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Adhesion-Free Mold-Stamping of Meniscus Inorganic Glass Lens Using N-Doped SiC Dies

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Abstract

Viscous inorganic glass works had a risk of adhesion to mold surface above the glass transition temperature during their mold-stamping process. Silicon carbide (SiC) mold was surface-modified to have massive carbon supersaturated layer via the high density plasma nitrogen doping. Upsetting process was utilized to describe the adhesion-free deformation on the contact surface of nitrogen-doped SiC dies to glass works. Mold-stamping process was also employed to demonstrate that non-spherical lens was net-shaped without adhesive wear and cracking.

1 Introduction

An adhesive wear or galling phenomenon, has been identified as the most essential issue in the process tribology to deteriorate the product quality and to induce many difficulties in manufacturing (Dohda 2015). Plastic strains and process temperature had significant influence on this adhesive wears as stated in (Dohda 2015, 2021). However, no engineering methods have been developed to make galling-free forming and forging of easy-to-adhesive inorganic work materials such as stainless steels, titanium and titanium alloys, and, oxide glasses (Sun, 2022). Various tool-steel dies and ceramic dies suffered from severe galling to deteriorate their formability (Kihara, 2019). A silicon carbide (SiC) was identified as a die substrate for mold-stamping of high Tg (glass transition temperature) glassy work materials because of its high heat resistance and thermal conductivity (Chen, 20). This new die material is still never free from galling or adhesion wear.

Massive carbon supersaturation (MCS) into tool steel dies plays a role of in situ formation of carbon based tribofilms onto the contact surface to stainless steel and titanium work materials in dry forging and fine blanking (Aizawa, 2023, 2024-August). The titanium eye-glass frame parts were net-shaped by dry forging together with their higher qualification under lower energy consumption. The titanium

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and stainless steel gears were also fine-blanked under MQL (Minimum Quantity Lubrication) without adhesive wear. After LCA (Life Cycle Assessment) in (Aizawa 2026-April), the environmental burdens by ejection of acid mixture wastes were completely diminished by saving the intermediate steps in manufacturing. This MCS to SiC dies was also useful to accommodate the in situ formation of carbon tribofilm to dry cold forging of titanium and titanium alloys (Aizawa, 2024-October). However, MCS with excess carbon contents had a risk to deteriorate the toughness of MCSed SiC die especially under hot forging. A new MCS process was proposed by nitrogen doping to SiC dies for hot mold stamping of glass works (Aizawa 2025, 2026-May).

In the present paper, a role of nitrogen doping into SiC dies for MCS is described by microstructural analysis. In situ formation of carbon based tribofilm during hot forging is analyzed by Raman spectroscopy. A boron silicate glass preform is shaped to optical element without adhesive wear onto the MCSed SiC dies. Meniscus N-doped SiC dies are also utilized to demonstrate that a nonspherical lens is hot formed and self-demolded without adhesive wear.

2 Materials and Methods

Hot CVD (Chemical Vapor Deposition) system is introduced to yield a thick SiC coating substrate. Plasma immersion nitriding system is also used to make nitrogen doping into this SiC die. Hot forging system was utilized for near-net shaping of boron silicate glass works.

2.1 Hot CVD Process

A monolithic SiC coating substrate with the thickness of 7 mm was synthesized using the hot CVD system, as schematically depicted in Fig. 1. A sintered SiC block with an average porosity of 0.5% was prepared as a substrate to build up a thick SiC coating via the thermal CVD process at 1700 K for 125 ks. Silicon chloride and methane gases were selected as the silicon and carbon sources, respectively. They were mixed with hydrogen gas and introduced using a flow rate of 500 mL/min to the thermal reactor in the present CVD system. After cooling down in the nitrogen gas atmosphere, the SiC-coated SiC block was directly cut using a diamond saw, polished using chemical buffing, and, laser-machined to shape the SiC-coated SiC dies.

