Thermal conductivity and mechanical properties of soda-lime glass with interfacially connected Au layer fabricated via sputtering and spark plasma sintering

Lei Liu* and Kenji Shinozaki*ab

*National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Japan; bPRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Japan

ABSTRACT
Glass is used for various substrates, but its thermal conductivity and mechanical properties are lower than ceramics. In this paper, we propose a new process for fabricating heat conduction paths using a small amount of metal. Au was coated on soda-lime glass powder via ion sputtering for 0, 20, 40, and 60 min, and the resultant powders were sintered via spark plasma sintering. The Au nanolayers precipitated between the soda-lime glass domains and were well connected to each other. Their thickness increased with increasing sputtering time. The thermal conductivity was enhanced by 10% with a small amount of precipitation less than 0.28 vol%, mainly resulting from the well-connected highly conductive Au nanolayers. The hardness and toughness were hardly affected by the precipitation of Au.

1. Introduction
Oxide glasses are transparent and formable, and thus have various applications. They have also been actively studied as matrices for dispersing various functional ceramics, as sealants, and as glass substrates in various fields [1–3]. However, they have disadvantages, such as lower thermal conductivity and lower toughness than ceramics. Owing to the random structure of glass, the free path of phonons cannot be increased significantly, making it difficult to improve the thermal conductivity significantly. In addition, glass becomes brittle owing to the stress concentration near the crack tip and the lack of toughening mechanisms, such as plastic deformation in metals [4–6]. The toughening of glass can be realized via the enhancement of the crack propagation resistance and the alleviation of stress concentration near the crack tip from the viewpoint of fracture mechanics. The addition of secondary phases, such as ceramic, fiber, and metal microparticles, contributes to the enhancement of toughness, and the toughening mechanisms (martensitic transformation of ZrO2, crack deflection and crack bridging, pull-out, etc.) are variable and depend on the additives[7]. Recently, the incorporation of metal nanoparticles has proven to be a promising method for improving the fracture toughness of glass through plastic deformation, crack deflection, and crack bridging [8–14].

Soda-lime glass is a typical commercial glass, but its low fracture toughness significantly limits its structural applications. Metal nanoparticles have been incorporated to increase fracture toughness [9,11,12]. Recently, we synthesized metal-nanoparticle-precipitated glasses with interfacial heterogeneity by sintering soda-lime glass particles with Ag particles deposited near the surface. In this glass, Ag nanoparticles are connected in a three-dimensional network like grain boundaries in ceramics, which improves the fracture toughness and thermal conductivity. However, this method is limited to metal particles that can be synthesized via ion exchange and heat treatment reduction. In this paper, we propose a new process using ion sputtering to produce the same morphology with various metal particles. Ion sputtering is a simple method for depositing metals with relatively uniform sizes[15], and the sputtering process causes limited damage to the specimen. In addition, the thickness of the metal can be controlled by changing the coating time. We produced metal-nanoparticle-coated glass particles by sputtering powders while stirring, and the powders were sintered to produce an interfacial precipitation of metal nanoparticles. The procedure is illustrated in Figure 1.

Au has high thermal conductivity and high ductility, and its valence can be controlled easily in the ion sputtering process. Therefore, a comparative study can be conducted under the simplest possible conditions. In this study, we investigated the effects of
interfacial Au layer connected in a three-dimensional connection on the thermal conductivity and fracture toughness.

2. Experimental procedure

Soda-lime glass (average particle size 22 μm, UNITIKA Ltd., Japan) was used as the starting material. Au coating was performed using an ion sputter (E-1030, Hitachi, Japan) with a vibratory rotation unit under a discharge current of 20 mA in an argon atmosphere (vacuum of 1 Pa), and the sputtering times were 0, 20, 40, and 60 min. The resultant powders were consolidated via spark plasma sintering (SPS) under a pressure of 50 MPa. The original and Au-coated soda-lime glass powders were densified at 600 and 700°C for 10 min, respectively, and the heating/cooling rates were 50°C/min. The sintered samples from glass powders coated for 0, 20, 40, and 60 min are denoted as SA-0-SPS, SA-20-SPS, SA-40-SPS, and SA-60-SPS, respectively.

