Selective component nanoparticle precipitation from Invar 42 during metal particle migration by laser irradiation in silica glass

Hirofumi Hidai, Tatsuki Iwamoto, Souta Matsusaka, Akira Chiba, Tetsuo Kishi and Noboru Morita

ARTICLE HISTORY
Received 4 November 2016
Accepted 9 April 2017

ABSTRACT
Laser illumination on a nickel sphere in silica glass has shown to migrate the sphere towards the light source with a nickel nanoparticle precipitated around the sphere. The selective nanoparticle precipitation by Invar 42 sphere migration in silica glass is reported. An Invar sphere is implanted into glass by laser illumination of an Invar foil. In addition to the sphere migration in glass, stripes are formed along the trajectory of the sphere. The stripes consist of metal nanoparticles with a diameter of several hundred nanometres. Nanoparticles precipitated on the laser-illuminated side are composed only of nickel and those on the non-illuminated side are composed of nickel and iron alloys. The reason for the difference in components is discussed.

KEYWORDS
metal nanoparticles; silica glass; laser; Invar 42

1. Introduction

The optical properties of glasses can be controlled by doping with metal nanoparticles. Nanoparticle-doped glasses are popularly fabricated by adding a metal oxide into the silicate melt and deoxidising by heat treatment [1]. Other techniques have also been proposed; for example, ion exchange by dipping into molten salt [2], electric-field-assisted ion exchange [3,4], ion implantation [5] and selective deoxidation by laser illumination [6,7]. However, multiple-component nanoparticle implantations in glass have not yet been reported.

The authors have previously reported that laser illumination is able to migrate a metal sphere in glass towards a light source [8]. Laser illumination is reported to heat the metal sphere while the surrounding glass is also heated and softened. The softened glass enables the metal sphere migration. The migration was reported to be caused by the non-uniformity of the interfacial tension between the metal and glass caused by the laser-induced temperature gradient [9,10]. Nickel nanoparticle precipitation accompanying the migration in silica glass has also been reported [11].

CONTACT
Hirofumi Hidai
hidai@faculty.chiba-u.jp
Department of Mechanical Engineering, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan. TEL/FAX: +81-43-290-3227

© 2017 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group
This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
In this paper, we report a selective nanoparticle precipitation by Invar 42 sphere migration in silica glass. A nickel nanoparticle was precipitated on the laser-illuminated side, and a nickel and iron alloy nanoparticle was precipitated on the non-illuminated side. The component analysis results and the reason for the difference in the components of the nanoparticles are provided.

2. Experimental procedure

The experimental set-up was similar to that described in [11]. The sample was stacked as follows: 5-mm-thick silica glass, 5-mm-thick borosilicate glass (Pyrex®, Corning 7440, Corning Inc.), 10-µm-thick Invar 42 foil (628,173, Nilaco Corp.) and silica glass to ensure a good contact between the borosilicate glass and the Invar 42 foil. The glass sheets were fixed with a jig and located on an XYZ stage. A continuous wave (CW) fibre laser (RFL-C020/A/2/A, WuhHan Raycus Fiber Laser Technologies Co., Ltd.) with a wavelength of 1064 nm illuminated the silicate glass side of the sample. The laser beam was focused with a lens (focal length: 40 mm, NYTL-30-40PY1, SIGMA KOKI Co., Ltd). A CCD camera was placed on the side of the sample and sphere migration was observed in the orthogonal direction of the optical axis. A band pass filter (centre wavelength: 440 nm) was placed in front of the CCD camera.

The Invar sphere implanted glass was cut and polished to intersect the sphere, and carbon was evaporated to obtain electric conductivity. The Invar sphere and precipitated particles were analysed with SEM-EDX (scanning electron microscope with electron-dispersive X-ray spectroscopy; JSM-7001F, EDX, JED-2300, JEOL Ltd., Tokyo, Japan).

3. Results and discussion

A sphere was implanted into the borosilicate glass by laser illumination of the Invar foil. Further laser illumination migrated the sphere towards the light source and penetrated into the silica glass. Along with the sphere migration in the silica glass, stripes were formed in the same manner as the case when a nickel foil was used [11]. A snapshot photograph taken during the migration is shown in Figure 1. The laser power was 12.4 W.

Figure 1. Snapshot of the Invar 42 sphere and precipitated particles around the sphere: (b) is a snapshot taken 5 s after that taken for (a).
and the beam diameter was calculated to be 184 μm. Compared with the nickel foil [11], no clear differences were observed although the stripes were thinner.

