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High temperature properties of an iron phosphate melt containing high chrome nuclear waste [☆]

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Abstract

Iron phosphate glasses are of interest for immobilizing high level nuclear waste (HLW). The high temperature viscosity and AC electrical conductivity of an iron phosphate melt containing 2.8 mass% chrome oxide were investigated in this work. The viscosity of this melt varied from 10 to 50 poise from 1350 to 1150 °C, respectively, while the activation energy for viscous flow was 82 and 126 kJ/mol during heating and cooling the melt, respectively. The viscosity of the melt at 1250 °C increased with time due to the reduction of Fe^{3+} to Fe^{2+}. The AC electrical conductivity of the melt varied from 45 to 65 S/m at 1050 and 1350 °C, respectively. The activation energy for AC electrical conductivity was 28 and 18 kJ/mol during heating and cooling, respectively. The weight loss rate of the melt at 1250 °C after 20 h was only 5×10^{-4} g/cm^2/h.

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1. Introduction

Iron phosphate glasses have properties that make them attractive for vitrifying high level nuclear waste (HLW) [1,2]. In some instances, iron phosphate glasses may be more technically suitable and less expensive than the borosilicate glasses now being used to vitrify certain types of HLW. This is especially true for those wastes containing significant amounts of phosphate, iron oxide, chrome oxide and heavy metal oxides, such as Bi_2O_3, La_2O_3 and U_3O_8 [3]. These oxides generally have a low chemical solubility in most borosilicate glasses and this lowers the waste loading, such that the radioactive waste volume becomes undesirably large.

Recently, it was reported that much of the HLW stored at Hanford WA, which contains up to 4.25 mass% chrome oxide (Cr_2O_3), could be vitrified by simply adding 25–30 mass% phosphate directly to the HLW and melting the mixture at 1250 °C for few hours [4]. The iron phosphate glasses made in this simple way, with a waste loading of up to 75 mass% HLW had an extremely high chemical durability, that met all of the DOE chemical requirements.

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For practical purposes, the high temperature properties of a melt containing several weight percent chrome oxide are important for selecting a method of melting the waste material, for designing a furnace with maximum output and for choosing the most corrosion resistant, melt-contact refractory. Since the fluidity of an iron phosphate melt is important to determining the temperature and time needed for melting, knowledge of the viscosity–temperature curve for a melt is useful in choosing the melting and pouring procedures. The viscosity of a melt can also have a strong effect on the degree to which the melt-contact refractory is wet and corroded by the melt. Similarly, the AC electrical conductivity of a melt is also important, if the material is to be melted in a joule heated melter (JHM) as is now being done at Savannah River site to vitrify HLW.

The aim of the present study was to measure the viscosity and AC electrical conductivity of an iron phosphate melt that contained 70 mass% of a simulated HLW that was representative of the high chrome containing wastes stored at Hanford, WA. The viscosity and AC electrical conductivity, along with the weight loss of the melt, were measured over the temperature range that would likely be used for melting from 1100 to 1350 °C.

2. Experiment procedure

2.1. Glass preparation

The composition of the simulated high chrome HLW that is representative of the high chrome containing wastes stored at Hanford, WA, along with the composition of the vitrified iron phosphate waste form, IP70W, that contained 70 mass% of the simulated HLW have been reported previously [4]. The composition of the IP70W iron phosphate waste form used in the present work, along with the starting raw materials are given in Table 1. The choice of raw materials is arbitrary, so other materials could have been chosen.

A batch that produced 100 g of IP70W glass was prepared by mixing the appropriate amounts of the raw materials listed in Table 1. Note, that the required P_2O_5 was added as sodium phosphate, but other sources of phosphate could have been used. To compensate for the potential volatilization of P_2O_5 during melting, an additional 5 mass% over the required amount of P_2O_5 was added to the batch. The batch materials were ground to pass a 100-mesh sieve and dry mixed by tumbling in a sealed plastic container. The batch was melted in an ordinary fireclay crucible at 1250 °C for 2 h in air, during which time the melt was stirred two times with a silica glass rod at 30 min intervals to aid homogenization. The melt was then poured on a cold steel plate to produce frit that was re-melted for the viscosity and AC electrical conductivity measurements.

