Anti-sticking Re-Ir coating for glass molding process

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ABSTRACT

The sticking of glass to the dies is a critical problem in glass molding process which limits the quality of products and lifespan of mold. Three kinds of protective coatings, including monolayer Re, Ir and Re/Ir multilayer were designed to mitigate the sticking and to improve the lifespan of mold. The interaction between barium crown optical glass and WC/Co mold materials (Co-10 at. %) with these three protective coatings was investigated. The results demonstrated that anti-sticking performance of multilayer coating is better than that of monolayer Re, Ir coating. The addition of interfaces resistance in multilayer is the main reason for improvement of anti-sticking ability of multilayer Re/Ir film. It was also verified that the Re/Ir multilayer coating possesses the highest nanohardness (24.5 GPa), as well as the largest wetting angle (168.1°).

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1. Introduction

Due to increasing market demand for glass components with high precise and reduced size, the glass lenses are required to be more diversified in sizes and shapes, better form accuracy/surface roughness, as well as more competitive in price. Conventional glass grinding and polishing techniques have advantage in producing spherical glass lenses. However, it costs considerable money and time to produce complex optical components such as micro lenses and aspheric lenses.

The introduction of glass molding process (GMP) to the precision optics industry has made it possible to manufacture high precision aspherical optical components at a high volume [1–5]. During glass molding process, the mold surface directly contacts with glass at an elevated temperature higher than glass transition temperature (T_g) [6]. Simultaneously, it also suffers from mechanical and thermal cyclic loads. Thus the chemical reaction easily occurs at the contact area between glass and mold, which leads to a premature mold failure.

Only particular materials such as tungsten carbide and silicon carbide can withstand such a harsh environment and meet the hardness requirement involved in GMP. However, without a protective coating, those materials are also not suitable for the application of GMP due to the interfacial reactions. In order to reduce the interfacial reactions, various coatings have been employed to protect mold, such as hard carbon thin films [7–13] and precious metal alloy films [8,14–16], including platinum-iridium (Pt-Ir), rhenium-iridium (Re-Ir) and so on. Previous studies [15] pointed out that a specially developed design for particular glasses was the most effective way to optimize the performance of

protective coating. Commercial dense barium crown optical glass has been widely used as aspherical glass lens in China. In this study, different protective coatings based on Re/Ir were prepared and the interfacial reactions for all kinds of coatings were compared and analyzed using high temperature wetting tests, in which the coatings directly contacts dense barium crown optical glass. Based on the results, a preferable coating design for mold of dense barium crown optical glass was proposed.

2. Experimental details

Re/Ir coating was deposited onto tungsten carbide (WC) substrate using RF magnetron sputtering technique. Cemented tungsten carbide substrates (WC-10 wt. % Co) with dimensions of $\Phi 15 \times 3 \text{ mm}^3$ were grounded and polished using 0.5 μm diamond paste. They were subsequently cleaned by the ion sources of 1250 V for 15 min to improve the adhesion with the substrate. Three types of protective coatings, monolayer Re, monolayer Ir and multilayer Re/Ir were generated. The substrate holder was heated to 300 °C. Ar flow rate was controlled at 30 sccm and the working pressure was $3.2 \times 10^{-1} \text{ Pa}$. Before protective

Table 1

The major constituents and T_g temperature of optical glass.

Glass	Diameter/mm	T _g /°C	T _s /°C	nd	vd	Composition
D-ZK3	7.6	511	546	1.58913	61.15	SiO ₂ 30–40% B ₂ O ₃ 20–30% CaO 0–10% Al ₂ O ₃ 0–10% BaO 10–20% Sb ₂ O ₃ 0–10%

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Fig. 1. SEM image of the cross-section of the monolayer (a) Re and (b) Ir protective coating.

coating deposition, a Ta interlayer with a thickness of 80 nm was deposited with a fixed input power of 120 W. The Re and Ir protective coatings were deposited with a fixed input power of 120 W and 100 W, respectively. Multilayer Re/Ir coating of 40 layers were achieved by alternative

Fig. 3. SEM image of the cross-section of Re/Ir multilayer coating.

deposition. The anti-sticking capacity of monolayer and multilayer coatings was studied employing the sessile-drop technique (Wetting test, DATAPHYSICS, Germany). The surface morphology of coatings were observed using field emission scanning electron microscope (FESEM, ZEISS SUPRA 55, Japan). Energy Dispersive Spectrometer (EDS, JSM-6510LA) attached to the scanning electron microscopy (SEM, JSM-6510A, JEOL, Japan) was employed to detect the elements diffused into its counterpart during the experiment. The electron accelerating voltage is 10 kV. The surface nanohardness was measured using a nano-indentation tester (Nano Indenter XP). The surface roughness and peak-valley were investigated using DEKTA 150 (U.S.A). Each experiment was repeated five times for more accurate results with a standard deviation.

