JOURNAL OF MATERIALS SCIENCE 10 (1975) 799–808

Microstructural studies of glass–metal composites produced by ion-exchange and hydrogen treatments

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Detailed electron micrographic studies have been carried out on float glass surface subjected to sodium ⇌ copper ion-exchange in molten salts followed by a reduction treatment in hydrogen. Spherical copper particles of diameters ranging from 50 to 300 Å are formed in the glass matrix depending on the ion-exchange and reduction temperatures. The nucleus density of these particles is maximum at around 450°C. Phase separation in glasses whether incipient or induced by ion-exchange, increases considerably the nucleus density when such samples are subsequently reduced. This is ascribed to the increase in the number of copper atoms surrounding the nucleation sites in the phase separated glasses. The optical absorption spectra of the glass-metal composites show two bands, namely at 17 400 cm^{-1} and 23 000 cm^{-1} respectively. The absorption maxima for both the bands occur for specimens reduced at temperatures between 450 and 500° C corresponding to the temperature of maximum nucleus density. The bands at 17 400 cm^{-1} and 23 000 cm^{-1} are assigned to the conduction resonance and plasma resonance respectively as predicted by Maxwell-Garnet theory on aggregated metal systems dispersed in a dielectric matrix.

1. Introduction

Glass surfaces when subjected to a suitable ion-exchange reaction followed by reduction in hydrogen develop a microstructure which consists of metallic particles having diameters ranging from 50 to 2000 Å dispersed in a glass matrix [1-2]. Such glass–metal composites have interesting physical properties. For instance, using silver as the exchanging ion for soda-glasses, memory switching and high-conductivity effects have been observed [1, 2]. The electrofloat process developed by Pilkingtons to produce solar-control coatings on window glass is based on field-induced ion-exchange followed by reduction, one of the exchanging species being copper. The morphology of such products has been shown to consist of metallic particles in a glass matrix [3]. Electron microscopic studies of glass surfaces subjected to sodium ⇌ silver ion-exchange, using molten silver salts, have shown that considerable changes in the surface structure can be induced by such an ion-exchange reaction [4]. The prior phase separation in glass systems has been shown to influence the subsequent formations of crystals in the glass matrix [5]. Since the first step in the electrofloat process is one of ion-exchange, it therefore seems likely that the microstructure of the float glass surface induced by the ion-exchange reaction will affect the nucleation and growth of the metal phase.

A systematic investigation was, therefore, undertaken with particular reference to metallic copper-phase formation in float and other related glass systems following sodium ⇌ copper ion-exchange from molten salts and subsequent reduction. The microstructural changes were studied by transmission electron microscopy and optical absorption measurements.

2. Experimental

The composition of the laboratory prepared "float glass" used for this investigation is shown in Table I. The glasses were prepared from reagent grade chemicals. Sodium, calcium, magnesium and potassium were introduced as carbonates and the others as the corresponding oxides. SO_3^- was introduced as sodium sulphate.

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TABLE I Composition of float glass

Oxide	Mol %
SiO_2	71.60
Na_2O	12.59
CaO	8.89
MgO	5.59
K_2O	0.38
SO_3	0.33
Al_2O_3	0.58
Fe_2O_3	0.04

The glass was premelted in an electric furnace for 1 h at 1400°C and then cast, crushed and sieved through 14 mesh before re-melting at 1450 to 1480°C for 3 h. After casting at 1350°C on to a stainless steel plate, the glass was annealed at 550°C for 2 h and brought to room temperature at a rate of 20°C h^{-1}. Samples were cut and ground to the dimensions 25 mm × 10 mm × 4 mm and the surfaces polished flat and parallel.

For sodium $\rightleftharpoons$ copper exchange, glass specimens were immersed into the molten bath of a copper salt, contained in a silica boat. Both anhydrous cupric chloride, $CuCl_2$ (Hopkin and Williams Analar) as well as cuprous chloride, CuCl (Fisons Scientific, Analytical Reagent) were used for this purpose. The microstructure and optical absorption of specimens ion-exchanged in the two salts respectively were found to be identical. Most of the experiments were, therefore, performed using the cuprous salt because of its easier handling characteristics. The ion-exchange treatments were carried out for 1 h at temperatures ranging from 500 to 650°C. After the diffusion run, the sample was removed from the bath and any adherent salt removed by scraping gently with a scalpel blade under running water.

The reduction treatments of the ion-exchanged specimens were carried out in a silica tube fitted with rubber stoppers and inserted into a wire-wound horizontal furnace. Reduction temperatures ranged from 400 to 600°C for periods extending to 48 h. Samples for reduction were placed on a refractory plate. The furnace was brought to the required temperature and the tube flushed with nitrogen gas for $\frac{1}{2}$ h. After equilibration at the required temperature for about 15 min, a mixture of hydrogen and nitrogen was admitted the flow rates of the gases being 100 cm^3 min^{-1} and 1 litre min^{-1} respectively.