Table 1
Composition, mass%, of the simulated high chrome waste, and iron phosphate melt containing 70 mass% (IP70W) of the simulated waste

Component	Simulated waste	IP70W melt	Chemicals used in batch
Al_2O_3	21	14.70	$Al(OH)_3$
Bi_2O_3	3	2.10	Bi_2O_3
CaF_2	3	2.10	CaF_2
Cr_2O_3	4	2.80	Na_2CrO_4
Fe_2O_3	9	6.30	Fe_2O_3
La_2O_3	1	0.70	La_2O_3
Na_2O	26	18.20	Na_2CO_3
P_2O_5	5	33.50	$NaH_2PO_4 \cdot 2H_2O$
SiO_2	16	11.20	$Na_2SiO_3 \cdot 5H_2O$
U_3O_8	9	6.30	UO_2
ZrO_2	3	2.10	ZrO_2

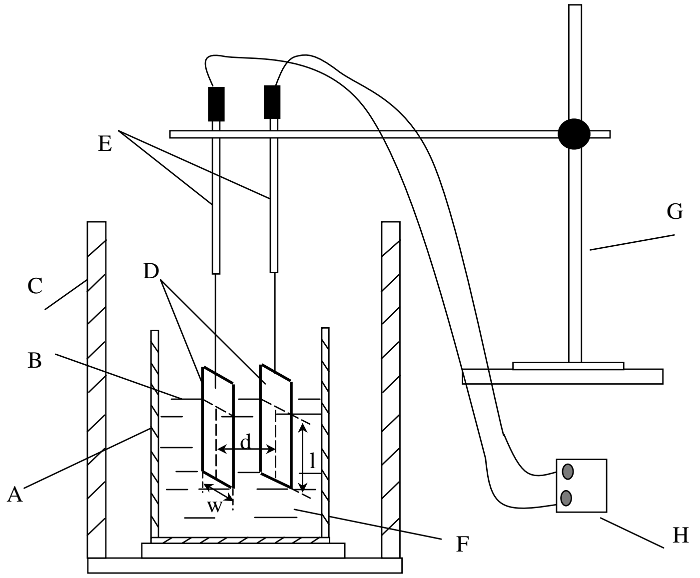
2.2. Viscosity measurement

The viscosity of the melt was measured from 1150 to 1350 °C with a Brookfield viscometer (Brookfield Engineering Laboratories, INC, MA 02072, USA). A non-standard alumina spindle was made from a 10 ml straight wall crucible. Three standard viscosity oils (965, 98.8 and 97.2 centipoise supplied by Brookfield Engineering Laboratories, INC, MA 02072, USA) were used to calibrate the viscometer. The error in the viscosity is estimated at $\leqslant 5\%$.

Before each measurement, the melt in an alumina crucible was thermally equilibrated at the chosen temperature for 30 min, whereupon, the preheated alumina spindle was immersed in the melt. The viscosity of the melt was measured three times at a spindle speed of 20 rpm. The viscosity was calculated from the calibration curve and the error for the average of the three measurements is estimated at ±5%.

2.3. Electrical conductivity measurement

The AC electrical conductivity of the melt in an alumina crucible was measured at 120 Hz and 1 kHz over the temperature range of 1050–1350 °C using the apparatus shown in Fig. 1. Fifty grams of glass were put into a 30 ml cylindrical dense alumina crucible (A), which sat on the base of an electric furnace (C) (Model 1700S KBL, Rapid Temp furnace, CM Furnace Inc. Bloomfield, NJ 07003, USA). The glass was re-melted at 1050 °C for 30 min. Two parallel platinum/rhodium electrodes (D) separated by a distance *d* and connected to an adjustable rack (G) were slowly lowered into the melt (F). When the electrodes touched the surface of the melt, the electrical resistance between the electrodes,



A: Alumina crucible, B: Melt level, C: Electric furnace, D: Platinum electrodes (40x20 mm), E: Refractory tube, F: Iron phosphate melt, G: Adjustable rack, H: L/C/R meter

Fig. 1. Schematic of the apparatus used to measure the AC electrical conductivity of the iron phosphate melt at a frequency of 120 Hz and 1 kHz.

as measured by a L/C/R meter (H) (Model LCR-500, IET Labs, Inc. Westbury, NY 11590, USA), suddenly decreased. The electrodes were then carefully lowered an additional distance (l) into the melt. The electrical resistance, R of the melt between the two electrodes was measured three times over a period of 5 min. The error in the average R value is <1%.