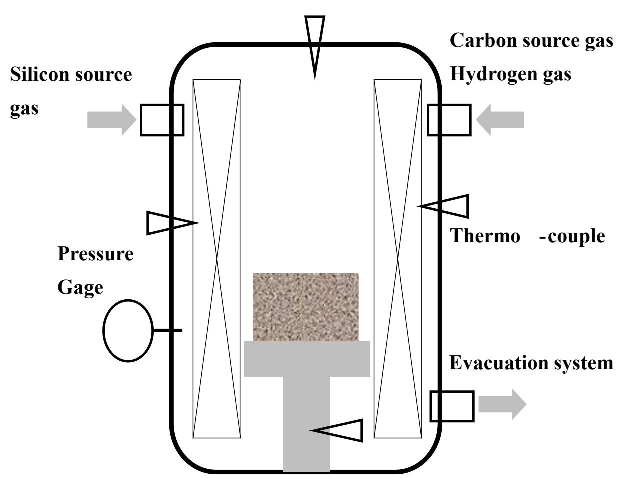

Figure 1: A schematic view on the hot chemical vapor deposition system to fabricate a thick SiC coating die-substrate.

2.2 Nitrogen-Doping Process

The RF (Radio-Frequency) – DC (Direct Current) plasma nitriding system with the use of the hollow cathode was utilized for nitrogen doping (or N-doping) to SiC coating dies as illustrated and shown in Fig. 2. SiC die was set in this hollow cathode and immersed into the nitrogen – hydrogen plasma sheath. After N-doping at 473 K for 21.6 ks by 50 Pa under the nitrogen and hydrogen gas flow rates by 160 mL/min and 30 mL/min, the N-doped SiC die was cooled down to RT under the nitrogen gas atmosphere.

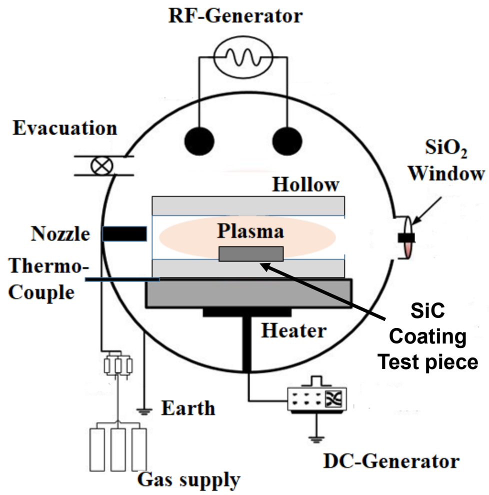

Figure 2: A schematic view on the nitrogen doping process by plasma immersion nitriding system.

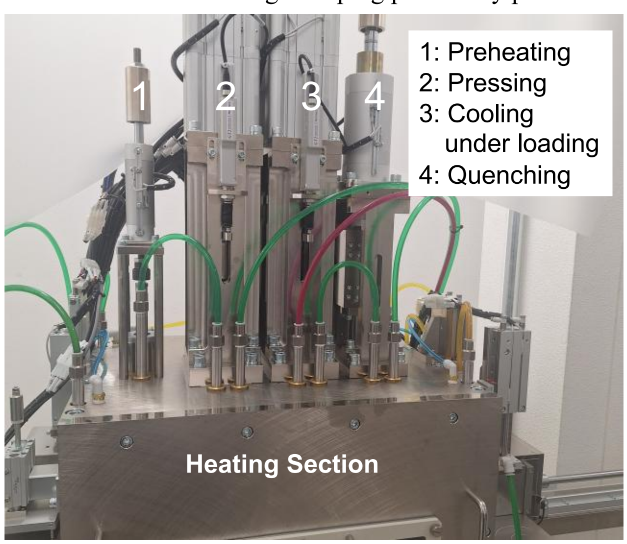

Figure 3: Four-step procedure in the mold stamping process.

2.3 Hot Mold-Stamping Process

CNC (Computer Numerical Control) hot stamping system was employed for near-net forming the boron silicate glass preform at 843 K by 300 N. As depicted in Fig. 3, heating, stamping and cooling processes were performed at each step using each stamping unit in the whole system. In the practical mold-stamping operation, a SiC die-set including the glass work materials was first preheated at the 1st step in Fig. 3 before pressing of glass work at the 2nd step. After pressing, the die-set was cooled down below T_g under the controlled loading sequence. In this 3rd step, the thermal transient must be precisely controlled to significantly reduce the risk of cracking and deterioration of glasses. Then, at the 4th step, the die-set was quenched to the ambient temperature to pick the glass product up.

3 Results

3.1 Preparation of Thick SiC Coating Die

A thick SiC coating die for mold-stamping of meniscus lens was prepared by laser machining and polishing the hot-CVD SiC substrate. As shown in Fig. 4, the core-cavity was shaped into the SiC mold to yield a non-spherical lens via the mold-stamping above T_g.

