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The Influence of Heat Treatment on Microstructural and Physical Properties of Silicate Glasses with High-Content Lead Oxide

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Abstract: Homogenization and heat treatment control plays a primary role in the production of lead glasses. Homogenization processes are applied in different ways. One of the important methods which is also industrially practical for other glass systems is fritting that is the process of melting and quenching of molten materials to form small glass particles. In the current research, the effect of homogenization and heat treatment on the thermal and physical properties of lead glasses is investigated. The fritting procedure is applied six terms for lead glass composition and the effect of fritting on thermal, physical, chemical resistance and homogeneity of glass are studied. While the effects of 3 times of heat treatment on these properties are studied. Finally, the result of micro-structural analyses of glass specimens are presented showing that an increase of the fritting period has an undesirable influence on different properties of glass samples and this process would be used in joint considering of other effected parameters.

Key words: Lead glass, homogenization, heat treatment, micro-structure, properties, Iran

INTRODUCTION

Lead Silicate Glasses (LSG) are considerably used in many different parts from ophthalmic biotechnology, electrode glass production and video-screen manufacturing to radiation protection (Azooz and ElBatal, 2009; Kanunnikova *et al*., 2002; Doan and Turul, 2001; Rahimi *et al*., 2009b; Chanthima *et al*., 2010; Ou *et al*., 2010).

The history of lead glasses production goes back to the start of soda glass manufacturing date. First, they were opaque but translucent lead silicate glass was reported for the 1st time from the 12-13th century (Robinet *et al*., 2008).

Glass has a remarkable transformation range with a change in temperature rather than a quick phase change at the freezing point. This transformation range is various in different glass type due to the glass composition. At the end of this range, annealing point is located, the temperature is sufficiently high and the viscosity suitably low which the stresses of the glass can be released. These kinds of stresses in glass come from two sources; thermal and structural. Thermal stress in glass arises from differences in temperature between the outer surfaces and the internal bulk of the glass. For small glass sample, thermal stress can be efficiently deliberated to be negligible (Rahimi *et al*., 2009a). The quantity of silicon has a considerable effect on the stability of the lead silicate glass. In pure silica, silica tetrahedronsare connected to each other with oxygen atoms settled at corners.

The PbO as a modifier gives rise to partial breakage of the direct interconnections and turn them into indirect connection. Consequently, the Pb ions affect the chemical durability of silica tetrahedrons in the LSG glass structure (Marotta *et al*., 1981).

These days, lead glasses are used in table glassware although, they have extended to other fields such as optical, electronic technologies and nuclear research. Usually, lead glasses are yellow but they can be produced as free from color as possible (Hampton, 1946).

Lead silicate glass is stable in comparison with alkali silicate glass and the network is not destructed due to the high amount of lead. This effect has been described by the lead unit formation in lead silicate glass either Pb_2O_4 polyhedron or PbO_4 pyramids that are network former (Robinet *et al*., 2008; Schultz-Munzenberg *et al*., 1998; Shaaban *et al*., 2009; Fayon *et al*., 1998).

Liquid-liquid phase separation and crystallization are two main processes that can change a micro-inhomogeneous structure of glasses during their heat treatment (Petrovskii *et al*., 2003). In this research,

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changes in structure and physical properties of the silicate glasses with the high lead content upon different heat treatment and a new method of homogenization (fritting) were investigated by chemical resistance results and scanning electron microscopy images.

MATERIALS AND METHODS

Experimental procedure: Glass samples with chemical compositions shown in Table 1 were produced from technical grade silica >99.9 (Iran, Hamedan), Pb_3O_4 (Iran) and reagent grade Na_2O, K_2O, ZrO_2, TiO_2 to As_2O_3 (Aldrich Chemical Co.) powders. About 500 g of mixed materials were weighed for each batch and an alumina crucible was used for material melting under atmospheric pressure at temperatures from 1200-1300°C in an electric furnace (Exciton Co., Iran) for 30 min. The glass melted was water quenched to achieve an acceptable homogeneity.

The produced frit was then ground to <60 μm and was well mixed in a ceramic mortar. The ground powder was melted and then divided to 2 parts. One part was cast in a preheated stainless steel mold to yield a solid piece and one part was water quenched again. This procedure repeated six terms and the samples named G1-G6, respectively. The samples annealed at about 10°C above the glass transition temperature for 2 h. After that the furnace was turned off and cooled down to room temperature.

After annealing, samples were cut into the size of 5×10×20 mm using a diamond saw for different heat treatment processes. These were then polished using a series of 240, 400, 600, 800 and 1000 grit SiC polishing paper followed by final polishing by the 1 μm cerium oxide slurry to give an optical finish.

