Ti_{0.55}Al_{0.40}Si_{0.05}N$ coatings. Fig. 2(a) shows the HRTEM image of the deposited $Ti_{0.55}Al_{0.40}Si_{0.05}N$ with an interlayer of TiN. The $Ti_{0.55}Al_{0.40}Si_{0.05}N$ layer possessed much denser structure than TiN due to the presence of Al and Si to form nanocomposite structure [21,22]. Fig. 2(b) shows the cross sectional TEM micrographs of $Cr_{0.46}Al_{0.48}Si_{0.06}N$ coating. The top figures showed high resolution TEM micrograph and the insets show diffraction patterns of area A and B obtained by making the Fourier transform. The HRTEM observation demonstrated the nanocrystalline structure of the deposited $Cr_{0.46}Al_{0.48}Si_{0.06}N$ and $Ti_{0.55}Al_{0.40}Si_{0.05}N$ coatings.

3.2. Oxidation resistance and wettability of the CrAlSiN, TiAlSiN and AlTiN coatings at high temperature

Annealing at high temperature of the deposited coatings was directed towards understanding both oxidation resistance and microstructural