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Author(s)	Ueda, Mikito; Matsunaga, Hajime; Ohtsuka, Toshiaki et al.
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RAPID PUBLICATION

Diffusion of Tl Ions into Glass Treated by Molten Salt Ion Exchange and Hydrogen Reduction

Mikito Ueda[1], Hajime Matsunaga[1,*], Toshiaki Ohtsuka[1] and Toshiharu Yamashita[2]

[1]*Research Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan*
[2]*Kawazoe Frontier Technology, Tokyo 193-0826, Japan*

To investigate the diffusion behavior of Tl ions, glass was immersed in $TlNO_3$–KNO_3 molten salt at 753 K for various lengths of time. The Tl ions embedded in the glass were then reduced to metallic Tl nano-particles by hydrogen at 803 K for 1 h. The depth of the ion exchange layer down to about 140 μm in the glass was found to be proportional to a square root of the length of immersion time. It was suggested that the ion exchange process is controlled by the diffusion of Tl ions from the surface to the inside. Reduction of Tl ions to metallic Tl with the hydrogen gas occurred only at the surface down to 4 μm. The concentration profile of the metallic Tl is discussed by nucleation-nucleus growth and the diffusion of Tl ions from deeper areas. [doi:10.2320/matertrans.M2011343]

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1. Introduction

Metallic nano-particles of gold, silver, and copper dispersed in glass have been used for fabricating color and functionally useful glass like optical filters. This functional glass has been produced by three methods: ion implantation,[1–3] sol–gel coating,[4] and ion exchange treatment.[5,6] Ion exchange treatment offers advantages over the other method, due to the simple process and lower cost. Dubiel *et al.*, reported that Ag nano-particles could be formed in soda glass using ion exchange treatment.[7] Varma *et al.*, reported on the mechanism of the ion exchange between Ag ions from molten salt and Na ions from glass in $AgNO_3$–$NaNO_3$ molten salt by FTIR.[8] Maurizio *et al.*, studied the ion exchange process of Tl from molten salt and Na from borosilicate glass in $AgNO_3$–$NaNO_3$ molten salt containing $TlNO_3$.[9]

Elsewhere the authors have applied ion exchange treatment to make a functional glass containing Tl nano-particles,[10] where molten sulfate salt was used as the medium of ion exchange, however, the originally flat glass surface became scabrous uneven with the ion exchange treatment. We have recently established that a flat glass surface can be maintained by using molten nitrate salt rather than sulfate salt.[10]

In the study here, diffusion of Tl ions during the formation of Tl nano-particles in glass in the ion exchange treatment and in the subsequent hydrogen reduction is discussed.

2. Experimental

The glass used for the ion exchange was B-270 super white 2 mm thick provided by Schott Desag AG (Germany), and composed of (mass%): 68-SiO_2, 9-Na_2O, 8-K_2O, 7-CaO, 2-BaO, 4-ZnO, 1-TiO_2, and 1-Sb_2O_3. The glass sheets were cut into 20 mm × 20 mm squares, fixed in a stainless steel holder, and immersed in a molten salt bath containing a mixture of 10 mol% $TlNO_3$ (Kanto chemicals, 99.5 mass%) and 90 mol% KNO_3 (Kanto chemicals, 99 mass%) for durations of 8, 24, 48, 96, and 196 h all at 753 K, and the glass sheets were vibrated with longitudinal oscillations while immersed in the molten salt. After the immersion, the glass sheets were cooled to room temperature at very slow cooling rates to prevent cracking and then washed with distilled water to remove solidified salt from the surface. To reduce the Tl ions that had penetrated into the glass matrix by ion exchange to metallic Tl nano-particles, the glass specimens were placed in a hydrogen atmosphere for 1 h at 803 K.

After the reduction by hydrogen, the samples were mechanically polished with emery paper No. 1500 and then polished by a cross-section polisher (JEOL SM-9010). The cross-sections of the glass samples were observed with a transmission electron microscope (TEM, JEOL 2010-FASTEM) and a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6500F). A qualitative analysis was conducted by an Energy Dispersive Spectroscope (EDS, JEOL 2010-FASTEM).

3. Results and Discussion

3.1 Ion exchange treatment of the glass

The glass samples are immersed in the molten $TlNO_3$ and KNO_3 mixture, results in an exchange between the cations in the glass and Tl ions in the molten salt. The glass samples subjected to this ion exchange at 753 K for 8–192 h do not color. Our previous paper reported that the ion exchange mainly occurs between Tl ions in the molten salt and Na ions in the glass[10] and in this experiment, diffusion distance of Tl for the glass was investigated.

