Journal of the University of Chemical Technology and Metallurgy, 47, 4, 2012, 409-414

ION - EXCHANGE COLOURING OF FLOAT GLASSES IN VAPOURS AND MELTS OF COPPER-CONTAINING SALT

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Received 12 January 2012
Accepted 12 July 2012

ABSTRACT

In this study we treated float glass samples with vapours and melts of CuCl and more complex compositions of chlorides. Due to the tin present on the glass surface, pink and redlike colors were obtained directly without using external reducing agents. We determined the experimental conditions (time and temperature of action) needed to change the intensity of the coloring. The cut-off wavelength of the light transmission is located near 300 nm. An absorption pick is observed near 570 nm. With AFM the formation of small crystals sized around 20 nm was established, while the roughness of the background surface is in the range 4-5 nm. The mechanism for the formation of the color layer includes surface interdiffusion of $Na^+ \longleftrightarrow Cu^+$*; reduction of the* Cu^+ *to* Cu^o *(favored by the presence of tin) and growth of colloidal Cu clusters by diffusion.*

Keywords: *glass, ion-exchange, copper.*

INTRODUCTION

Research devoted to ion-exchange processes between melt and glass surface was highly intensively in the 70s of last the century in relation to modifying of some properties: increasing of mechanical and chemical resistance and coloring. By ion-exchange alkaline ions, Ag, Au and Cu particles in the glass matrix are implanted [1-9]. New researches concerning to ion-exchange processes are concentrated on obtaining different functional materials, such as nonlinear optical materials [10-12] and planar waveguide [13,14]. The nanosized metal particles in the amorphous matrix, generating optical properties and the coloring of the new materials are analyzed by Surface Plasmon Resonance (SPR) [15-20].

In the department “Technology of the silicates” of UCTM during the period of 1970-1980 intensive research were made related to coloring of the glasses and increasing their mechanical strength by ionexchange processes. One of the essential results was modifying the color of industrial glasses in melts of copper and silver salts ($AgNO_3$, $CuSO_4$ and CuCl). We have developed a method for the transformation of green colored glass obtained by ion-exchange ($Cu^{2+} \longleftrightarrow M^+$) into red colored by UV and X-ray irradiation at appropriate thermal treatment. This phenomenon is due to the formation of colloidal Cu particles ($Cu^{2+} \longleftrightarrow Cu^0$) [21, 22].

One of the unsolved problems related to the ion-exchange processes at high temperatures is the corrosion of the glass surface and the poor reproducibility of the color. However, all previous research were made with industrial glasses produced by the old technologies (Pitsberg and Furko). Now new industrial glasses are produced by the so called float method and they contain small amount of tin on the surface. Due to this fact the ion-exchange processes for this type of glasses have to be investigated and a new method for treatment in the melt has to be devepoled. Some interesting results have been obtained by several authors for the distributions of the tin [23, 24] and coloring by silver [20, 25] and copper [8, 26].

This study is a continuation of our previous experiments. The subject of the ion- exchange treatment is commercial soda-lime float glass. The aim is to determine the conditions for thermal treatment of a float-glass in copper chloride vapor depending on temperature, time and composition of the melt and concentration of CuCl. We have also to compare the results of the samples treated in vapor of CuCl with those treated in copper chloride melts. The influence of additional thermal treatment on optical characteristics of the glasses has to analyzed also.

EXPERIMENTAL

The experiments were made on float-glass samples with composition $72SiO_2.13Na_2O.8CaO.4MgO.2Al_2O_3$ (%mass). They were treated in vapors or melts of the salt mixtures, presented in Table 1.

The ion-exchange process was accomplished in a vertical furnace. The glass plates were immersed in a molten bath in a porcelain crucible or were attached

Table 1. Chemical compositions of salt baths.

Composition	CuCl, mol %	KCl, mol %	Color
1	50	50	uncolored
2	60	40	Colored
3	80	20	Colored

over it. The temperatures and time of ion-exchange treatment in chloride melts were respectively: 500-550°C, 10-60 min The samples were subsequently removed from bath, cooled to room temperature and washed in H_2O.

The ion-exchanged samples were subjected of additional thermal treatment at 600°C, 1 - 3 h.

UV-VIS spectra were recorded on UV-VISSIBLE (Cary100-Varian) spectrophotometer in the range 300-800 nm. The size of the particles and the roughness of the surface after treatment were registered with AFM (Anfatec Instruments AG).

RESULTS AND DISSCUSIONS

The results of the ion-exchange indicate that glasses processed in melts and vapors of chloride compounds visualy are colored in pink, pink-brown to redlike. The ion-exchange conditions are given in Table 2.