The electrical conductivity, σ, was calculated from the equation: $\sigma = (Kd)/(wlR)$, where d is the distance between the electrodes, w is the width of the electrode, l is the depth of the electrodes in the melt and K is the cell constant of the apparatus. The cell constant, K, was determined by measuring the conductivity of three KCl solutions, at room temperature, of different concentrations (0.75, 7.47, and 76.58 g KCl/kg H_2O whose conductivity was 0.141, 1.285 and 11.13 S/m, respectively). The cell constant K was 0.8014 for this apparatus. After the iron phosphate melt had been at the chosen temperature for 30 min, the resistance, R of the melt was measured from 1050 to 1350 °C at 50 °C intervals.

2.4. Weight loss rate measurement

A nominal 30 g of quenched glass frit, whose weight was measured to ±0.01 mg was re-melted in a 50 ml platinum/rhodium crucible at 1250 °C. After being at 1250 °C for a selected time, the melt and the crucible were cooled to room temperature and reweighed (nearest ±0.01 mg). The weight loss per hour per square cm of melt surface was calculated from the weight change (assuming that the weight of the platinum crucible remained constant).

To measure the concentration ratio of $Fe^{2+}/(Fe^{2+} + Fe^{3+})$, Mossbauer spectra was obtained at 23 °C on an ASA 600 spectrometer. The estimated measurement error was ±4%.

3. Results

3.1. Viscosity

The viscosity of the melt at 1250 °C increased with the time as shown in Fig. 2.

The viscosity of the IP70W melt varied with temperature as shown in Fig. 3. As melt was first heated from 1150 to 1350 °C and then cooled, the viscosity decreased with increasing temperature and then increased during cooling as expected. However, the viscosity during cooling was higher than that during heating and the difference between the two viscosity curves increased with decreasing temperature, see Fig. 3.

Over the temperature range from 1150 to 1350 °C, the viscosity for the IP70W melt was significantly higher

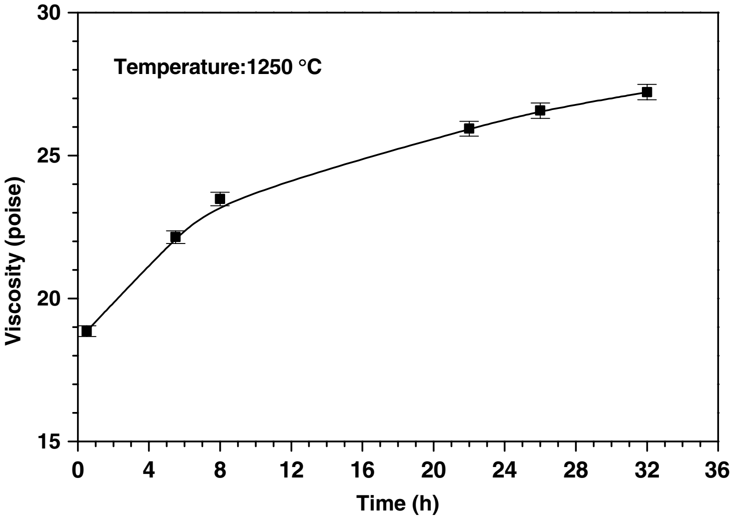


Fig. 2. Viscosity of the IP70W melt at 1250 °C as a function of time. Spindle speed was 20 rpm.

