

## Reply to “Comment on ‘Influence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ Ratio on the Crystallization of Iron-Rich Glasses Made with Industrial Wastes’”

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OUR previous paper<sup>1</sup> described studies on modification of the crystallization ability and spinel/pyroxene ratio, as induced by thermal treatment and carbon addition, in high-iron-content glasses obtained from jarosite (J) and electric arc furnace dust (EAFD). The composition of these wastes is variable and complex.<sup>2</sup> As an example, J-glass generated from one of the main zinc producers in the world (and a partner in the Brite-Euram CT94-018 project) has been reported in a simplified form; all the elements are not shown (the glass also has fractional amounts of cadmium, indium, silver, arsenic, antimony, mercury, germanium, and sulfur, or traces of nickel, cobalt, and thallium<sup>2</sup>). The loss on ignition is very high, usually 35%–40%, because of the presence of  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  species; fractions of sulfur remain in the glass. This aspect introduces some uncertainties in the evaluation and tries to explain the results as a trend of behavior of the system under the investigated experimental conditions, i.e., powder (P) and bulk (B) glasses heated in air and nitrogen. It is also evident that these silicate glasses from industrial waste cannot be considered as model glasses, nor should their behavior be considered similar or compared to a phosphate model glass.<sup>3</sup>

The first comment notes that the weight gain due to the  $\text{Fe}^{2+}$  oxidation, obtained via thermogravimetry (TG), is higher than that expected, according to the reported  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio in the parent glass. The associated TG experimental error has been estimated to be  $\sim 0.1\%$  and  $\sim 0.2\%$  in the temperature intervals of  $20^\circ\text{--}500^\circ\text{C}$  and  $20^\circ\text{--}1000^\circ\text{C}$ , respectively. Therefore, the measured weight gain in the  $500^\circ\text{--}1000^\circ\text{C}$  interval for the P-air, J-0 glass (jarosite glass without carbon)—0.44%, reported as  $\sim 0.5\%$  of the total weight gain—is in fair agreement with the theoretical value of 0.22%. The uncertainty on the determination of  $\text{Fe}^{2+}$  ions and total iron, which influences the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio by  $\pm 5\%$ , also must be considered.

A great difference is observed in the P-air, J-2 sample (jarosite glass with 2% carbon addition), where the theoretical value should be 0.82% but a value of 1.62% (reported as  $\sim 2\%$ ) was measured in the  $500^\circ\text{--}1000^\circ\text{C}$  interval.<sup>1</sup> This anomaly is explained by the presence of carbon in the glass batch, which might have reduced some of the  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pb}^{2+}$  ions, as well as the other minor elements, to the elemental form. Previous research<sup>4</sup> has assumed that, in silicate melts obtained in a reducing atmosphere, iron exists simultaneously in the following forms:  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Fe}^0$ . This assumption is confirmed by the large crystallization field of iron in the phase diagram of the  $\text{FeO}\text{--}\text{Fe}_2\text{O}_3\text{--}\text{SiO}_2$  system.<sup>5</sup> Metallic iron has not been observed via X-ray diffractometry (XRD), probably because of the amorphous structure. Metallic drops have been observed in EAFD glass with 5% carbon addition. In this case, an oxidation weight gain of  $\sim 6.5\text{ wt}\%$  is observed in the  $700^\circ\text{--}1100^\circ\text{C}$  temperature range and is accompanied by a very intensive and large exothermic effect that overlaps the crystallization peak,

at  $\sim 760^\circ\text{C}$ , and the endothermic melting effects in the  $1100^\circ\text{--}1300^\circ\text{C}$  range.