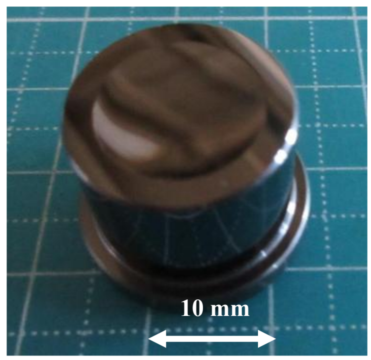

Figure 4: Meniscus SiC die prepared for mold-stamping.

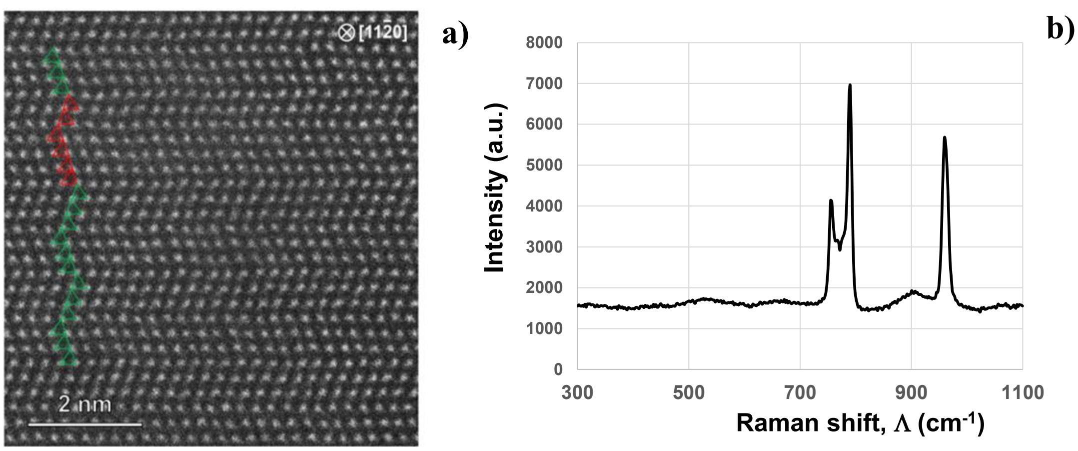

Figure 5: Microstructure of monolithic SiC coating die. a) STEM (Scanning Transmission Electron Microscopy) image on the SiC die, and b) Raman spectrum of SiC die surface.

STEM (JOEL, Tokyo, Japan) was utilized to analyze the crystalline structure of CVD coated SiC die. As stated in (Nakaya, 2025), a silicon carbide has polymorphous structure such as cubic, hexagonal and rhombohedral structures with various periodicity. As shown Fig. 5a, this SiC coating die has hexagonal and six-stacked structure. This 6H SiC has more stable crystalline structure than 3C-SiC. To be noticed, this 6H-structured SiC die has higher thermal conductivity than conventional 3C-structured SiC substrates. It is preferable to reduce the thermal stress transients at the vicinity of interface between the SiC die and the glass works during cooling process in Fig. 3. Figure 5b shows the measured Raman spectrum on the SiC coating die surface. This spectrum was characterized by three peaks; e. g., double peaks at $\Lambda = 767$ cm^{-1} and 798 cm^{-1}, and, a single peak at $\Lambda = 964$ cm^{-1}. After (Bauer, 2009), these peaks prove that this SiC die has 6H structure. These analyses in the above reveal that thick SiC coating die surface has stable 6H-structure.

3.2 Nitrogen doping to SiC die

The N-doped SiC dies were prepared by the plasma immersion nitriding system as depicted in Fig. 2. SEM (Scanning Electron Microscopy) – EDS (Electron Dispersive x-ray Spectroscopy) were used to make microstructural analysis and to describe the distribution of nitrogen and carbon solutes. As shown in Figs. 6a to 6c, the SiC grains have grain boundaries where the carbon agglomerates partially distribute.