Table 2. Ion-exchange conditions of treated samples.

Sample	CuCl : KCl mol %	Ion-exchange treatment T(^{0}C)	τ (min)	Additional treatment T(^{0}C)	τ (h)	absorption peak λ nm	Transmission %
S_0	Untreated	---	---	----	----	---	----
S_1	80 : 20(in vapor)	500	10	---	----	565	87.10
S_2	80 : 20(in vapor)	500	15	---	----	563	80.01
S_3	80 : 20(in vapor)	500	30	----	----	567	77.22
S_4	80 : 20(in vapor)	500	45	----	----	565	67.06
S_5	80 : 20(in vapor)	500	60	----	----	563	50.81
S_6	80 : 20(in vapor)	550	30	----	----	562	36.68
S_7	80 : 20(in vapor)	550	30	600	1	561	36.48
S_8	80 : 20(in melt)	500	10	----	----	567	60.16
S_9	80 : 20(in melt)	500	15	----	----	561	34.18
S_{10}	80 : 20(in melt)	500	30	----	----	562	6.38
S_{11}	80 : 20(in vapor)	500	30	600	1	562	42.54
S_{12}	80 : 20(in vapor)	500	30	600	3	561	56.56
S_{13}	50 : 50(in vapor)	500	60	----	----	565	87.10
S_{14}	60 : 40(in vapor)	500	60	----	----	565	59.62

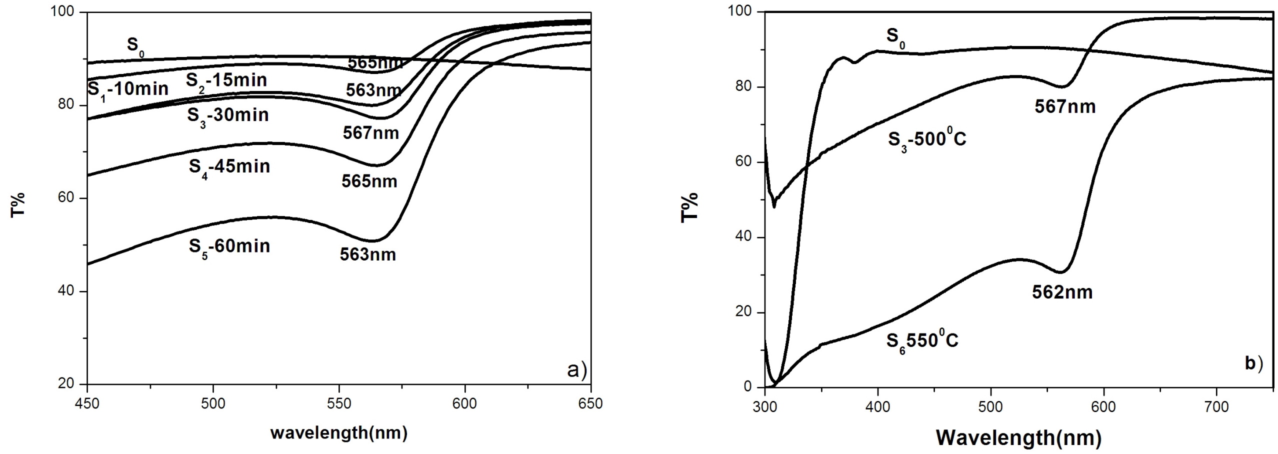

Fig. 1. Spectral transmission of float glasses treated in the vapor of a chloride melt containing 80 mol % CuCl, 20 % KCl: a) constant temperature 500^0C, time of the treatment 10-60 min ; b) influence of the temperature 500, 550°C for 30 min exposition.

UV-VIS spectra show that the transmission of the glasses decreases with increasing the ion-exchange time in comparison with an untreated sample S_0 (Fig. 1a). The increasing of the ion-exchange temperature leads to significant decrease of the transmission (Fig.1b). That phenomenon is connected with the deeper penetration of more copper particles into the glass surface [27].

The same tendency is observed for the glasses treated in melts, but the decreasing of the transmission is more significant (Fig. 2). After the ion-exchange process a peak in the 560-570 nm range is observed. Its area increases with the increasing of temperature and processing time. That peculiarity in the spectrums is related to formation of colloidal size copper particles. The increasing of their concentration and sizes is a result of the diffusion of copper ions dependent on the experimental conditions [5, 8, 9, 15, 25].

In Fig. 3 are shown UV-VIS spectra of float-glasses treated in copper chloride vapors (500°C, 30 min) which are additionally treated after washing at 600°C in air atmosphere for different time (1-3h). The exposition for 1h decreases transmission and leads to more intensive coloring. However, the treatment for 3 h causes color lightening. This could be explained by the displacement of the equilibrium $Cu^+ \longleftrightarrow Cu^0$ to the left [28, 29].