Transformation temperatures were clearly determined by differential thermal analysis. The density of the prepared glasses was measured using the Archimedes method. The test for chemical resistance of glass powder samples were carried out in boiled 0.01 mol L^{-1} nitric acid solution for 1 h.

The glass powder was chemically analyzed by the wet chemical method. Surface characterization of the glasses after dissolution experiments was done by meaning of a scanning electron microscope (Philips, XL30) equipped.

Table 1: Chemical composition of studied lead-silicate glass samples

Compound substance	As_2O_3	B_2O_3	Na_2O	TiO_2	ZrO_2	PbO	SiO_2	K_2O
Wt. (%)	0.4	4	1.21	1.2	2.4	70	21.7	0.18

RESULTS AND DISCUSSION

Figure 1 shows changes in lead content versus melting term in various samples. This curve is based on the results of wet chemical analysis of glass samples which were melted from 1-6 terms. As shown in Fig. 1, the amount of lead has been decreased with the increase of melting terms. This reduction can be related to evaporation of lead that has an undesired effect on radiation absorption and density of glass samples (Rahimi *et al*., 2009a, b). Figure 2 shows the results of differential thermal analysis of glass samples. In the Fig. 2, the transition Temperature (Tg) of the glasses is shown. As is clear from this curve with the increase of melting points, the transition temperature of glasses has been shifted from 470°C for G1 to about 520°C for G6. It seems that by reducing the amount of lead in the combination, the relative amount of SiO_2 to lead oxide has been increased with increasing melting terms. This leads

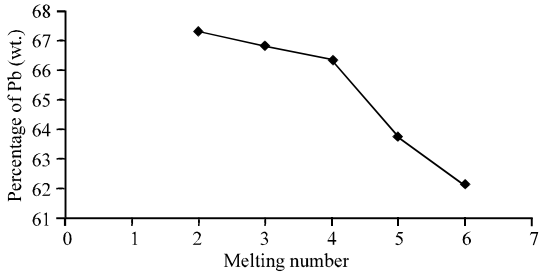

Fig. 1: Effect of different terms of making ferrite on lead amount of glass samples

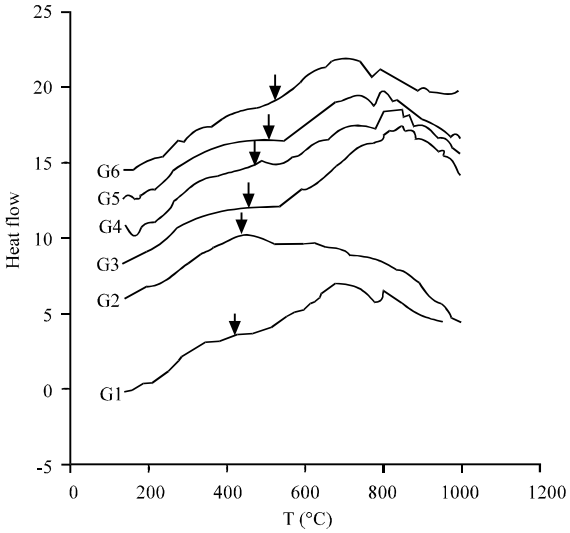

Fig. 2: Thermal analysis curves of different samples of lead glass (soft point temperature range marked with flash)

to an increase in Tg temperature. Tg temperature is important in determining annealing temperature for glasses (Xu *et al*., 1991; Levelut *et al*., 2006). Thermal stresses are created during the cooling of glass melt that cause cracks in the structure of glass. The annealing process will ultimately lead to the preparation of glass without defects and micro-cracks.

Endothermic peak in the 800-900°C temperature range is related to the melting temperature of the samples. Figure 3 shows the results of measuring acid resistance of the glass samples. This curve is based on the amount of weight loss of glass powder versus terms of melting. The weight losses of glass samples were determined according to Eq. 1:

$$\Delta WG = (W_0 - W_s)/S \quad (1)$$

Where:

ΔWG = The weight loss
W_0 = The initial sample weight
W_s = The sample weight after dissolution experiment
S = The sample surface area

As it is shown in Fig. 3, the increase in terms of melting up to 4 in G4 sample has minor influence on acid resistance. While in G5 and G6 samples, acid resistance has been severely reduced. If composition of glass be considered as the only effective parameter on acid