In regard to the two exothermic effects in the differential thermal analysis (DTA) trace of the J-0 sample, the first—large and with low intensity, corresponding to a weight gain of  $\sim 0.4\%$ —was attributed to a diffusion-controlled process with low reaction order (i.e., surface oxidation). In the temperature range where this exothermic effect was noticed (the first onset at  $620^\circ\text{C}$  is close to the glass transition ( $T_g = 580^\circ\text{C}$ )), the viscosity is very high ( $\sim 10^{10}\text{--}10^{12}$  dPa·s); the crystallization processes are very slow and cannot be identified via DTA. On the other hand, several studies were dedicated to the identification of the crystallization peaks in the TG-DTA of iron-rich jarosite glasses, presented in literature<sup>6–8</sup> referenced in our previous paper.<sup>1</sup> In particular, Karamanov *et al.*<sup>6</sup> investigated a glass composition similar to that of the J-0 sample. The crystallization peaks, at a heating rate of  $10^\circ\text{C}/\text{min}$ , were observed at  $780^\circ$ ,  $805^\circ$ , and  $875^\circ\text{C}$  for the P- $\text{N}_2$ , B-air, and P-air samples, respectively. A clear oxidation exothermic effect in the P-air sample was observed at  $720^\circ\text{C}$ , with a weight gain of  $\sim 0.6\%$ . In that work, the degree of phase transformation ( $\alpha$ ) at  $680^\circ\text{C}$  was measured using density variation<sup>7</sup> and XRD methods for the P and B samples. For the B sample, a consistent variation of density, which was related to magnetite and pyroxene formation, was observed, whereas for the P sample, the crystallization was negligible, even after 300 min. This result was attributed to the oxidation of the P sample with consequent inhibition of the crystallization process. Therefore, the weight gain was detected at  $620^\circ$  and  $680^\circ\text{C}$  and the oxidation was related to a simple diffusion process (square-root-of-time dependence). If we report the  $\alpha$  value of the B sample and the weight gain for the P sample on the same timescale, the plot in Fig. 1 is obtained. Thus, after 20 min, the crystallization is negligible, whereas oxidation comprises 30% of the total weight gain. Therefore, we concluded that, in these powder glasses, oxidation occurs at low temperature and inhibits the crystallization of magnetite and pyroxene. Figure 2 shows the isothermal crystallization “S” curve at  $620^\circ$  and  $660^\circ\text{C}$

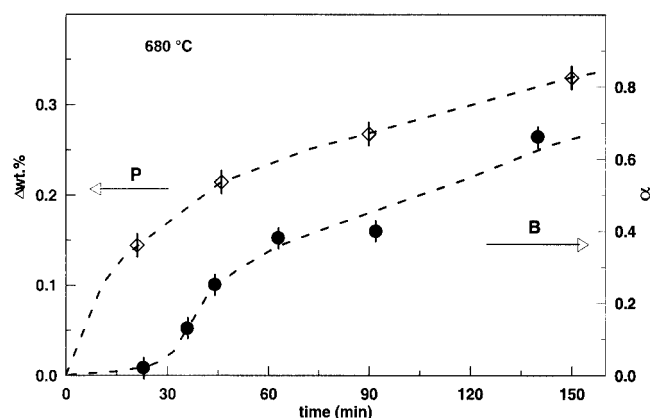


Fig. 1. Weight gain of the P sample and degree of transformation ( $\alpha$ ) of the B sample, as a function of time at  $680^\circ\text{C}$ .

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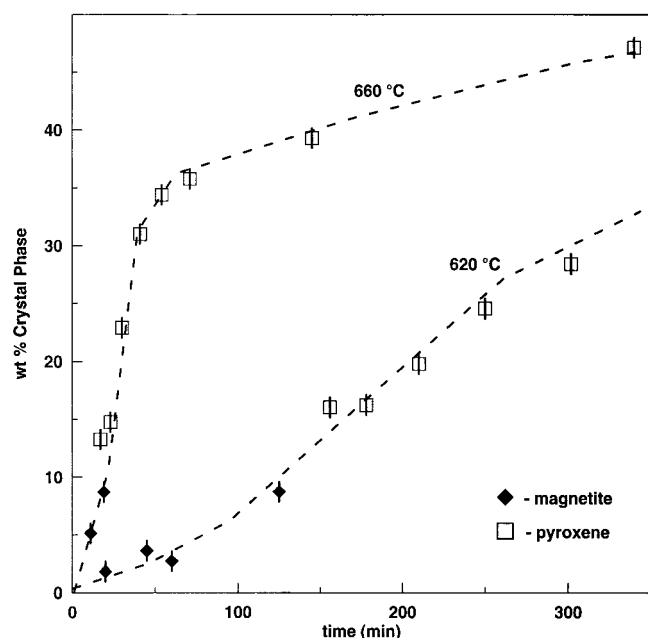