During the high temperature wetting test, the D-ZK3 optical glass balls, which are dense barium crown optical glass manufactured by CDGM GLASS Co., LTD, P. R. China, were placed onto the WC/Co substrate in an environment of vacuum. The pressure was controlled at 10^{-3} Pa while the temperature was around 631 °C (120 °C above T_g of optical glass, 511 °C) for 30 min. Then the contract angle of optical

Fig. 2. SEM images and EDS analysis of the residual reactant left at the contacted area of optical glass with monolayer Re (a) SEM (b) EDS, Ir (c) SEM (d) EDS protective coatings after wetting tests.

Table 2

Surface quality and mechanical properties of Re, Ir monolayer and Re/Ir multilayer coatings.

Protective coatings	Surface accuracy		Mechanical properties	
	Ra/nm	PV/nm	Young's Modulus/GPa	Hardness/GPa
Monolayer Re	3.5 ± 0.7	42.9 ± 29.9	338.2 ± 36.1	11.7 ± 1.4
Monolayer Ir	4.1 ± 0.4	35.9 ± 11.6	304.5 ± 37.1	12.9 ± 1.5
Multilayer Re/Ir	2.9 ± 0.6	20.8 ± 25.8	627.0 ± 21.3	24.5 ± 1.2

glass on coating was measured. The major constituents and Tg of optical glass are listed in Table 1. The constituents of glass can be basically divided into three categories namely network formers, network

modifiers, and intermediates. Network formers (e.g. SiO₂, B₂O₃, etc.) are the main structure of the glass. Network modifiers (e.g. K₂O, Na₂O, CaO, BaO, etc.) including mostly the oxides of IA, IIA elements play a role of breaking up the network and intermediates. The intermediates (e.g. Zn, F, Al₂O₃, etc.) act as network formers or network modifiers. In order to make it easy to mold the optical glass at a low temperature, the molding glasses normally have a high proportion of network modifiers.

3. Results and discussion

Fig. 1 shows the SEM image of the cross-section of the monolayer (a) Re and (b) Ir protective coating. The microstructure of monolayer Re and Ir protective coating exhibits a typical columnar structure. The thickness of protective coating is 400 nm. The interlayer Ta with a thickness of 80 nm not only acts as a diffusion barrier, but also plays an important role in enhancing adhesion between protective film and substrate.

Fig. 2 shows the SEM images and EDS analysis of residual reactant around contact area after wetting test of single Re, Ir films. Ca, Ba elements of glass were detected at the contact area of Re film (Fig. 2a and b), which indicated that network modifiers elements were easier to diffuse into the coatings [15]. It is because that the dissociation energy of CaO and BaO are 257 and 260 kcal/g-atom, respectively, which are lower than that of Si (424 kcal/g-atom) and B (356 kcal/g-atom). Thus CaO and BaO are easier to be decomposed [17]. Subsequently, the escaped Ca and Ba elements condensed on the surface of the coating and formed CaO and BaO. The presence of black scraps and Si at the contact area of Ir film indicated the adhesion of glass on Ir film (Fig. 2c and d). The melting of glass and coating may be attributed to mechanical locking caused by the tensile stress existed in the Ir film.

To improve the anti-sticking performance of the protective coating, the Re/Ir multilayer film was designed. Fig. 3 illustrates the microstructure of multilayer film which exhibits the coexistence of a columnar and nano-laminated structure. The Re/Ir multilayer coating contains twenty bilayers of Re/Ir. The thickness of each Re/Ir bilayer is nearly 50 nm.

The roughness and peak-valley value of different protective coatings are listed in Table 2. The nanohardness of Re/Ir multilayer film is much higher than that of monolayer Re, Ir, which can be explained by the Hall-Petch reinforcement theory [18]. All of the deposited films show a roughness (Ra) less than 5 nm and P-V less than 150 nm, which meets the requirement of precision mold surface accuracy.