By increasing the temperature of the ion exchange it is possible to obtaine the same result without additional thermal treatment (Fig. 4).

The copper concentration in initial batches also causes change of the coloring intensity. According to most literature data, pure copper chloride is used to

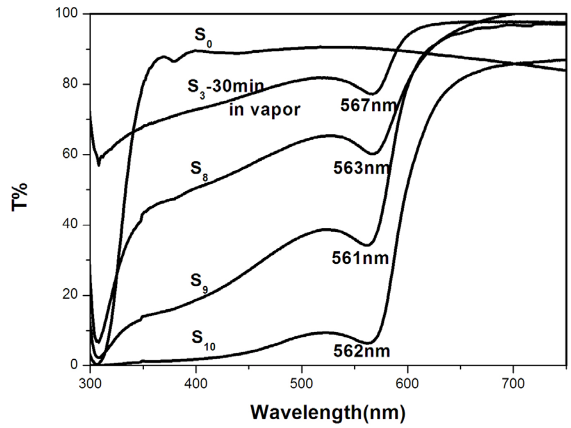

Fig. 2. Spectral transmission of float glasses treated in the melt of a chloride mixture containing 80 mol % CuCl, 20 % KCl at 500°C for different time, 10-30 min.

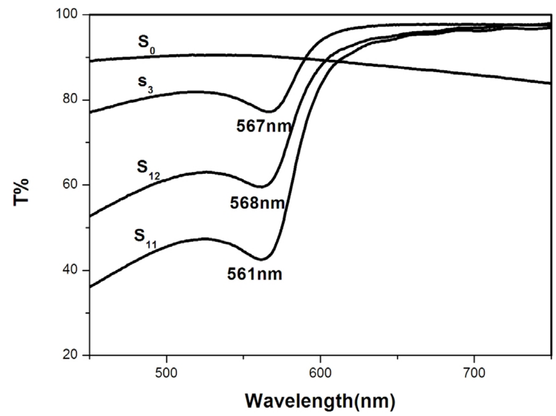

Fig. 3. Spectral transmission of float glasses treated in vapors of a chloride melt containing 80 mol % CuCl, 20 mol % KCl at 500°C, 30 min and additionally heat treated in air atmosphere at 600°C for 1-3h: S_0- an untreated glass sample; S_3- an ion-exchanged sample without additional treatment; S_{11}- an ion-exchanged sample additionally heat treated for 1h; S_{12} - an ion-exchanged sample additionally heat treated for 3h.

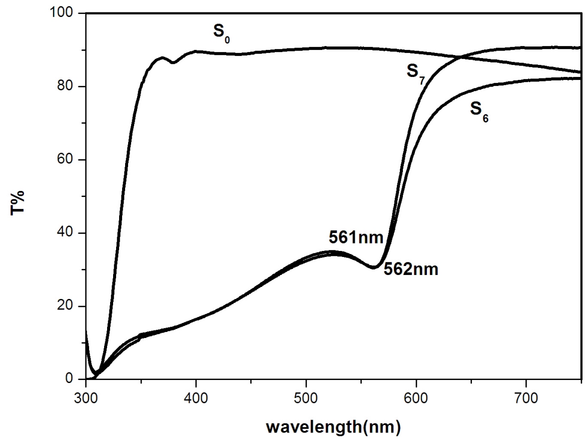

Fig. 4. Spectral transmission of float glasses treated in vapors of a chloride melt containing 80 mol % CuCl, 20 mol % KCl at 550°C for 30 min; S_6- an ion-exchanged sample without additional treatment; S_7 – an ion-exchanged sample additionally heat treated at 600°C for 1h.

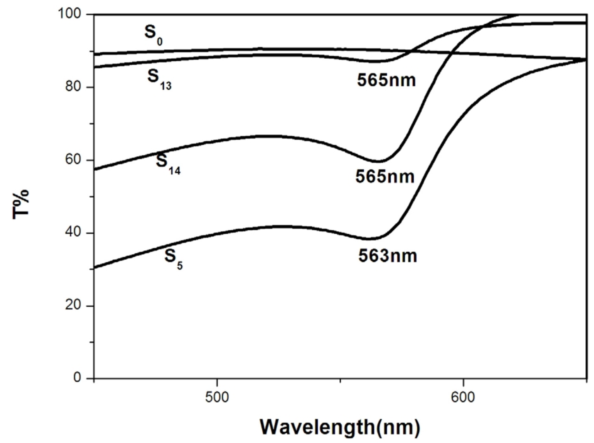

Fig. 5. Spectral transmission of float glasses treated in the vapors of chloride melts at 500°C containing different concentration of CuCl for 60 min: S_{13}- 50 mol %; S_{14} - 60 mol %; S_5- 80 mol %.