Fig. 2. Percentage of crystal phase (magnetite and pyroxene) formed, as a function of time at 620° and 660°C in a jarosite bulk glass.

for a 24% iron oxide bulk jarosite glass.<sup>7</sup> The isothermal kinetic curve is continuous; i.e., pyroxene crystallization immediately follows the magnetite formation and no step is evident between the two phases of formation. Under nonisothermal conditions, such as those in a TG-DTA test, the glass shows a single exothermic crystallization peak and two melting endothermic peaks. The crystallization peak, at a heating rate of 10°C/min, is observed at 746°, 755°, and 821°C for the P-N<sub>2</sub>, B-air, and P-air samples, respectively; an oxidation exothermic effect in the P-air sample was observed at 720°C. XRD spectra<sup>8</sup> obtained from samples treated at 730°C in air and nitrogen showed that, after 30 min, crystallization was completed in the P-N<sub>2</sub> sample, with the formation of 8–10 wt% magnetite and 33–35 wt% pyroxene, whereas only 4–6 wt% magnetite and 5–7 wt% pyroxene were formed in the P-air sample. The activation energy of crystal growth, the Avrami parameter, and the percentage of crystal phase formed in the B-air and P-N<sub>2</sub> samples are similar; in the P-air sample, the crystallization occurs at a higher temperature with a lower reaction order (i.e., 1.5, compared to 3 for the B-air and P-N<sub>2</sub> samples<sup>8</sup>).

The J-2 glass was obtained by adding 2% of carbon to the glass batch, to decrease the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio (which was 2.1, compared to 10.5 for the J-0 sample). The results, shown in Fig. 3 of the previous paper,<sup>1</sup> are also the subject of the comment and need additional explanation.

By decreasing the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio, the magnetite/pyroxene ratio and the rate of crystallization have been increased. All the crystallization peaks in the DTA traces occurred at lower temperatures than that of the J-0 glass. The Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio of 2.1 is similar to that of magnetite (FeO·Fe<sub>2</sub>O<sub>3</sub>), and the amount of spinel formed in the bulk of the J-2 glass (~22%) is similar to the stoichiometric value, if zinc is considered. The rate of magnetite formation is so fast that completely amorphous glasses can be obtained only via rapid quenching. Therefore, the results reported in Fig. 3 of the previous paper<sup>1</sup> can be explained, assuming that most of the Fe<sup>2+</sup> ions enter into the spinel structure. Then, more time or higher temperature is required for Fe<sup>2+</sup> oxidation and the corresponding exothermic peak in the DTA trace for J-2 glass occurs at higher temperatures than that for J-0 glass. Similar behavior was demonstrated in Fig. 5 in the previous paper<sup>1</sup> by the EAFD glass, where the TG variation has been recorded in the same temperature interval as the crystallization peak. The oxidation exothermic effect overlaps the very intensive crystallization peak and is not clearly distinguished.

A low-angle XRD technique was used to investigate the distribution of the phases formed on the surface of the glass during heating.<sup>6,7</sup> A glass sample was heat-treated for 2 h at 950°C. After polishing the surface to some fraction of a millimeter, the analysis was repeated. The comparison highlighted that, under air conditions, hematite (Fe<sub>2</sub>O<sub>3</sub>) was prevalent on the surface of the glass in a concentration of ~35 wt%, which is higher than the total iron content in the parent glass. In the bulk of the glass, pyroxene was the main crystal phase. Optical microscopy confirmed the presence of a red-brown hematite phase ~0.1 mm thick on the surface of the glasses.

Therefore, we have concluded that iron migration is preferred over the oxygen diffusion mechanism, which, on the other hand, cannot be excluded. More specific investigation is required to clarify this complex mechanism, which is influenced by several variables such as glass composition, surface tension, and diffusion coefficients.

## References

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