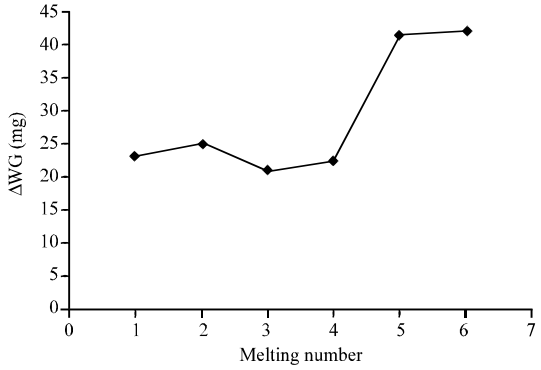

Fig. 3: Effect of different terms of making ferrite (melting number) on acid resistance of lead glass samples

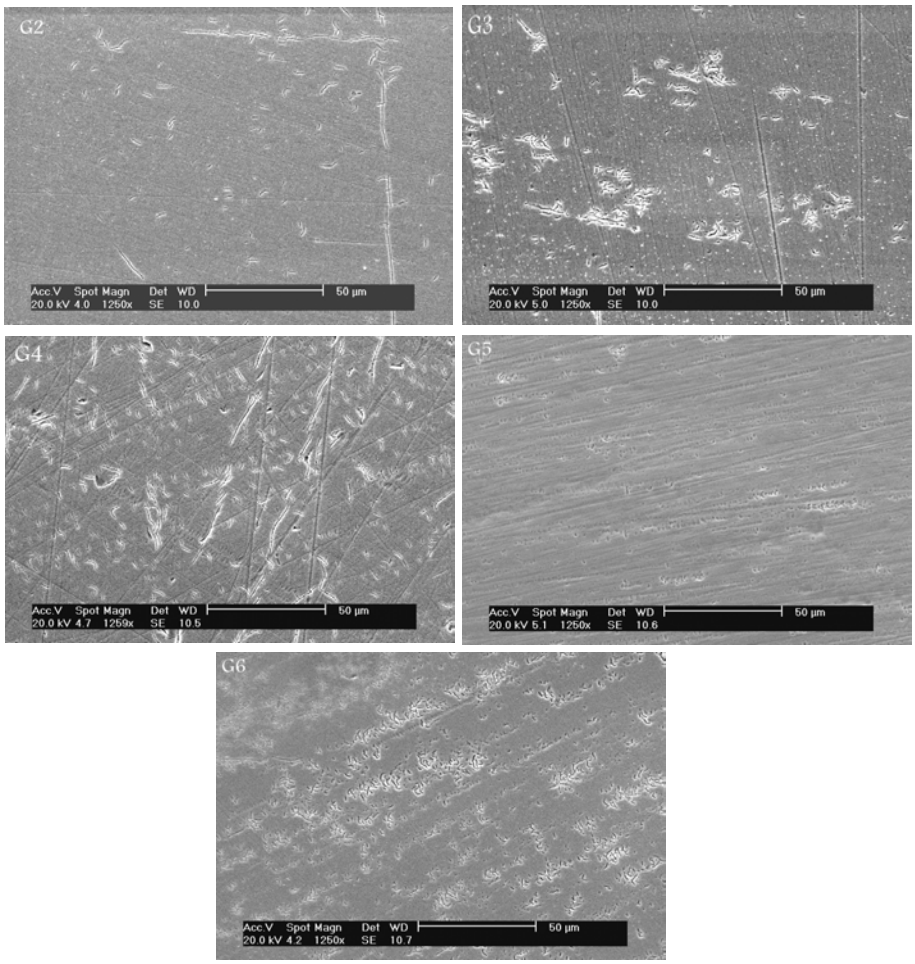

Fig. 4: Scanning electron microscopic images of glass samples (G2-G6) after 2 h heat treatment (1250 X)