Measurements of the optical absorption spectra of all samples were performed after both the ion-exchange and reduction steps using a Unicam SP 700 double beam recording spectrophotometer. All spectra were measured using air as the reference. Absorption measurements on reduced samples were performed after grinding off one of the coloured surfaces. Thus the data refer to a single surface only.

The transmission electron micrographs of the specimens were taken after both ion-exchange and reduction on a Philips EM 300 electron microscope. The specimens were prepared by a method described elsewhere [2].

3. Results and discussion

3.1. Absorption measurements after ion-exchange

Fig. 1 shows optical absorption spectra of float glass before and after ion-exchange. The spectrum before ion-exchange shows two absorption bands – a broad band with a maximum of ~ 9500 cm^{-1} due to absorption by Fe^{2+} ions [6], whilst the weak absorption at 26 300 cm^{-1} is due to Fe^{3+} ions [7]. After ion-exchange an additional broad absorption band is observed with a maximum at ~ 12 500 cm^{-1} which is characteristic of Cu^{2+} ions [8, 9]. All the ion-exchanged glasses also exhibit a weak yellow fluorescence under u.v. illumination, which has been assigned to Cu^+ ions [10, 11]. The presence of both monovalent and divalent copper ions in the ion-exchanged specimens imply that Cu^+ ions from the molten bath diffuse into the glasses and subsequently a Cu^+/Cu^{2+} equilibrium is established.

3.2. Microstructure after ion-exchange

Fig. 2 is an electron micrograph of the glass surface before ion-exchange which shows that the structure is homogeneous. However, this finding does not preclude the presence of incipient phase separation, as will be discussed later, but implies that if such phase separation is present before ion-exchange it is not directly observable by this technique. The micrographs of specimens after ion-exchange for 1 h at 550 and 600°C, respectively, are similar to Fig. 2. It is, therefore, evident that the exchange of sodium for copper ions at 550 and 600°C does not give rise to phase separation. However, an interconnected microstructure results from exchange at 650°C as is shown in Fig. 3. This phase separation arises due to the injection of copper ions into the glass and not due to the heat-treatment at 650°C. This has been con-

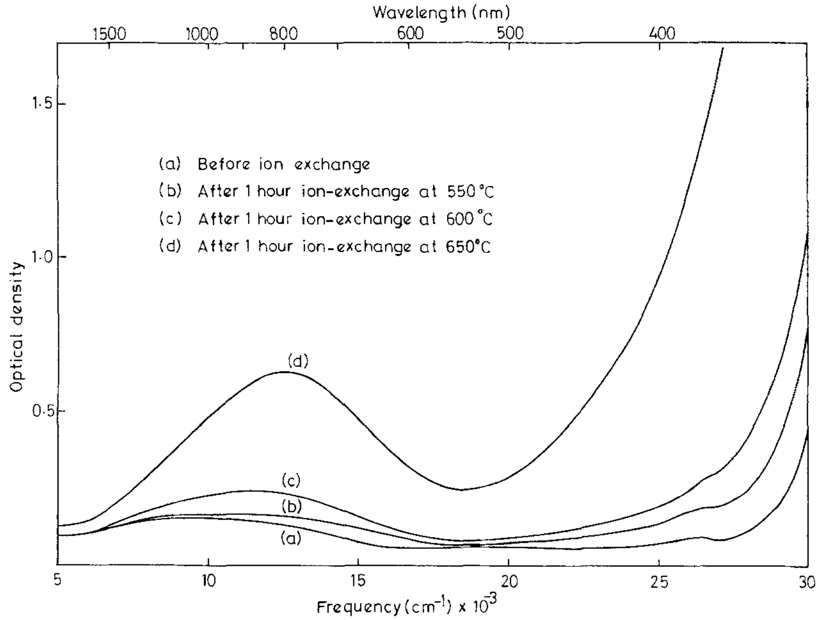

Figure 1 Optical absorption spectra of float glass before and after ion-exchange.

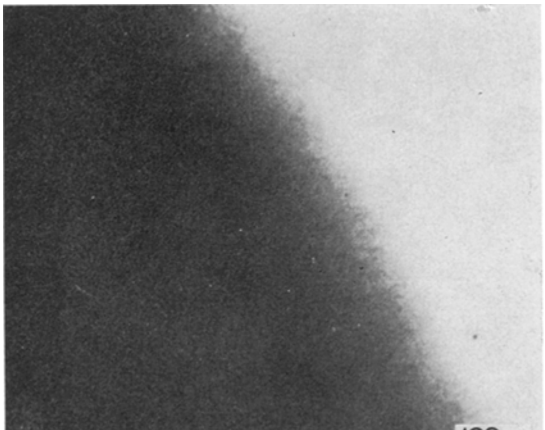

Figure 2 Transmission electron micrograph of float glass before ion-exchange.