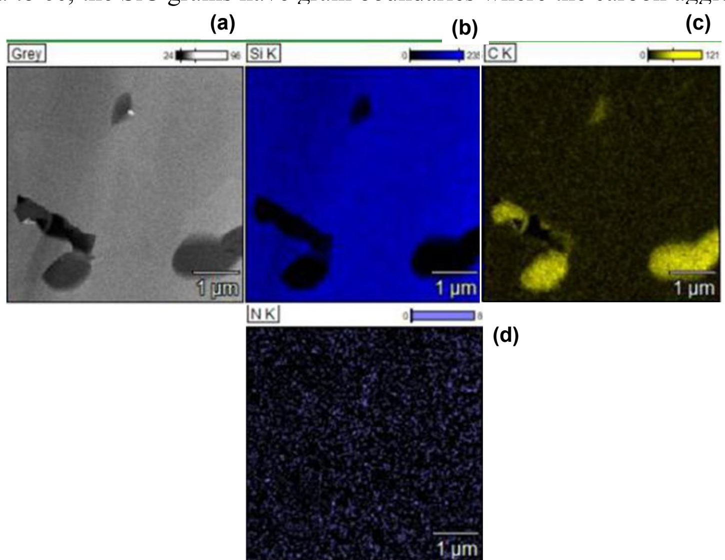

Figure 6: SEM and EDS analysis at the center of cavity of SiC die. a) SEM image at the center of cavity, and b-d) silicon, nitrogen and carbon mapping, respectively.

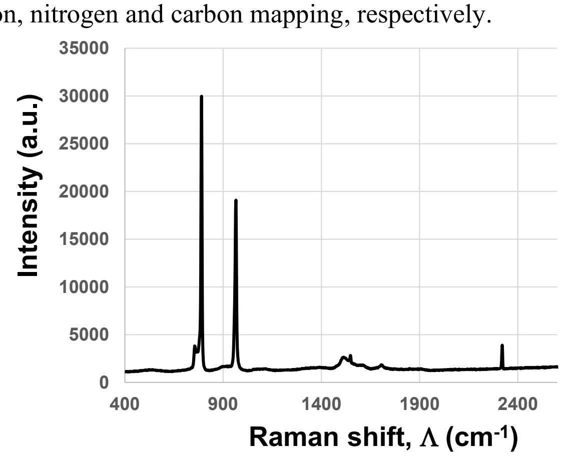

Figure 7: Raman spectrum at the center of cavity.

Since no carbon solutes are present in the 6H-structured SiC before N-doping, this carbon agglomerates along the grain boundaries must be synthesized during N-doping. On the other hand, the impinged nitrogen atoms homogeneously distribute into SiC grains as shown in Fig. 6d. This implies that nitrogen atoms substitute the carbon sites in SiC and that carbon were exiled from the inside of SiC grains to grain boundaries to agglomerate there by themselves. Raman spectrum measured at the surface of N-doped SiC die was shown in Fig. 7. Besides for the characteristic double and single peaks to 6H-SiC, a sharp peak pair were detected around $\Lambda = 1600\ cm^{-1}$ and $2300\ cm^{-1}$. After analyses in (Li, 2023) and (Rabia, 2019), the sp1-structured carbon atoms, or, carbon wires, were synthesized along the gran boundaries after N-doping to SiC. No D- and G-peaks were detected to characterize the amorphous carbon state.

3.3 Hot mold-stamping

A boron silicate glass preform was utilized for hot mold-stamping. Figure 8 depicts the glass work after mold-stamping by using the meniscus SiC mold. A cylindrical glass work was shaped to a glass lens in the reduction of thickness by 30% without adhesive damage.

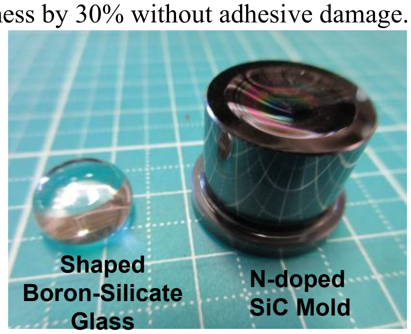

Figure 8: Mold-stamping of boron-silicate glass work with the use of meniscus SiC mold.