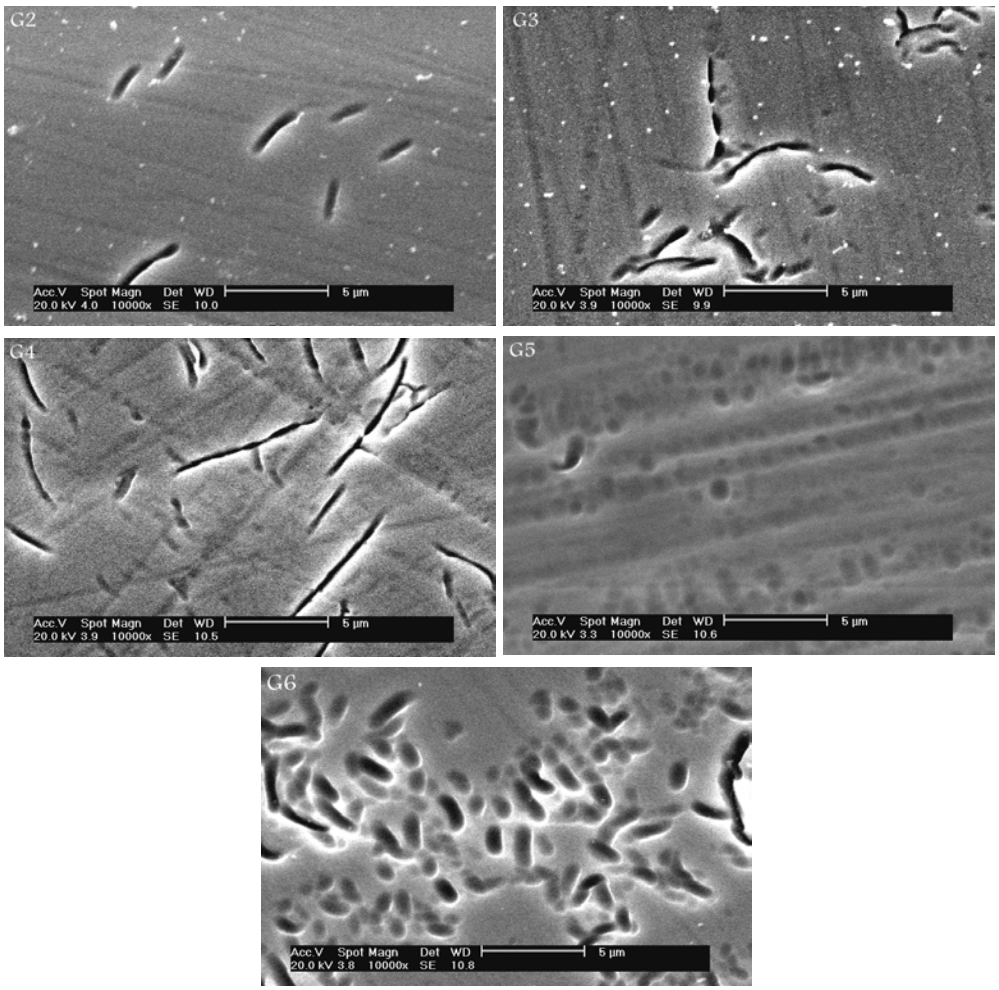

Fig. 5: Scanning electron microscopic images of glass samples (G2-G6) after 2 h heat treatment (10000 X)

resistance, it is expected that by reducing the amount of lead oxide and increase in the relative amount SiO_2 for G5 and G6 samples (Fig. 1), acid resistance is increased. It seems that different factors rather than composition affect properties of these glass samples. Microstructures shown in Fig. 4 and 5 confirm this issue. As it is clear in these Fig. 4 and 5, all glass samples have heterogeneous microstructures although in G5 and G6 samples, the value of heterogeneous structures are more intensive. The increase of heterogeneous regions in the samples has negative effects on acid resistance. It is noted that these microstructures cannot indicate phase separation phenomenon in these glasses. Phase separation phenomenon is visible by the microscopic methods with high magnification. Figure 6 shows the scanning electron microscope image (100000 X) of the G4 sample. Figure 6 does not show any phase separation. Such

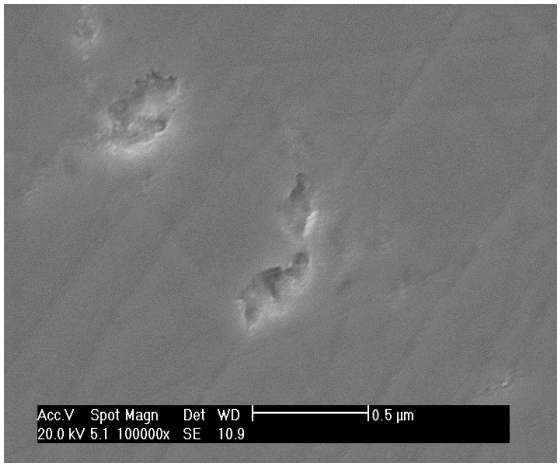

Fig. 6: Scanning electron microscopic images of glass sample (G4) after 2 h heat treatment (100000 X)

microstructures were observed in other studied samples. It seems that the heterogeneous microstructures are due to difference of density in the molten lead glasses which is largely created when molten glass is discharged in the mold. Regarding to increasing of melting terms, it was expected to have a high level of the homogeneous area in samples G5 and G6.