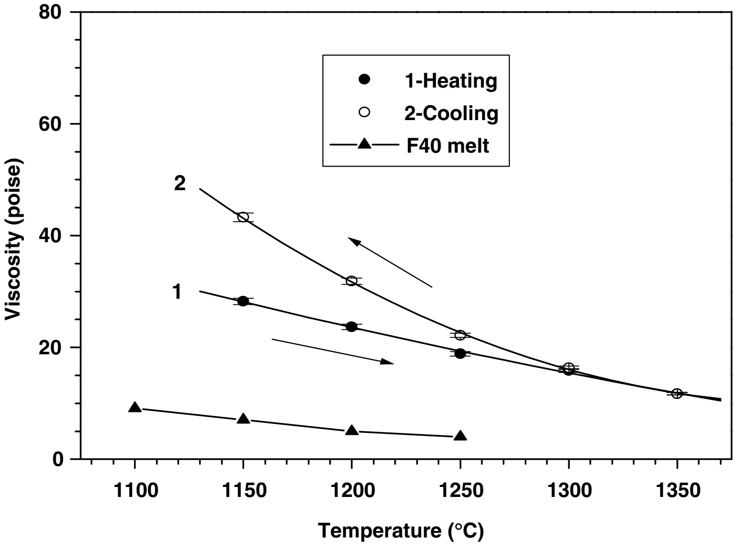


Fig. 3. Viscosity of the IP70W melt as a function of temperature at a spindle speeds of 20 rpm measured during heating (1) then cooling (2). Viscosity for the F40 melt ($43Fe_2O_3 \cdot 57P_2O_5$ mass%) is from Ref. [4].

than that for the alkali-free F40 phosphate glass [5] (composition is $43Fe_2O_3 \cdot 57P_2O_5$ mass%). The activation energy for viscous flow for IP70W melt was calculated from the Arrhenius plot in Fig. 4.

3.2. AC electrical conductivity

The AC electrical conductivity of the IP70W melt increased only slightly with temperature, as shown in Fig. 5. The conductivity was measured at a frequency of 120 and 1000 Hz, but the electrical conductivity at 1000 Hz was only 1 or 2 S/m less than the conductivity at 120 Hz. Thus, only the conductivity at 1000 Hz is shown in Fig. 5 and the activation energy for charge migration for IPW70 melt was calculated from the Arrhenius plot in Fig. 6.

The electrical conductivity, σ, of the IP70W melt only varied from 45 to 65 S/m over the temperature range used. The σ for IP 70W is about three times larger than that (14–25 S/m) for the sodium containing F40N15 melt, whose composition is $40Fe_2O_3 \cdot 53P_2O_5 \cdot 7Na_2O$ mass% [6].

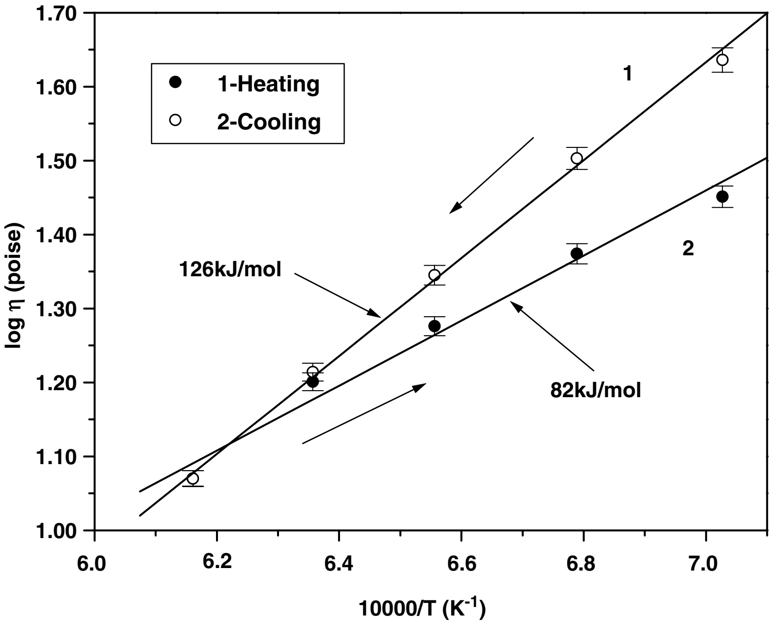


Fig. 4. Arrhenius plot of log η (poise) versus inverse temperature for the IP70W melt during heating (1) followed by cooling (2). The activation energy for viscous flow was calculated from the slope of the line.