To analyse the Invar sphere and stripes, the sample was cut and polished to intercept the Invar sphere. An optical image and backscattered electron images are shown in Figure 2(a) and Figure 2(b–d), respectively. Metal spheres with a diameter of ∼10 μm

Figure 2. Cross-sectional image of Invar sphere in silica glass: (a) optical micrograph; (b)–(d) SEM micrograph of cross section of Invar 42 sphere Ni sphere; (c,d) the magnified images marked in (b); (e) X-ray spectrum obtained at the position marked in (b); (f) atomic components obtained from (e); (g) atomic components of the metal sphere and particles.
and particles were recognised where the stripes were observed by the optical micrograph. The Invar sphere and the particles marked by the rectangle in Figure 2(b) are magnified in Figure 2(c,d). This result shows that the stripes consisted of particles with diameters of several hundreds of nanometres.

The Invar sphere and precipitated particles were analysed by EDX. The result is shown in Figure 2(e) and the analysed points are marked in Figure 2(b). For a comparison, the spectra of silica glass and the Invar foil are also plotted. Silicon, oxygen, iron, nickel and carbon that were used as a coating for the SEM observation are detected.

The elemental composition calculated from the EDX spectrum is shown in Figure 2(f). The carbon component was eliminated. The quantity of the elements obtained from silica glass and Invar was matched with the original components. At the sphere (marked by A), the component ratio of the nickel was larger and that of iron was smaller compared with the foil. In addition, silicon was detected. The silicon did not originate from the surrounding silica glass, because the diameter of the sphere (~10 μm) was much larger than the spatial resolution of the EDX (~1 μm). In addition, if silicon in the glass was detected, oxygen was also detected, but no oxygen was detected at point A. To clarify when the sphere contained silicon, the sphere just after implantation into the borosilicate glass was also analysed. The elemental components are indicated in Figure 2(f) noted as ‘sphere in BG’. The result indicates that silicon was contained just after implantation.

As silicon was contained in the glass just after the implantation, the silicon was contained while the Invar foil was melted and implanted into the glass. Ellingham’s diagram shows that the Gibbs’s energy was decreased in the order of silicon, iron and nickel. Therefore, the reduction of silicon by the oxidation of iron and nickel was not explained. In addition, oxygen was not contained in the sphere and where the deoxidised oxygen was located was unclear. The mechanism of the implantation from the Invar foil to the borosilicate glass was also unclear and clarification of the process was attempted.

The metal sphere contained silicon; hence, the precipitated particle was also expected to contain silicon. The precipitated particles were smaller than the spatial resolution of the EDX; hence, the components of the surrounding silica glass were also detected. It was proposed that the ratio of silicon and oxygen in the surrounding silica glass was the same as that in the raw silica glass. In Figure 2(f), the amount of silicon derived from the surrounding silica glass was expressed as ‘silicon in glass’ and the remaining silicon was proposed to be derived from the metal particles and was expressed as ‘silicon in Invar’. To understand the elemental components of the metal particles, the elemental components without oxygen and silicon in the glass are expressed in Figure 2(g).

The sphere in borosilicate glass contains a larger ratio component of nickel and smaller ratio component of iron than those in the Invar foil. The sphere in silica glass contains a larger ratio of the nickel component. The particles on the laser-illuminated side or the side of the sphere migration (marked by B, C and D) were composed of nickel and contained a small amount of silicon. In contrast, the particles in the path where the metal sphere had passed (marked by E) contained iron and the ratio of the components was almost the same as the Invar sphere in silica glass (marked by A). The atomic component ratio (Fe/Ni) of the particle marked by E was 13%. Note that the glass in the vicinity of the area marked by E was also analysed and the components were the same as those in silica glass; hence, it was confirmed that iron was not contained in the glass and the components of the particle are shown in Figure 2(g). Several particles were also analysed. Iron
and nickel were detected from the central zone (marked by F and G in Figure 2(b), respectively) where the metal sphere had passed. The atomic component ratio of Fe/Ni was 13%–15%. Only nickel was detected in the peripheral zone (marked by D, H, I and J). No differences were observed in each stripe.

The difference of the components was discussed. Only nickel was detected in the particle on the laser-illuminated side (marked by B and C) and in the peripheral zone (marked by D, H, I and J); therefore, nickel can be detected in the region far from the Invar sphere. The laser illumination heated the sphere. The metal ions and/or non-valent metals were dissolved into the silica glass and were diffused. The metals were precipitated in the area far from the sphere. These mechanisms were discussed by using other silicate melts, because only a few reports have reported the diffusion and precipitation in silica glass.