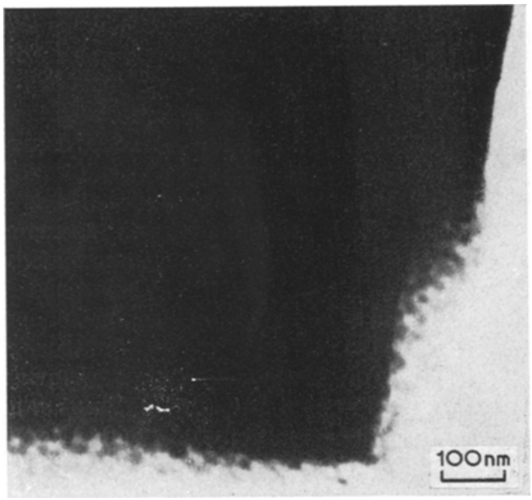

Figure 3 Transmission electron micrographs of float glass after ion-exchange at 650°C for 1 h.

firmed by studying the microstructure of samples which were heated at 650°C for up to 16 h. Such treatment does not induce any phase structure typified by Fig. 3. It is, therefore, concluded that the copper-rich glass formed after ion-exchange has a region of immiscibility around 650°C whereas glass of the original composition clearly does not.

3.3. Microstructure after reduction

Fig. 4 gives the microstructures of glasses ion-exchanged at 550°C for 1 h and reduced at different temperatures. The dark spheres shown in the micrographs were identified as copper particles by selected-area electron diffraction [3]. For glasses ion-exchanged at 600 and 650°C

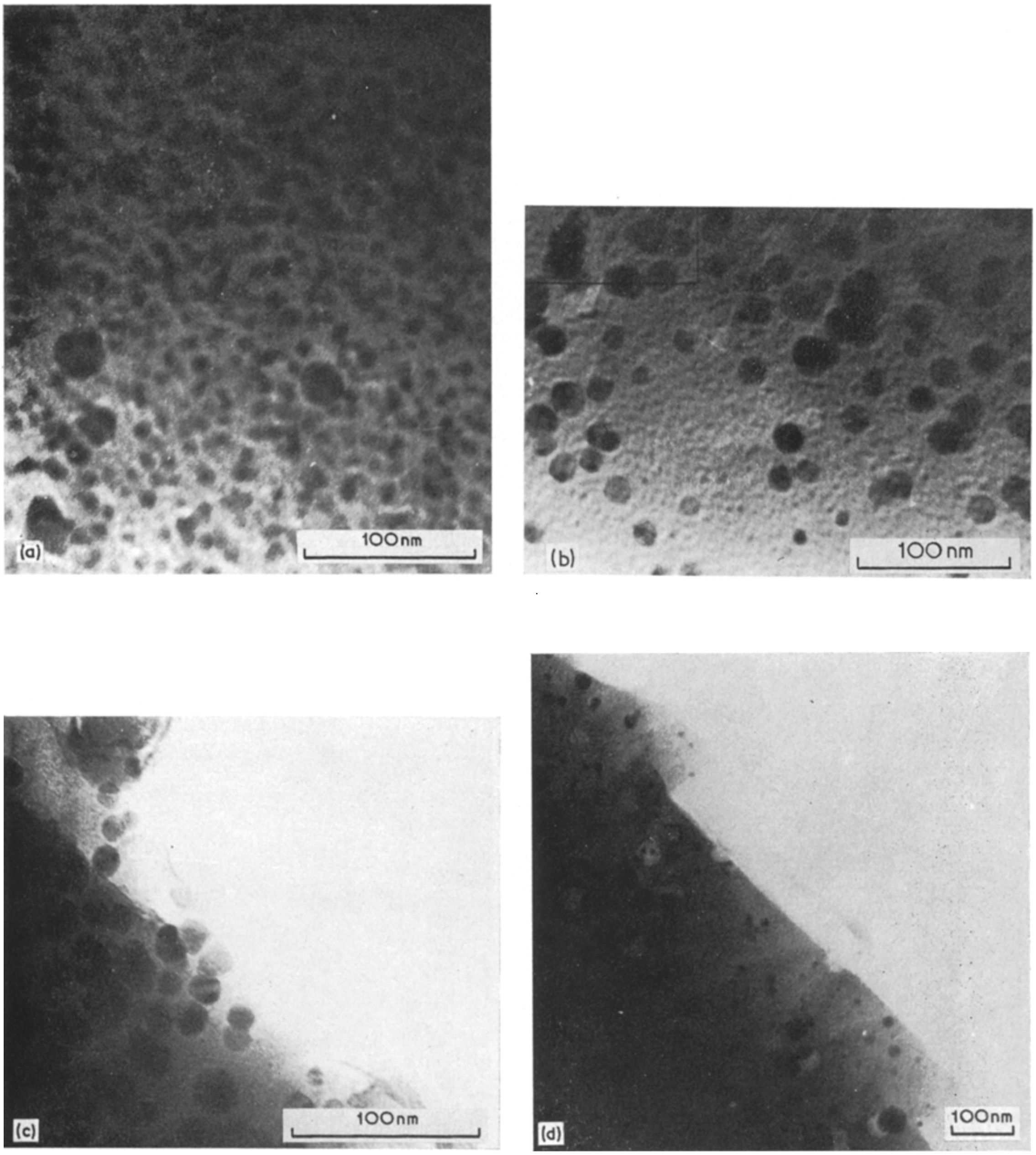

Figure 4 Transmission electron micrograph of float glass after ion-exchange and reduction. Ion-exchange treatment: 550°C for 1 h. Reduction (a) 400°C for 48 h, (b) 450°C for 4 h, (c) 500°C for 4 h, (d) 550°C for 4 h.