It is well known that high temperature induces inter-diffusion between coating and glass. The severer the reaction is, the smaller the wetting angle is [10]. Fig. 4 shows the wetting angle of optical glass on various protective coatings. Monolayer Re has the smallest wetting angle of 134.2°, while multilayer Re/Ir coating has the largest wetting angle of 168.1°. Previous studies [19,20] showed that ordered nano-

Fig. 4. High temperature wetting angle of optical glass in liquid state on different protective coatings surfaces (a) monolayer Re, (b) monolayer Ir, (c) multilayer Re/Ir.

Fig. 5. The wetting angle of optical glass on different protective coatings at 631 °C.

Fig. 6. Surface appearance of optical glass gobs after high temperature wetting tests with different coatings: (a) monolayer Re coating, (b) monolayer Ir coating, (c) multilayer Re/Ir coating.

Table 3

Optical glass state and dimension of contact area after the high temperature test with various coatings.

Different coatings	Optical glass state after wetting test	Dimension of the glass contact area/mm
Monolayer Re	Translucent	7.2
Monolayer Ir	Transparent	6.1
Multilayer Re/Ir	Transparent	1.7

structure enhanced the bonding between Re and Ir at interface, making it difficult for Ca, Ba of glass network modifiers elements to penetrate in protective films, and alleviate adhesion of glass. The diffusion resistance [21,22] of monolayers are mainly caused by grain boundaries. The addition of interfaces increased the diffusion resistance of multilayer, preventing elements of substrate from initiating the interfacial reaction.

The wetting angles of substrates with and without coatings are illustrated in Fig. 5. The wetting angle of WC (10 wt. % Co) is lower than 130°. Monolayer Re, Ir has a contact angle larger than 140°, whereas multilayer coating exhibits larger wetting angle. This indicates that Re/Ir multilayer coating can offer better protection than Re, Ir monolayer films.

The surface appearance of optical glass after high temperature wetting tests was also evaluated (Fig. 6). In general, the glass loses its transparency and turns into translucent as the reaction progresses [8]. The glass on monolayer Re coating is translucent, while the glasses on monolayer Ir and multilayer Re/Ir coating stay transparent.

The more violent the reaction is, the larger the dimension of the glass contact area is. The dimension of the contact area after the high temperature wetting tests is shown in Table 3. The glass on monolayer Re coating has the largest contact dimension of 7.2 mm. However, the glass on Re/Ir coating has the smallest contact dimension of 1.7 mm. The result is consistent with the result of the high temperature wetting test. The SEM

image and EDS analysis of residual reactant left on Re/Ir multilayer coatings after high temperature wetting test are shown in Fig. 7.

Compared to the results shown in Fig. 2, anti-sticking performance has been significantly improved for Re/Ir multilayer coating. There are no glass elements left on the contact surface. It means that Re/Ir multilayer coating has better anti-sticking performance than Re, Ir monolayer coating for the optical glass. The Re/Ir multilayer is considered as an improved protective coating for molding the optical glass.

4. Conclusions

The anti-sticking ability of monolayer Re, Ir and multilayer Re/Ir with barium crown optical glass was evaluated by high temperature wetting tests at 631 °C ($T_g + 120$ °C). Multilayer films exhibited better anti-sticking ability than monolayer coatings, which is probably due to the addition of interfaces resistance. The Re/Ir multilayer films show a nanohardness of 24.5 GPa, which is much higher than those of monolayer Re (11.7 GPa) and Ir (12.9 GPa). Ca and Ba elements with low dissociation energy in network modifiers play an important role in triggering the reaction between protective coatings and glass. Optical glass after wetting test with Re/Ir multilayer coating has the smallest contact area of 1.7 mm. The Re/Ir multilayer coating shows the largest wetting angle of 168.1°, which indicates that Re/Ir multilayer coating possesses a better anti-sticking ability. Based on the results, Re/Ir multilayer film is considered as the preferable candidate for the mold of barium crown optical glass.

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Fig. 7. SEM image (a) and EDS analysis (b) of residual reactant left on Re/Ir multilayer coatings after high temperature wetting test with optical glass.

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