However, it was found that initial glass composition has more effect on the glass microstructure. With increasing terms of melting, evaporation of volatile components such as lead oxide in the composition (Fig. 1) leads to reduce largely homogeneous composition on the glass surface. This heterogeneous microstructure has undesirable effects on the optical properties of the glass (Levelut *et al*., 2006; Golubkov *et al*., 1999). Micro structural analysis of glass samples heat treatment at annealing temperature for 10 and 20 h was performed.

In Fig. 1-6, heterogeneous areas are created due to differences in combination and resulting in differences in density in the glass so that the etching procedure causes more corrosion of these regions. Silicon atoms make the glass network whereas the lead and other modifying cations are located in the interstitial locations in the LSG glass.

The network former intermediate elements such as Al, Ti and Zr participate in the glass structure as resulting of the presence of the large amount of the modifying cations. In spite of modifiers cooperation in structure of the glass network, their amounts in connection with Si are very low regarding to Table 1.

The glass network will have shrinkage due to break downing of the glass network when the silica bonds hydrolyze. Therefore, the shrinkage of the lead silicate glass during the decomposition process depends on the Si amount of the glass. As shown in Fig. 7-9a,b,

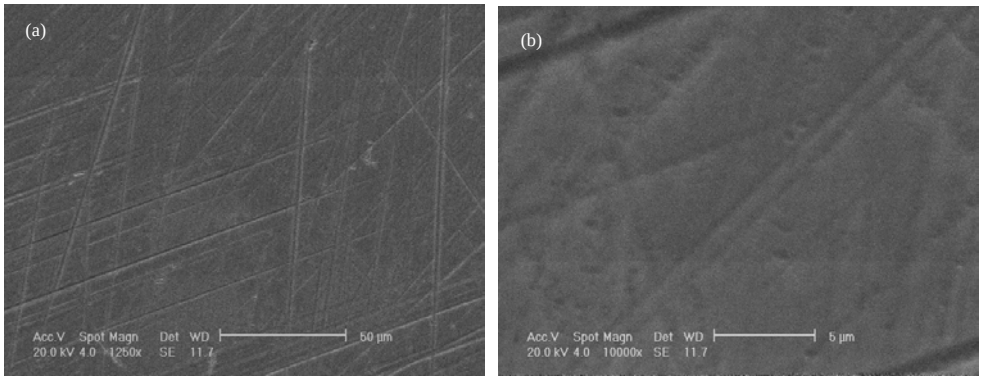

Fig. 7: Scanning electron microscopic images of glass sample (G2) after 10 h heat treatment; a) 1250 X and b) 10000 X

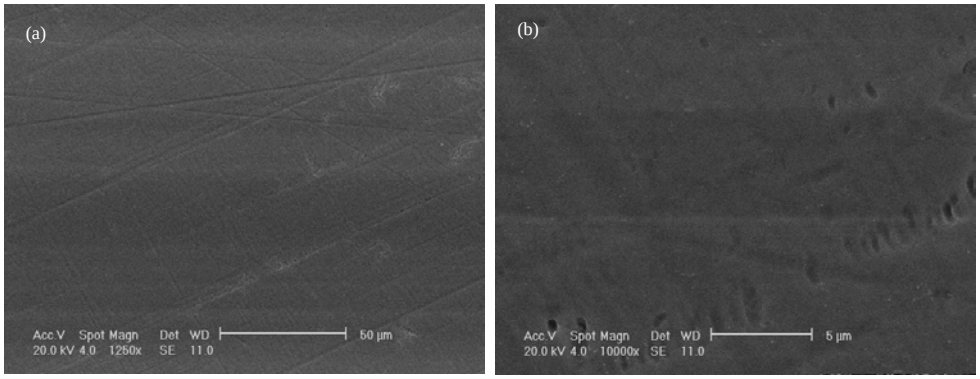

Fig. 8: Scanning electron microscopic images of glass sample (G3) after 10 h heat treatment; a) 1250 X and b) 10000 X