respectively before reduction the microstructures obtained are similar but the nucleus densities increase as the ion-exchange temperature increases. This effect is illustrated by Figs. 5 and 6 which show the micrographs of reduced specimens ion-exchanged at 600 and 650°C respectively. The diameters and the nucleus density of the copper phase were determined from the micrographs by using standard techniques [5, 12]. Table II summarizes the particle diameters in ion-exchanged glasses reduced at different temperatures. It is evident from these results that the particle diameter increases as the reduction temperature is increased for all the

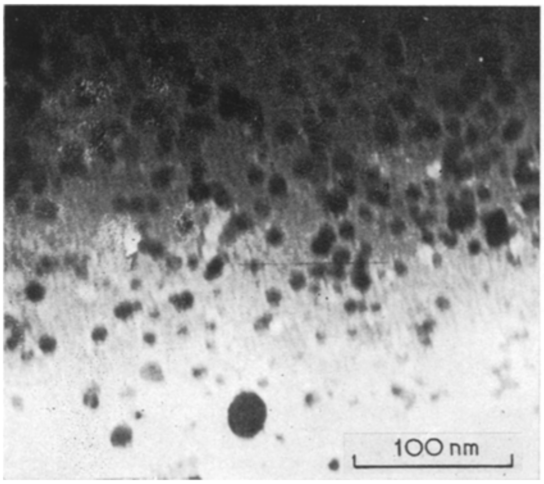

Figure 5 Transmission electron micrograph of float glass ion-exchanged at 600° C for 1 h and reduced at 450° C for 4 h.

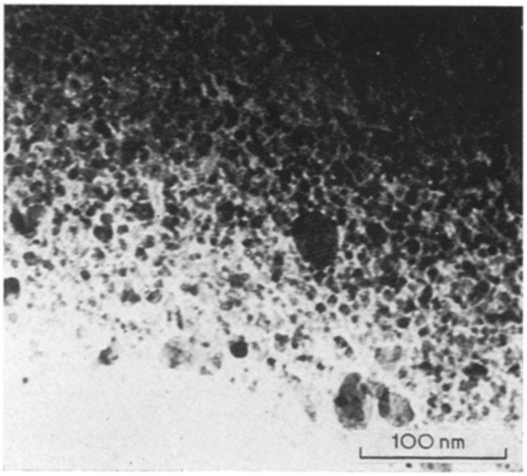

Figure 6 Transmission electron micrograph of float glass ion-exchanged at 650° C for 1 h and reduced at 450° C for 4 h.

ion-exchange temperatures. This is to be expected because the growth of the copper nuclei must proceed by a diffusion mechanism involving the copper atoms. For glasses ion-exchanged at 650° C the particle diameters are much less than those corresponding to 550 and 600° C respectively. This implies that the phase morphology of the glass surface has a significant effect on the subsequent crystallization of the copper metal phase. In the present case, a fine-grained structure of the copper phase has been obtained in glasses already having some phase separation.

Fig. 7 gives the variation of the nucleus density as a function of reduction temperature for specimens ion-exchanged at three different temperatures. It is evident that the nucleus density is maximum at around 450° C for all the ion-exchange temperatures. However, the maximum density value increases from $\sim 6 \times 10^{15}$ to $\sim 5 \times 10^{16}$ cm^{-3} as the ion-exchange temperature is increased from 550 to 650° C.

For homogeneous nucleation, the rate is given by [13]

$$N = A \exp[-(\Delta f^* + \Delta f_{\mathrm{D}})]/kT \tag{1}$$

where, Δf^* is the activation energy for nucleation,

TABLE II Copper particle diameters in float glasses ion-exchanged and reduced at different temperatures

Ion-exchange treatment		Reduction treatment		Average diameter (Å)
Temperature (° C)	Time (h)	Temperature (° C)	Time (h)	
550	1	400	4	80
550	1	450	4	150
550	1	500	4	250
550	1	550	4	230
600	1	400	4	100
600	1	450	4	150
600	1	500	4	200
600	1	550	4	200
650	1	400	4	50
650	1	450	4	60
650	1	500	4	65
650	1	550	4	65