The density was measured using the Archimedes method. The phase identification of the sintered glass samples was performed via X-ray diffraction (XRD) with Cu Kα radiation. Field-emission scanning electron microscopy (FE-SEM; SU-8000, Hitachi, Japan) operated at 1 keV was conducted to observe the microstructure of the sintered glass samples, and the distribution of elements was determined using energy-dispersive X-ray spectroscopy (EDS). To obtain enough signal, FE-SEM for EDS was operated at 15 keV. The Young’s modulus was measured using an ultrasonic technique. The Vickers hardness and fracture toughness were determined using indentation methods, and a load of 4.9 N was applied for 10s. The toughness values were obtained based on the following equation: [16]

$$K_C = 0.016 \left( \frac{E}{H_V} \right)^{1/2} \left( \frac{P}{C^{1/2}} \right)$$

where \( P, H_V, E, \) and \( C \) are the load, Vickers hardness, Young’s modulus, and crack length, respectively. The thermal conductivity was determined via the laser flash method (TC-7000, ULVAC-RIKO) using samples with the dimensions of \( \Phi10 \times 2 \) mm. Disk-shaped samples with the dimensions of \( \Phi10 \times 2 \) mm were used to measure the thermal diffusivity (\( \lambda \)) and specific heat (\( C_p \)) via a laser flash method (TC-7000, ULVAC-RIKO). The thermal conductivity (\( \kappa \)) was calculated using the equation \( \kappa = \lambda C_p \rho \).
3. Results and discussion

Elemental distribution of Au coated glass particles is shown in Figure 2. White spots on glass particles can be seen in the SEM, but their shape changes irregularly during observation and disappears when the voltage is reduced, indicating that they are caused by charge-up. From EDS, it can be seen that Au is coated over the entire surface of all glass particles.

Fully densified (relative density of 99.5%) soda-lime glass was fabricated at 600°C, whereas the Au-nanoparticles-incorporated soda-lime glass was densified at 700°C. The XRD patterns of the SA-0-SPS, SA-20-SPS, SA-40-SPS, and SA-60-SPS samples are shown in Figure 3. A broad peak was observed for the sintered soda-lime glass. The Au-spattered samples showed peaks attributed to Au. The peak intensity increased with increasing coating time. Assuming that the relative densities of all the samples were the same, the volume fractions (f) were estimated using the following equation: \( d_s = f d_c + (1 - f) d_g \)

Here, \( d_s \), \( d_c \), and \( d_g \) are the densities of the sample, crystal, and glass, respectively. The volume fractions were determined to be 0.08 vol%, 0.20 vol%, and 0.28 vol% for the SA-20-SPS, SA-40-SPS, and SA-60-SPS samples, respectively. By combining the sputtering and SPS methods, for the first time, we synthesized glasses with interfacial precipitation of well-connected metal phases with extremely small volume fractions.

The low-magnification SEM images of the SA-20-SPS, SA-40-SPS, and SA-60-SPS samples are shown in Figure 4(a-c), and the corresponding high-magnification SEM images are presented in Figure 4(d-f).

**Figure 3.** XRD patterns of the SA-0-SPS, SA-20-SPS, SA-40-SPS, and SA-60-SPS samples.

**Figure 4.** (a,b,c) Low-magnification and corresponding (d,e,f) high-magnification SEM images of the SA-20-SPS, SA-40-SPS, and SA-60-SPS samples.
The XRD (Figure 3) and EDS (Figure 4) results indicate that the white part is Au distributed between the soda-lime glass grains. As shown in Figure 4(a), Au nanoparticles were precipitated in the SA-20-SPS sample, but the precipitated Au domains were not connected well. With increasing sputtering time, the Au domains became coarser and connected, as shown in Figure 3(c). Au nanoparticles were distributed near the interface between glass particles, and the coarsening near the triple junctions of the glass particles was more evident (Figure 4(e)). Figure 5 shows the elemental distribution in the SA-40-SPS sample, and the Au nanoparticles were discretely distributed near the interface.

The micrograph around the Vickers indentation and the obtained Vickers hardness and fracture toughness of the Au-incorporated samples are shown in Figure 6 (a-c). The incorporation of Au nanoparticles did not influence the Vickers hardness or fracture toughness. Recently, we reported that Ag nanoparticles distributed homogeneously near the interfaces with the glass particles improved the fracture toughness[9]. However, the discrete distribution of Au nanoparticles resulted in a slight decrease in the fracture toughness.

Figure 5. Elemental distribution in the SA-40-SPS sample.

Figure 6. Optical microscope images of the Vickers indentations for the (a) SA-0-SPS and (b) SA-40-SPS samples. (c) Vickers hardness and fracture toughness of the Au-incorporated samples.
Conclusions

In this study, Au layers were successfully incorporated into soda-lime glass via ion sputtering and subsequent SP5 at 700°C. The thickness of Au nanolayer increased with increasing sputtering time. The Au layers precipitated between the glass domains and were connected to each other three dimensionally. The hardness and toughness were hardly affected by the precipitation of Au. Although the Au precipitation was very small (less than 0.28 vol%), the thermal conductivity was improved by 10% owing to the well-connected highly conductive Au network in the glass.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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ORCID

Kenji Shinozaki  http://orcid.org/0000-0002-0967-8710

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