Metal diffusion is subjected to Fick’s laws and the diffusivity $D$ follows the Arrhenius relationship, that is, $\log D$ is linearly correlated with the reciprocal temperature. Experimental results have been reported, for example, silicon and oxygen diffusion in silica glass [12] and metal-ion diffusion in silicate melts [13]. The diffusivity of Ni$^{2+}$ and Fe$^{3+}$ in silicate melts at 800–1300 °C was reported to have similar values [13]. The value of $\log D$ (in m$^2$/s) was 10 (Fe$^{3+}$) and 10.1 (Ni$^{2+}$) at 1300 °C from Figure 6 in [11]. It was not revealed whether the diffusing metal exhibited ion valence or was a non-valent metal. In addition, the diffusivity data of any of the metal ions or atoms have not been reported.

The precipitation of cristobalite in silica glass has been reported [14]. The crystal growth rate $u$ was expressed as

$$u = f \frac{D}{a} [1 - \exp(-\Delta G/k_B T)].$$  \hspace{1cm} (1)

Here $f$ is the fraction of surface sites on the crystal which can participate in crystal growth, $D$ is the self-diffusion coefficient across the glass–crystal interface, $a$ is the jump distance, $k_B$ is the Boltzmann constant and $T$ is the temperature. $\Delta G$ is expressed as

$$\Delta G = \frac{H_m(T_m - T)}{T_m}. \hspace{1cm} (2)$$

$H_m$ is the latent heat of fusion per molecule of cristobalite, $T_m$ is the melting temperature of the separated crystal.

From Equations (1) and (2), the size of the cristobalite particle was increased when the temperature was lower than the melting point and was decreased when the temperature was higher than the melting point. The observation using a microscope validated the result.

Iron particle precipitation in a silica glass has been reported. A film consisting of SiO$_2$ and Fe$_2$O$_3$ was deposited by sputtering SiO$_2$ and Fe$_2$O$_3$ simultaneously. Annealing the film resulted in the precipitation of iron nanoparticles. The size of the particles increased from 5 to 50 nm with increasing the temperature [15]. The melting point of iron is 1538 °C and the result that the particle size increases with increasing the temperature up to the melting point is consistent with the results obtained from cristobalite.

The thermal spike model is known to explain the mechanism of the particle size change [16]. In brief, the metal nanoparticles in a silica matrix are heated after a swift heavy ion is
implanted. Calculations elucidate that the smaller particles would be heated more. The small particles are heated above the boiling point and dissolve into the surrounding silica matrix. The dissolved metal promotes the growth of the surrounding larger nanoparticles by the Ostwald ripening process. The larger nanoparticles are not heated enough to reach the boiling point and are, therefore, able to grow. In this study, laser illumination heated the sphere to above the melting temperature and the metal ion/atom diffused into the glass. The boiling point of iron (3135 K) is lower than that of nickel (3186 K); therefore, iron should be detected far from the path of the sphere based on the thermal spike model. However, nickel was detected far from the path of the sphere. Hence, this observation cannot be explained by the thermal spike model.

As mentioned above, no clear difference between the diffusivity of Ni\(^{3+}\) and Fe\(^{2+}\) was observed. From Equation (2), the difference in the precipitation between iron and nickel was expected to arise from the difference in the melting points. The melting point of nickel (1728 K) is lower than that of iron (1811 K) and could be precipitated at the low temperature area far from the metal sphere (points B, C, D, H, I and J). The Invar sphere passed near to points E, F and G and was sufficiently heated, where iron was also precipitated and an alloy was formed.

The calculations confirmed that the temperature gradient was large; for example, the temperature difference between the laser illuminated and non-illuminated sides was larger than 300 K [9,10]. In addition to self-diffusion, the Soret effect may affect the diffusion. However, the temperature dependence of the solubility of metal ions and non-valent metals has not been reported and sufficient fundamental data have not been obtained for understanding the phenomena.

The size of the precipitated particles did not grow to more than several hundred nanometres even under long-term laser illumination. Further growth was prevented by the laser heating. The spot size of the laser beam was calculated to be 184 \(\mu\text{m}\) at the Invar sphere; hence, the laser also illuminated the precipitated particles. When the particles grew to several hundred nanometres, the particles absorbed the laser irradiation and were heated so that growth was ceased.