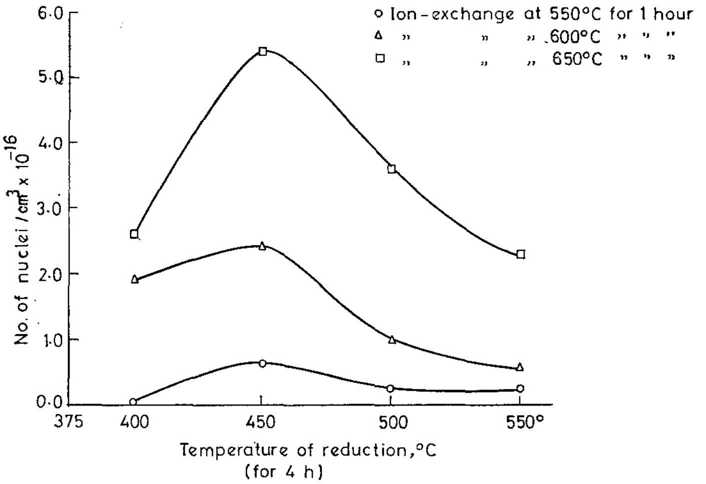

Figure 7 Variation of copper nucleus density as a function of reduction temperature for specimens ion-exchanged at different temperatures.

Δf_D is the activation energy for diffusion, k is Boltzmann's constant, T is the temperature in degrees kelvin, and A is the constant which depends on the number of available neighbouring atoms to nucleus which can migrate to the latter for its subsequent growth. Assuming the nuclei to be spherical, Δf^* can be shown to be given by [13]

$$\Delta f^* = \frac{16\pi\gamma^3 T_0^2}{3(\Delta H_V \Delta T)^2} \qquad (2)$$

where, γ is the interfacial free energy per unit area between the parent and the product phases, T_0 is the temperature at which the phase transformation takes place, ΔH_V is the enthalpy change at T_0 and $\Delta T = T_0 - T$ is the supercooling.

It is evident from Equations 1 and 2 that Δf^* value decreases very rapidly as the temperature drops and as a result the nucleation rate increases. At a sufficiently low temperature, however, Δf^* becomes negligible compared to Δf_D and Δf_D thus dominates Equation 1 and N then decreases with temperature. Consequently, there is a maximum in the homogeneous nucleation rate. This has been observed in the present investigation the temperature for maximum nucleation rate being 450°C. There are two possibilities for the increase in the nucleation rate at higher ion-exchange temperatures. This could be either due to a decrease in Δf^* caused by a reduction in the interfacial energy γ or due to an increase in the pre-exponential factor A because of the larger number of copper atoms available as nearest neighbours of the copper nuclei. The first possibility also predicts an increase in temperature at which the maximum nucleation occurs. However, our results show clearly that the temperature for maximum nucleation density does not change as a function of ion exchange temperature. Therefore, the increase in nucleation rate in the present system is believed to be due to increase in the number of copper atoms surrounding the nucleation sites which is a direct consequence of the phase separated structure induced in these glasses by ion-exchange at higher temperatures.

This effect of phase separation on the kinetics of nucleation of copper particles was confirmed by studying the morphological changes in a glass of composition 10 Na_2O, 10 CaO, 80 SiO_2 (mol %) heat-treated at various temperatures before ion-exchange and reduction treatments. Fig. 8 gives the surface replica electron micrographs of specimens heated at different temperatures and showing varying degrees of phase separation. The transmission electron micrographs of the same samples do not show any phase separation which illustrates the relative insensitivity of this technique to the direct observation of phase separation in low electron density materials. Fig. 9 shows the transmission electron micrographs of these samples taken after ion-exchange at 600°C for 1 h. The struc-