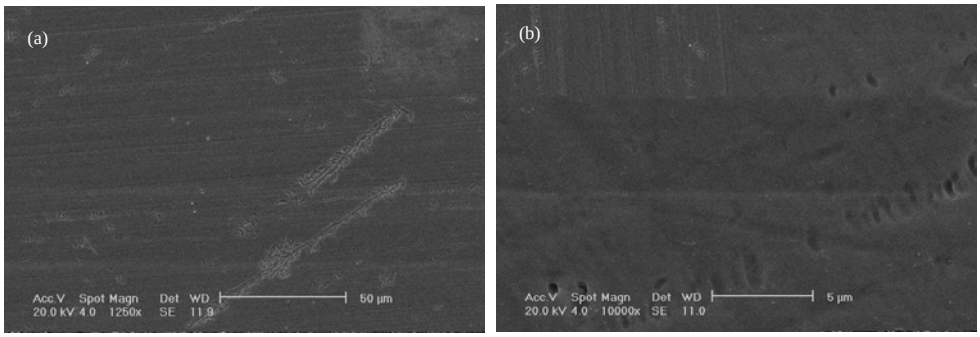

Fig. 9: Scanning electron microscopic images of glass sample (G4) after 10 h heat treatment; a) 1250 X and b) 10000 X

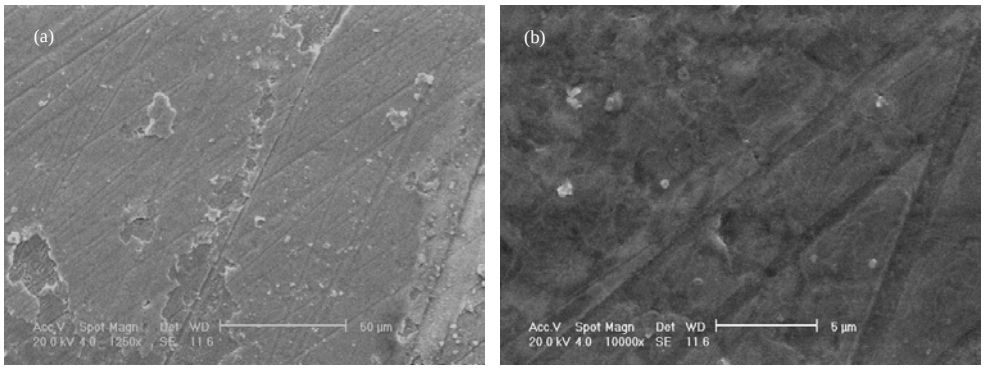

Fig. 10: Scanning electron microscopic images of glass sample (G2) after 20 h heat treatment; a) 1250X and b) 10000 X

increasing in heat treatment for 10 h the samples are obviously homogeneous and heterogeneous areas are seen with less intensity in the microstructure of glass. Whereas increasing of the heat treatment time to 20 h causes the destruction of the samples surface and significant cracks are observed on the glass surface (Fig. 10-12).

Since, the time of heat treatment of these samples was higher, it seems that evaporation of lead oxide from surface layer of the glass, differences in composition of surface and lower layers and different thermal expansion coefficients cause that these microstructures generate.

Figure 13 and 14a-f shows the microstructure of G5 and 6 samples melted 5 and 6 terms, respectively. As it is mentioned before for the other samples in these samples with increasing of annealing time to 10 h, the amount of heterogeneous areas has reduced. It is noteworthy that for samples that were heated to 20 h, surface layer in G6 sample is totally different from other samples and it is visible like a lattice surface.

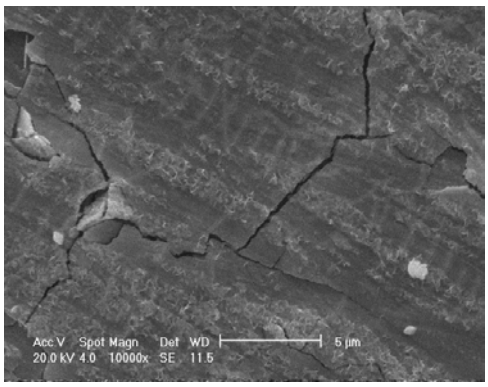

Fig. 11: Scanning electron microscopic images of glass sample (G3) after 20 h heat treatment (10000 X)

Surface cracks were not seen in this sample. This microstructure can be related to more terms of melting and longer annealing time in this sample that results higher evaporation of lead. Figure 1 shows this opinion and G6 sample has the lowest amount of lead (Golubkov *et al*., 1999).