The results of the line analysis for Tl in the cross-section of the glass samples are shown in Fig. 1 as a function of the length of immersion time. Figure 1 shows that the concentration of Tl at the surface is about 7 mol% independent of the immersion time, and the concentration gradients assume flatter slopes for longer immersion durations. The diffusion distance of Tl reaches 142 μm in 192 h immersion. The relationship between the diffusion distance of Tl in the glass samples and immersion time is shown in Fig. 2, where the depth of diffusion is plotted against the square root of the immersion time. The depth of diffusion is shown to be

*Graduate Student, Hokkaido University

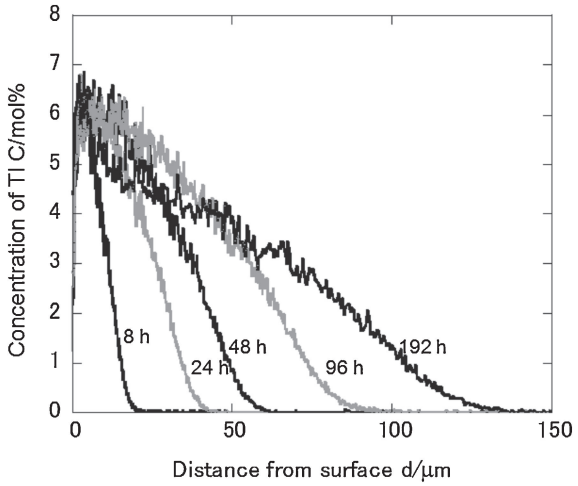

Fig. 1 Concentration profiles of Tl in the glass after ion exchange treatments from 8 to 192 h at 753 K.

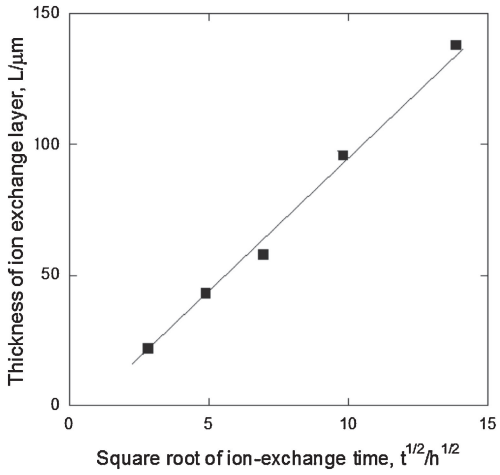

Fig. 2 Relationship between the thickness of the ion exchanged layer of the glass and the square root of the duration of the ion exchange.

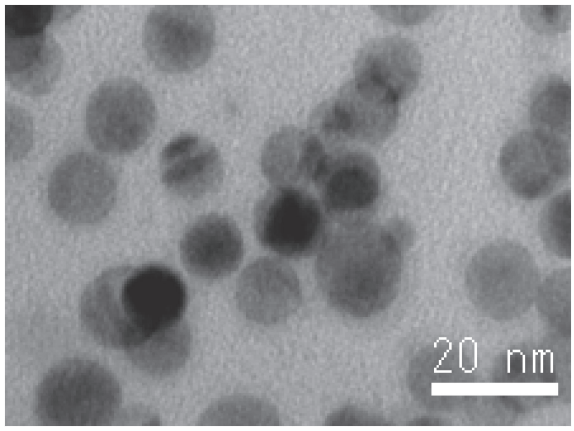

Fig. 3 TEM image of suraface of glass after ion-exchange treatment at 753 K for 48 h and hydrogen reduction for 1 h.

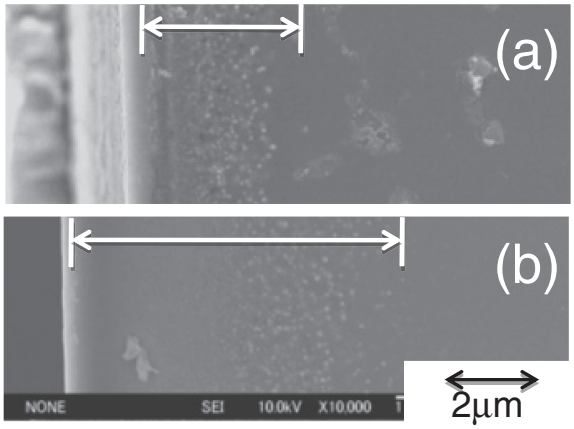

Fig. 4 Cross sectional SEM images of the surface regions of the glass after ion exchange treatment for 48 h and (a): hydrogen reduction for 1 h; (b): hydrogen reduction for 5 h.

proportional to the square root of the immersion time, suggesting that the ion exchange process between Tl ions in molten salt and Na ions in the glass sample is controlled by the diffusion of Tl ions moving from the surface to the inner parts of the glass.

3.2 Hydrogen reduction treatment of the glass

The glass samples subjected to the ion exchange were reduced in a hydrogen atmosphere for 1 h at 803 K. The Tl ions in the glass are reduced to metallic Tl by hydrogen, the reacted hydrogen becomes hydrogen ions and remains in the glass. The glass sample thus reduced assumed colors from light to dark brown, darker with longer durations of immersion. Figure 3 shows a TEM image of the top surface of a glass samples reduced by hydrogen following ion exchange treatment at 753 K for 48 h, showing dark particles dispersed in the glass. The dark particles were found to be metallic Tl by EDS and diffraction analysis, and the sizes of the metallic Tl particles were from 10 to 15 nm. The EDS analysis showed a low Tl content in the bright parts of the TEM image, and it is assumed that ionic Tl is presents in the bright parts and metallic Tl in the dark parts of the glass.