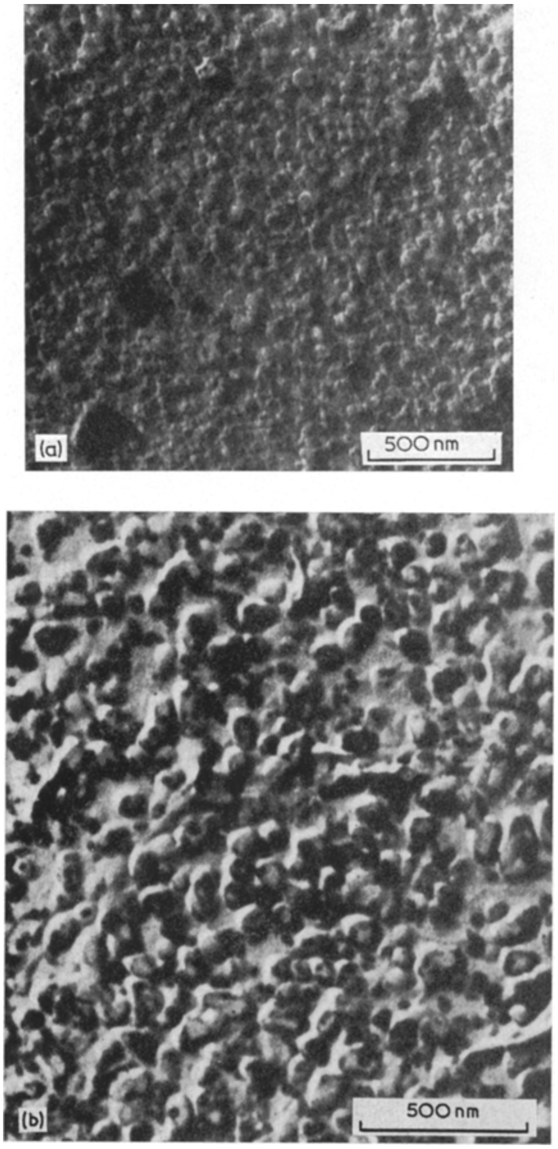

Figure 8 Replica electron micrographs of specimens of composition 10 Na_2O, 10 CaO, 80 SiO_2 (mol %). (a) As-cast, (b) heated at 660°C for 16 h.

tures observed are similar to those given in Fig. 8 indicating that the incorporation of copper has increased the contrast and sensitivity of the transmission micrographs. In Fig. 10 are shown the transmission micrographs of these ion-exchanged samples after reduction at 400°C for 16 h. The effect of phase separation on the nucleus density is clearly demonstrated by these figures. It is evident that the nuclei are concentrated in the copper-rich phase and also the nucleus density in this phase is much higher than that developed in the homogeneous glass. Table III summarizes the morphological characteristics of these micrographs.

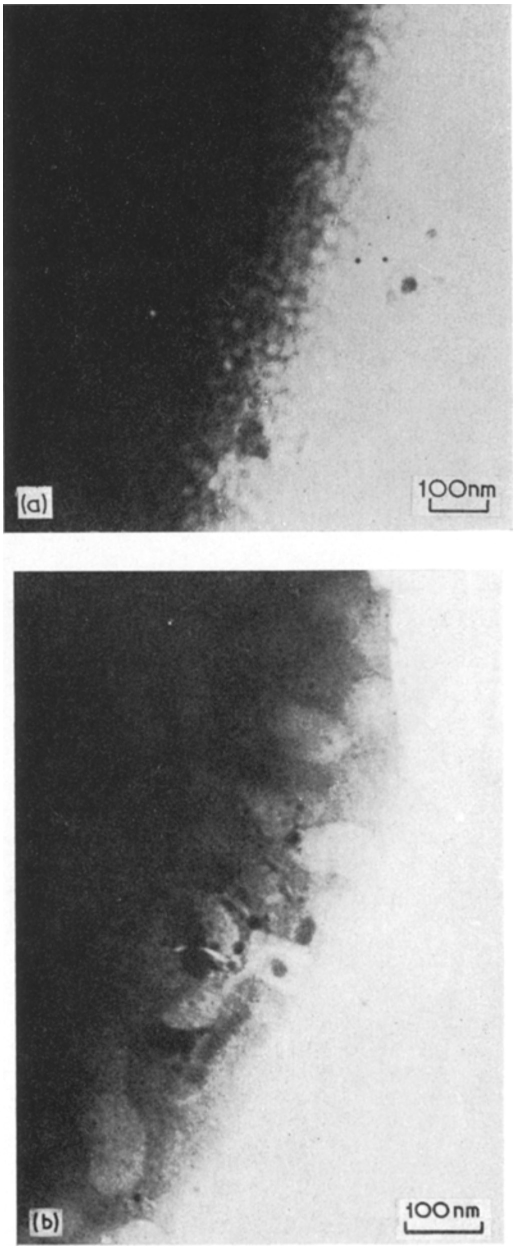

Figure 9 Transmission electron micrographs of specimens of composition 10 Na_2O, 10 CaO, 80 SiO_2 (mol %) ion-exchanged at 600°C for 1 h after various heat-treatments. (a) As-cast, (b) heated at 660°C for 16 h.