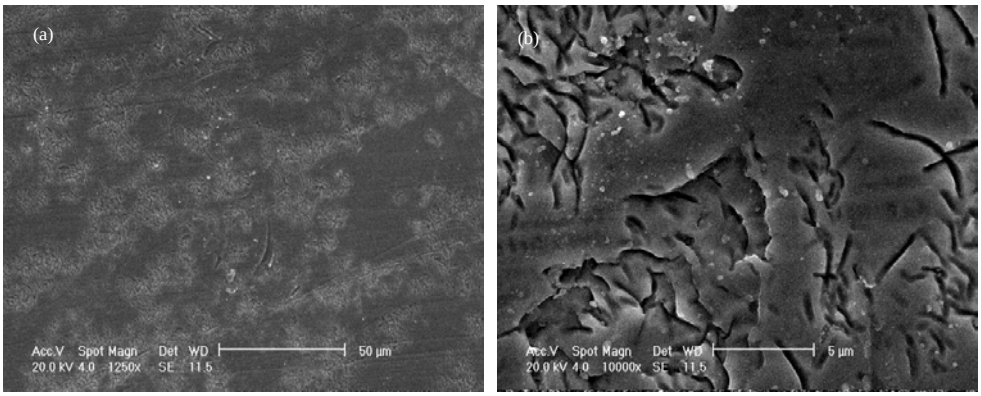

Fig. 12: Scanning electron microscopic images of glass sample (G4) after 20 h heat treatment; a (1250 X) and b (10000 X)

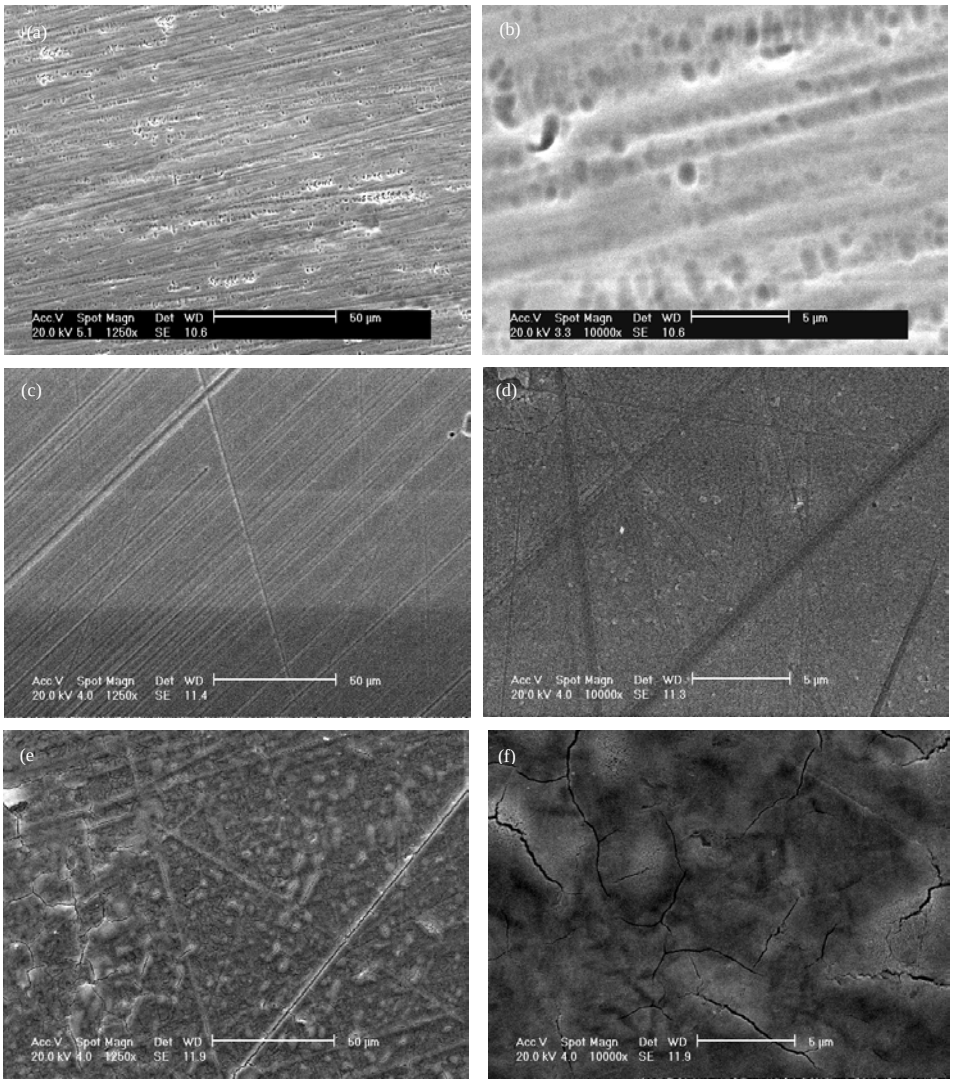

Fig. 13: Scanning electron microscopic images of glass sample (G5); a) 2 h heat treatment (1250 X); b) 2 h heat treatment (10000 X); c) 10 h heat treatment (1250 X); d) 10 h heat treatment (10000 X); e) 20 h heat treatment (1250 X) and f) 20 h heat teatment (10000 X)