Considering the above discussion, the selective precipitation mechanism was explained as follows. The laser illumination heated the Invar sphere. The Invar sphere was heated to above the melting point. The metal ions or non-valent metals were dissolved into the glass. At the same time, the non-uniformity of the interfacial tension caused the metal sphere migration. Explaining the situation at each point on the optical axis, the temperature was increased closer to the Invar sphere. Nickel diffused from the sphere and began to be precipitated. In addition to nickel, iron was also precipitated, as the Invar sphere was approached and the temperature increased. After passing the metal sphere, the temperature decreased and precipitation ceased. Nanoparticles composed of nickel and iron were formed.

4. Conclusion

In summary, selective nanoparticle precipitation by Invar 42 sphere migration in silica glass was reported. The components of the nanoparticle precipitated by the Invar sphere were investigated. The diameter of the nanoparticles was several hundred nanometres. Nickel nanoparticles were precipitated on the laser-illuminated side, and nickel and iron
alloy nanoparticles were precipitated on the non-illuminated side. By using this phenomenon, laser illumination of the metal sphere with temperature control enables selective nanoparticle precipitation in glass.

**Disclosure statement**

The authors declare that they have no financial competing interests.

**Funding**

Support by the Japan Society for the Promotion of Science under a grant-in-aid for scientific research [grant number 24656096] is gratefully acknowledged.

**References**

[1] Zayat M, Einot D, Reisfeld R. In-situ formation of AgCl nanocrystallites in films prepared by the sol-gel and silver nanoparticles in silica glass films. J Sol-Gel Sci Technol. 1997;10(1):67–74.

[2] Ramaswamy RV, Srivastava R. Ion-exchanged glass waveguides: a review. J Lightwave Technol. 1988;6(6):984–1000.

[3] Matsusaka S, Kobayakawa T, Hidai H, et al. Laser micro-machinability of borosilicate glass surface-modified by electric field-assisted ion-exchange method. J Phys Conf Ser. 2012;379:012035.

[4] Matsusaka S, Naotomo M, Hidai H et al. Formation of a buried silver nanowire network in borosilicate glass by solid-state ion exchange assisted with forward and reverse electric fields. Appl Phys Lett. 2014;105(10):103102.

[5] Gonella F. Nanoparticle formation in silicate glasses by ion-beam-based methods. Nucl Instrum Methods Phys Res Sect B. 2000;166–167:831–839.

[6] Qu S, Qiu J, Zhao C, et al. Metal nanoparticle precipitation in periodic arrays in Au2O-doped glass by two interfered femtosecond laser pulses. Appl Phys Lett. 2004;84(12):2046–2048.

[7] Marquestaut N, Petit Y, Royon A, et al. Three-dimensional silver nanoparticle formation using femtosecond laser irradiation in phosphate glasses: analogy with photography. Adv Funct Mater. 2014;24(37):5824–5832.

[8] Hidai H, Yamazaki T, Itoh S, et al. Metal particle manipulation by laser irradiation in borosilicate glass. Opt Express. 2010;18(19):20313–20320.

[9] Hidai H, Matsushita M, Matsusaka S, et al. Moving force of metal particle migration induced by laser irradiation in borosilicate glass. Opt Express. 2013;21(16):18955–18962.

[10] Hidai H, Matsushita M, Matsusaka S, et al. Moving force of metal particle migration induced by laser irradiation in borosilicate glass: erratum. Opt Express. 2014;22(21):25194–25195.

[11] Hidai H, Matsushita M, Matsusaka S, et al. Laser-induced nickel sphere migration and nanoparticle precipitation in silica glass. Opt Mater Express. 2015;5(5):1006–1015.

[12] Ferreira Nascimento ML, Zanotto ED. Diffusion processes in vitreous silica revisited. Eur J Glass Sci Technol B. 2007;48(4):201–217.

[13] Claussen O, Russel C. Diffusivities of polyvalent elements in glass melts. Solid State Ion. 1998;105(1–4):289–296.

[14] Wagstaff FE. Crystallization Kinetics of Internally Nucleated Vitreous Silica. J Am Ceram Soc. 1968;51(8):449–453.

[15] Masubuchi Y, Sato Y, Sawada A, et al. Crystallization and magnetic property of iron oxide nanoparticles precipitated in silica glass matrix. J Eur Ceram Soc. 2011;31(14):2459–2462.

[16] Ghosh S, Kumar H, Singh S P, et al. Subsecond annealing of advanced materials: annealing by lasers, flash lamps and swift heavy ions. Cham: Springer International Publishing; 2014. Chapter 6, Sub-nanosecond thermal spike induced nanostructuring of thin solid films under swift heavy ion (SHI) irradiation; p. 107–121.