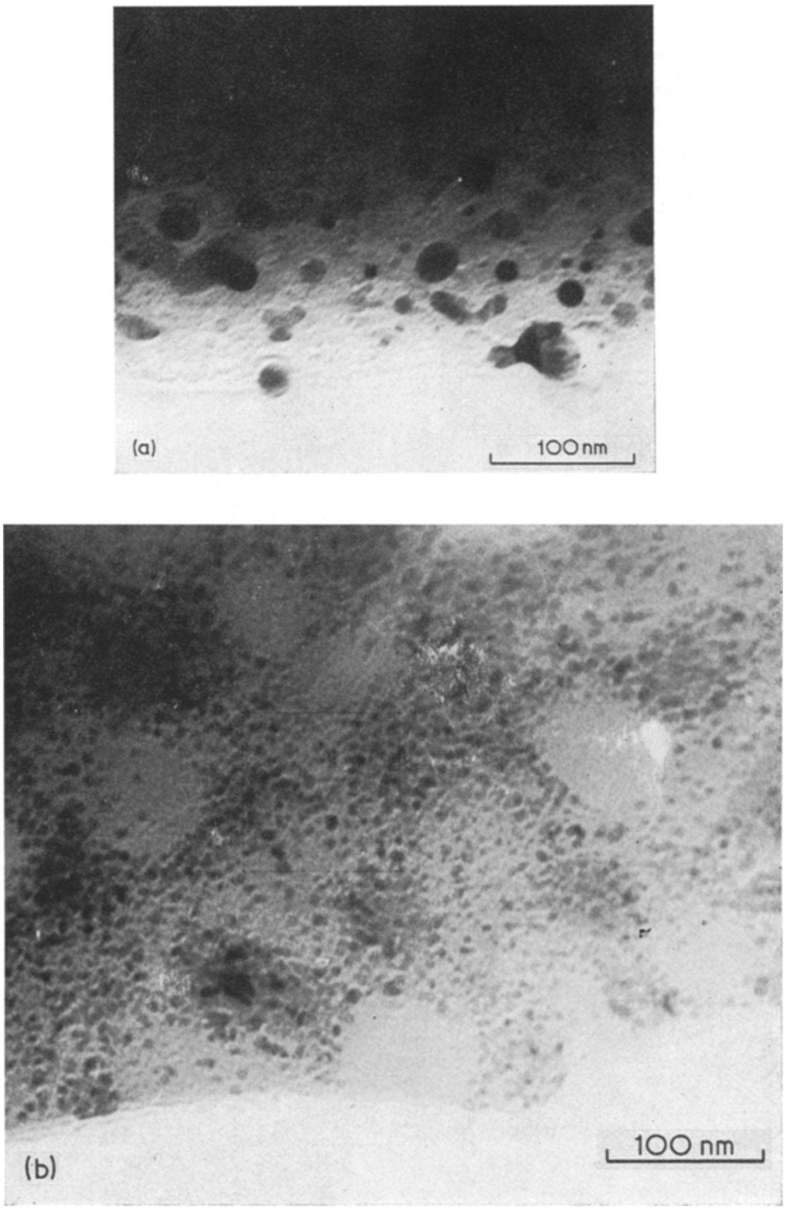

Figure 10 Transmission electron micrographs of specimens of composition 10 Na_2O, 10 CaO, 80 SiO_2 (mol %) heat-treated at various temperatures before being ion-exchanged at 600°C for 1 h and subsequently reduced at 400°C for 16 h. (a) As-cast, (b) heated at 660°C for 16 h.

3.4. Absorption measurements after reduction

Fig. 11 shows the optical absorption spectra for samples ion-exchanged at 550°C for 1 h and then subjected to reduction treatment at different temperatures for 4 h. Two absorption bands are observed – a sharp band around 17 400 cm^{-1} and a broad band with a maximum around 23 000 cm^{-1}. Similar results are obtained for specimens ion-exchanged at 600 and 650°C respectively. The absorption increases, however, as the ion-exchange temperature is increased. This is shown in Fig. 12 where the optical densities at the absorption maximum around

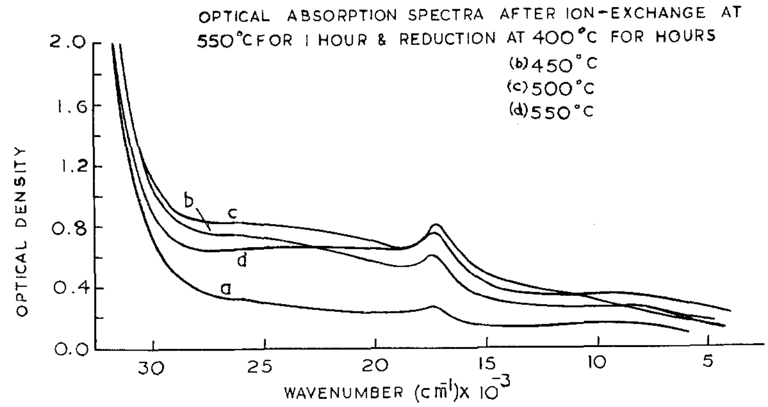

Figure 11 Optical absorption spectra of float glass ion-exchanged at 550°C for 1 h and subsequently reduced at different temperatures.

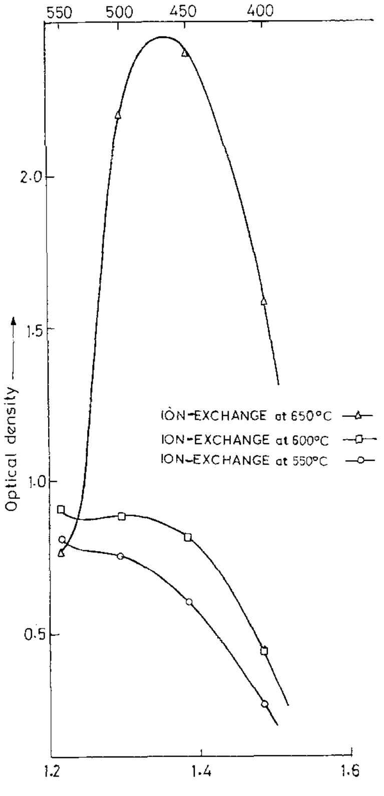

Figure 12 Optical densities at absorption maximum around 17 400 cm^{-1} versus reduction temperature (4 h) for different ion-exchange treatments.