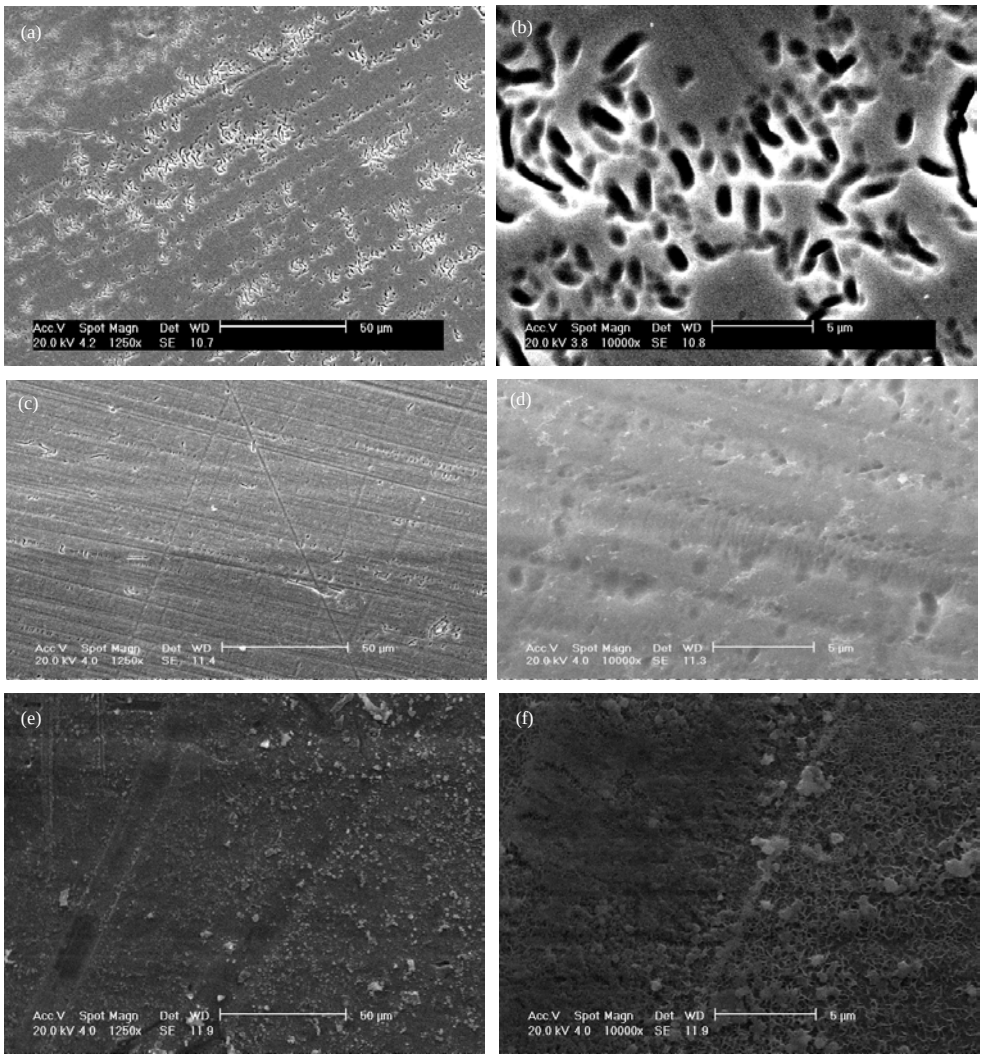

Fig. 14: Scanning electron microscopic images of glass sample (G6); a) 2 h heat treatment (1250 X); b) 2 h heat treatment (10000 X); c) 10 h heat treatment (1250 X); d) 10 h heat treatment (10000 X); e) 20 h heat treatment (1250 X) and f) 20 h heat treatment (10000 X)

CONCLUSION

The results of this study shows that for increasing homogeneity in lead silica glasses regard to high lead oxide values and high capability evaporation of lead oxide, Fritting method should be done more circumspectly. There is no direct relationship between increasing the terms of melting and increasing the homogeneity of the molten glass.

It seems that the fine structures created due to lead oxide evaporation will have a major role in using this method to help increase the homogeneity in molten glass lead. According to microscopic investigations conducted in this study, increasing annealing time will have a direct impact on improving the homogeneous areas and transparency of lead silica glass. Considering the lead-rich composition of this glass to determine the exact time for annealing is very important with regard to its effect on the micro-structure of the glass.

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