Cross sectional SEM images of the surface region of the glass after ion exchange treatment for 48 h and hydrogen treatment at 1 and 5 h are shown in Fig. 4. In Fig. 4(a) with 1 h of hydrogen reduction, the bright particles are the metallic Tl, and the thickness of the layer with metal particles is about 3 μm. In Fig. 4(b) with 5 h of hydrogen reduction, the thickness of the layer with Tl particles is about 7 μm. This suggests that irrespective of the length of ion exchange treatment, the depth of formation of metallic Tl particles in the glass is determined by the length of the hydrogen treatment.

Figure 5 shows a cross sectional SEM view in the surface region of the glass for a glass specimen reduced for 1 h at 803 K following 48 h of ion exchange process at 753 K. Figure 5 also plots the Tl content before the reduction (dotted line) and after the hydrogen reduction (solid line). The bright particles down to 3 μm in the SEM image are metallic Tl particles and the size of the particles increased with depth (from 50 to 200 nm). There were no Tl particles in areas deeper than 3 μm but Tl was detected in the deeper areas by the EDS analysis. It is, therefore, assumed that Tl ions were not reduced in the areas deeper than 3 μm, and as shown by the dotted line in Fig. 5, the Tl concentration decreased slightly towards the inside of the glass from the 6.7 mol% at

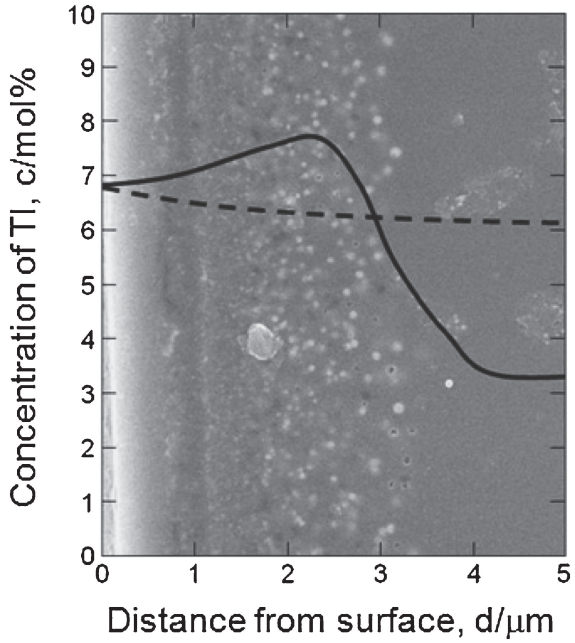

Fig. 5 Cross-sectional SEM image of the glass after hydrogen reduction and concentration profile of the Tl in the glass subjected to ion exchange for 48 h at 753 K: dotted line before and solid line after the hydrogen reduction of the glass.

the glass surface before the reduction. As shown by the solid line in Fig. 5, the Tl concentration was 6.8 mol% at the glass surface, it increased to 8.0 mol% at 2.5 μm depth, and then decreased to 3.2 mol% deeper in the glass. The distribution of metallic Tl may be explained as follows: Tl ions in the glass are reduced to metallic Tl only in the surface region, down to about 4 μm, though Tl ions have penetrated several tens of μm into the glass. The differences in the distribution of metallic Tl and Tl ions before and after the hydrogen reduction may be due to the depth of penetration of hydrogen in the glass. The reduced metallic Tl forms nano-sized particles through a nucleation-nucleus growth process at the surface region. Since Tl ions are reduced and captured by a nucleus during the Tl particle growth process, the concentration of Tl ions decreases in the surface region. Diffusion of Tl ions from the deeper regions towards the surface may be induced due to the lower concentrations of Tl ions in the surface region. At the outer most surface, however, the reduction rate from Tl ions to metallic Tl is also occurring and the growth of the nuclei may be restricted to this layer. At the glass surface, 1–3 μm from the surface, the density of nuclei may not be high at relatively low partial hydrogen pressures. The nuclei grows in this region resulting in diffusion of Tl ions from the region deeper than 4 μm from the surface, therefore, the concentration of Tl exhibits a maximum in the glass after the hydrogen reduction.

4. Conclusions

To investigate the diffusion behavior of Tl ions, ion exchange treatment of the glass was carried out in $TlNO_3$–KNO_3 molten salt at 753 K for various time periods.

(1) It was suggested that the ion exchange process is controlled by diffusion of Tl ions from the surface to the inner part of the glass.

(2) After the hydrogen reduction treatment at 803 K for 1 or 5 h, metallic Tl nano-particles formed at the surface of the glass. The thickness of the region where nano-particles form depends on the duration of the hydrogen reduction treatment, thicknesses of 3 and 7 μm formed by the 1 and 5 h hydrogen reduction, respectively.

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