TABLE III Variation of particle diameter and density with phase-separation in 10 Na$_2$O, 10 CaO, 80 SiO$_2$ (mol %) glass ion-exchanged at 600°C for 1 h and subsequently reduced at 400°C for 16 h

Heat-treatment prior to ion-exchange and reduction	Particle diameter (Å)	Particle density (cm^{-3})
Nil	150–250	1.4×10^{16}
660°C, 16 h	50– 60	7.0×10^{16}

17 400 cm^{-1} are plotted as a function of reduction temperature for different ion-exchange treatments. It is evident from these figures that the maxima occur at temperatures between 450 and 500°C. This is also the temperature range in which the maximum nucleation density has been observed (Fig. 7).

The occurrence of two absorption bands can be explained on the basis of Maxwell-Garnet theory applied to the case of metal aggregates dispersed in a dielectric matrix [14]. According to this theory the complex dielectric constant for such a system $\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$ is expressed in terms of the complex dielectric constant $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$ of the metal aggregates and the volume fraction q of the metal phase by the following relation:

$$\frac{(\varepsilon_1 - 1 + i\varepsilon_2)}{(\varepsilon_1 + 2 + i\varepsilon_2)} = \frac{q(\epsilon_1 - 1 + i\epsilon_2)}{(\epsilon_1 + 2 + i\epsilon_2)} . \quad (3)$$

Assuming free-electron processes to contribute to the dielectric constant of the metal phase and concentrating only on resonance-type solutions, the above equation has been solved analytically [14] for w, the angular frequency of the incident radiation. Two roots for w result from such analysis – the higher frequency ascribed to plasma resonance and the lower one to conduction resonance. These solutions also predict that the plasma resonance frequency should increase as a function of q, the volume fraction of the metal phase, whereas the conduction resonance frequency should decrease as q increases.

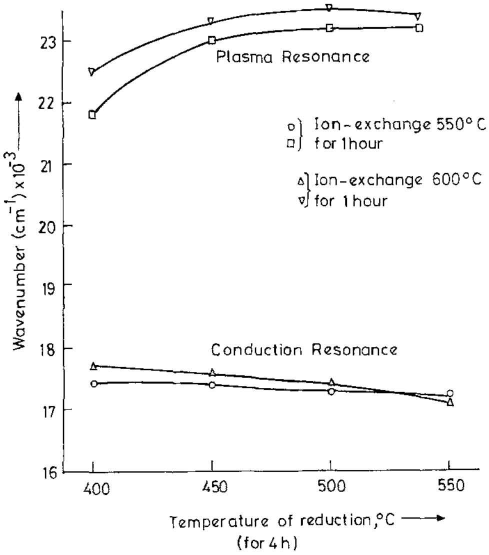

Figure 13 Variation of resonance wave numbers of 17 400 and 23 000 cm^{-1} bands as a function of reduction temperature (4 h) for different ion-exchange treatments.

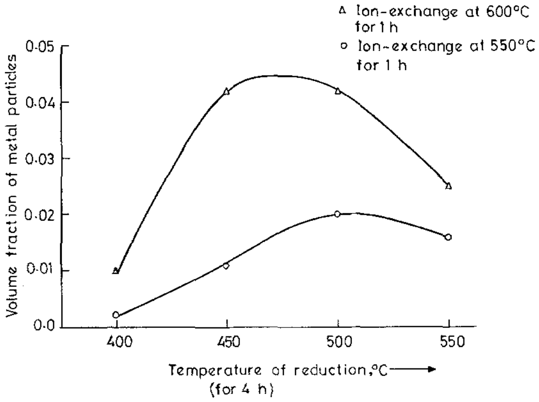

Figure 14 Variation of the volume fraction of metal particles as a function of reduction temperature (4 h) for different ion-exchange treatments.

In the present investigation, the frequency at which the maximum absorption occurs for both the bands mentioned before is found to be dependent on the reduction temperature. This is illustrated in Fig. 13 in which the wavenumbers corresponding to absorption maximum of the two bands are plotted as a function of temperature for specimens ion-exchanged at two different temperatures. It is evident that for the 17 400 cm^{-1} band the frequency decreases with the increase in reduction temperature whereas for the 23 000 cm^{-1} band the trend is just the opposite. The increase in volume fraction of the metal phase as a function of reduction temperature has been estimated from the electron micrographs described before and the results are shown in Fig. 14. On the basis of this analysis it is therefore concluded that the 17 400 and 23 000 cm^{-1} bands correspond to conduction resonance and plasma resonance respectively in the present aggregated metal system.

Acknowledgements

The authors wish to thank the Directors of Pilkington Brothers Limited, and Dr D. S. Oliver, Director of Group Research and Development for permission to publish this paper.

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Received 11 October and accepted 4 November 1974.