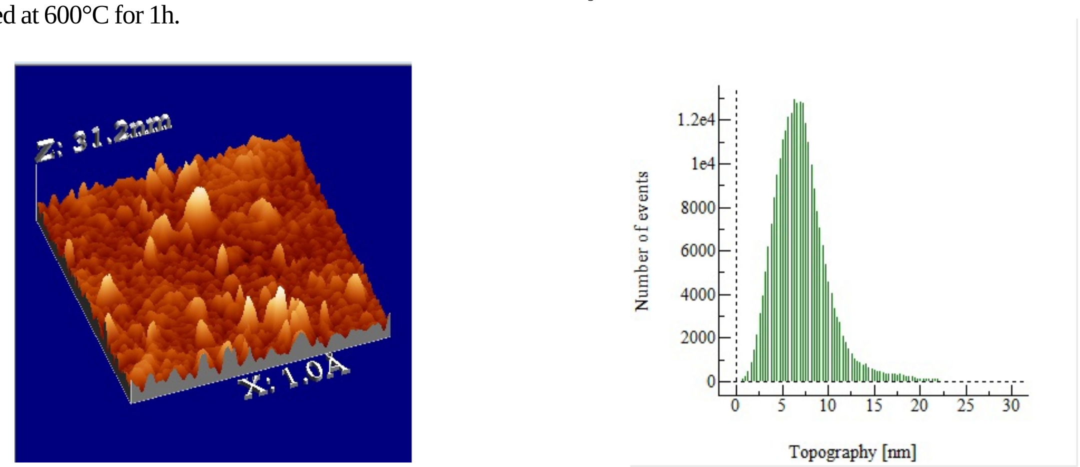

Fig. 6. AFM images of a glass sample after ion-exchange treatment at 500°C for 30 min.

color the glasses. We prepared mixtures with different ratio of copper to potassium chloride. The presented spectral results show that the visible coloration can be obtained in the bath containing more than 60 mol % CuCl (Fig. 5).

The size of the colloidal particles is determined by the three-dimensional AFM images (Fig. 6). The nanoparticles are in range of ~ 20 nm, while the roughness of the background surface is in the range 4-5 nm.

The absorption of the glasses in the visible spectrum is due to ions of the transition elements characterized by incomplete 3d levels.The color induced is caused to d-d transitions and depends on the oxidation state of the transition ion. The spectral characteristics of the samples show a peak at 550-570 nm which is due to the surface plasmon resonance, in proof of the formation of copper colloidal particles causing red coloring. Shifting of the peak to the right, increasing the area and changing its shape are an evidence for increasing the concentration, size and shape of colloidal particles, forming clusters [3, 9, 15, 21, 28].

Our experiments confirm the formation mechanism of red ruby layers on the glass surface:

- interdiffusion ion-exchange ($Na^+ \leftrightarrow Cu^+$);- reduction of Cu^{1+} to Cu^0 favored by less oxidation forms of the tin (Sn^0, Sn^{2+}) located in the surface layer;

- formation and growth of copper metal particles.

The color intensity and the spectral transmission changes are determined by the size of the colloidal particles, which are a function of the temperature and time of ion -exchange. It can be explained by the deep penetration in the glass matrix of a significant amount of copper particles [26, 27].

The significantly decrease of the transmission can be associated with a change in to physical and mechanical properties. It has been shown that decreasing of spectral transmission is accompanied by an increase in microhardness and strength of the glass and mainly determined by the concentration of copper particles in the surface glass layers [8]. Applied to our results this shows that the samples treated in copper chloride melts have higher concentration of copper nanoparticles penetrated to considerable depth in the glass matrix, respectively better mechanical properties, compared with samples treated in vapor.

CONCLUSIONS

The conclusions that can be made on this stage of our experiments are:

• Colored pink glasses with different intensity are obtained in dependence of the time and temperature of ion-exchange treatment.

• In all spectrums of ion-exchange glasses is registered an absorption peak in the 560-570 nm range which is due to the formation of copper colloidal particles.

• We have determined that the minimum concentration of CuCl in the salt mixture necessary to achieve a noticeable coloration is 60 CuCl mol %.

• It was found that with increasing the ion exchange time and temperature, the transmission in the visible range decreases. However the transmission increased again above 600 nm (in the near infrared range) compared to that of the initial comercial glass.

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