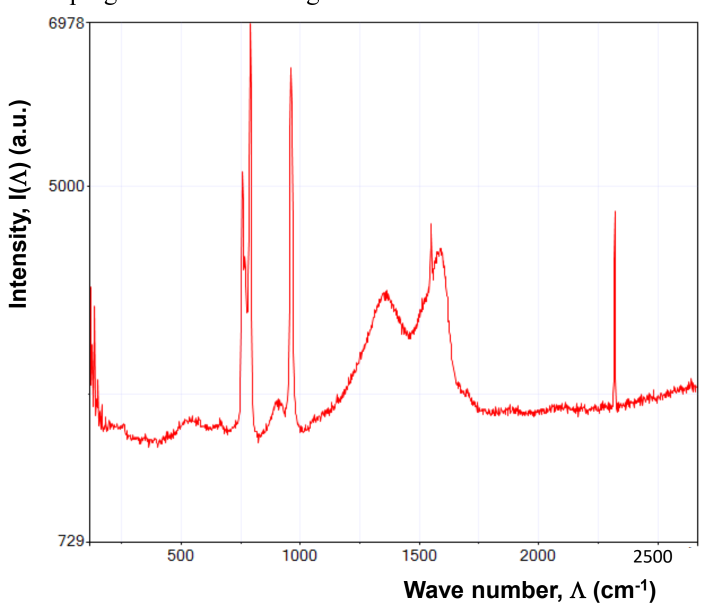

Figure 9: Raman spectrum measured at the center of contact surface between the glass preform and the N-doped SiC die.

3.4 Contact surface

Raman spectroscopy was utilized to describe the contact surface condition between the glass work and the N-doped SiC die. Figure 9 depicts the Raman spectrum measured at the center of contact surface. In addition to the characteristic peaks to 6H-SiC and the intense peak pair around $\Lambda = 1600$ cm^{-1} and 2350 cm^{-1} for sp1-structured carbon, a broad peak pair was detected at $\Lambda = 1320$ cm^{-1} and 1600 cm^{-1}. After precise analysis in (Fukue, 2024), (Haddock. 2016) and (Yuan, 2025), amorphous carbon film was synthesized on the contact surface. Since no peaks were detected at $\Lambda \sim 1320$ cm^{-1} and 1600 cm^{-1} outside of the contact surface, the amorphous carbon films must be in situ formed only onto the contact surface during mold-stamping. This carbon film works as a solid lubricant on the contact surface between the glass work and the N-doped SiC, so that no adhesion wear takes place on the contact surface.

4 Discussion

During hot mold-stamping process, the glass work deforms visco-elastically in contact to the die surface and fills into the mold cavities. This process has lots of chances for glass works to adhere onto the mold surfaces. Using the N-doped SiC molds, the glass works are prevented from direct contact to glass preform surfaces. This adhesion-free forming has three superiorities to conventional mold-stamping. The molded products demold by themselves from the mold . The glass work accurately fills into the mold cavity; the geometric accuracy is improved after single-shot operation. Little residual stresses are left in the formed glass product, so that its optical properties are also improved.

Raman spectroscopy before and after mold-stamping proves that amorphous carbon film is in situ formed only on the contact surface. No carbons are isolated from stable 6H-structured SiC. The amorphous carbons in film come from the sp1-structured carbon wires through the grain boundaries. Different from the carbon base coatings such as DLC coatings, this in situ formed tribofilm is supported by these carbon wires at the vicinity of SiC die surface.

The isolated carbon solute content by substitution of impinged nitrogen atoms exiled from SiC grain structure and agglomerate along the grain boundaries of monolithic SiC grains. Each carbon solute aligns as an inhomogeneity along the narrow grain boundary. This self-organization of carbon agglomerates drives the sp1-structure at the vicinity of SiC die surface.

In case of mold-stamping the high Tg glass preforms, the die material must be designed to have high heat resistance, engineering durability and thermal conductivity. The N-doped SiC provides the most suitable selection to production of high Tg optical elements including the silica lens without loss of the high heat resistance and thermal conductivity whish is original to monolithic 6H-structured SiC.

5 Conclusion

The nitrogen doping technique accommodates the in situ solid lubrication to monolithic SiC dies for hot forming of inorganic glass preforms to optical elements without adhesive and abrasive wears. Due to no adhesion of glass works to contact die surface, the glass work demolds by itself from the die. In situ formation of amorphous carbon film onto the contact surface is responsible for this adhesion-free hot forging. Different form amorphous carbon coatings, this tribofilm is formed from the N-doped SiC grain boundaries with sp1-strcture carbon solutes. This tribo-system works even in hot adhesion-free forming of high T_g glass preforms and imprinting the well-designed microtextures onto the glass product surface.

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