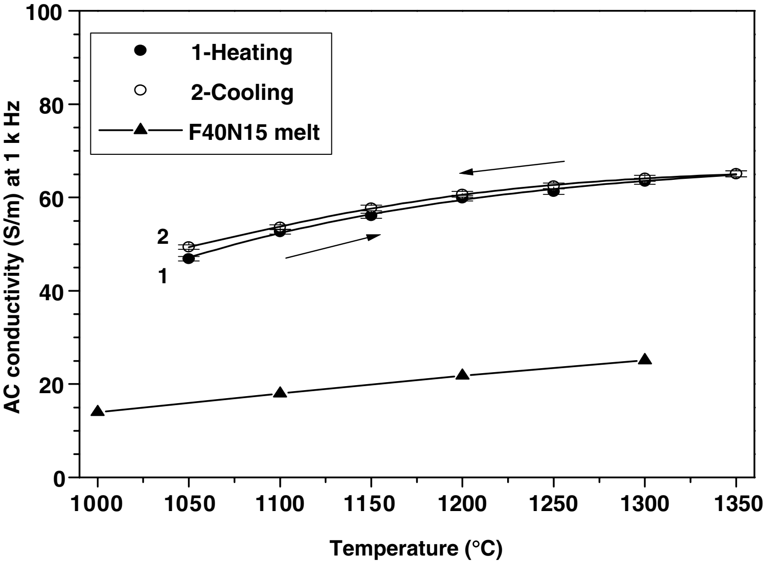


Fig. 5. AC electrical conductivity of the IP70W melt as a function of temperature during heating (1) then cooling (2) at the frequency of 1 kHz, data for the F40N15 iron phosphate melt ($40Fe_2O_3 \cdot 53P_2O_5 \cdot 7Na_2O$ mass%) are from Ref. [6].

3.3. Weight loss

The total weight loss for the 30 g IP70W melt in the platinum/rhodium crucible (the melt surface area in contact with air was 12.57 cm^2) was 405.50 mg and the rate of weight loss was 5.0×10^{-4} g/cm^2/h after 40 h at a temperature of 1250 °C. The weight loss rate decreased with the time as shown in Fig. 7. The weight loss rate at 1250 °C decreased at first and then became nearly constant after 20 h.

Table 2 shows the Mossbauer hyperfine parameters calculated from the relevant spectra. The ratio of

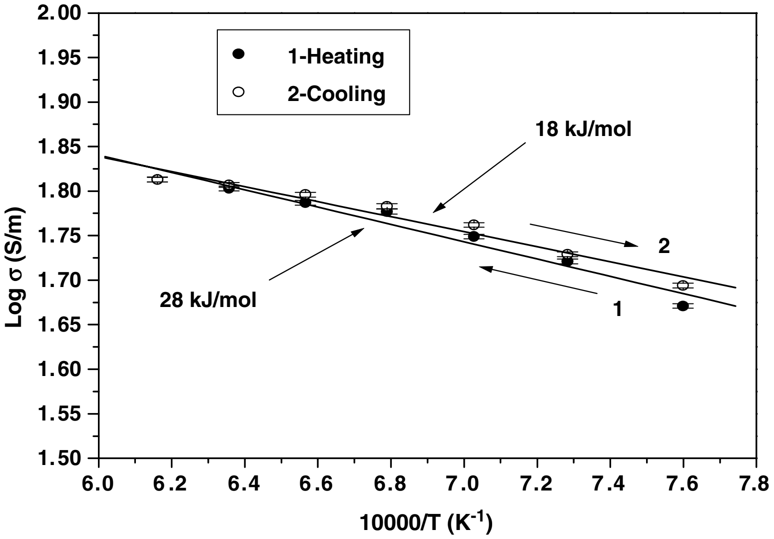


Fig. 6. Arrhenius plot of log σ (S/m) versus inverse temperature during heating (1) followed by cooling (2). Activation energy of IP70W melt for charge migration is obtained from the slope of the line.

Table 2
Room temperature Mossbauer spectra parameters for IP70W samples melted at 1250 °C for 2 and 40 h (IS = isomer shift, QS = quadrupole shift)

Sample	IS (mm/s)		QS (mm/s)		% Fe(II) fraction
	Fe(II)	Fe(III)	Fe(II)	Fe(III)	
2 h	0.95	0.41	2.16	0.89	7
40 h	0.89	0.43	2.56	0.86	35

$Fe^{2+}/(Fe^{2+} + Fe^{3+})$ for the glasses melted at 1250 °C for 2 and 40 h were 7% and 35%, respectively.

4. Discussion

4.1. Viscosity

The reason for the increasing viscosity of the IP70W melt with time, see Fig. 2, is believed to be related to the redox reaction, where the Fe^{3+} ions in the melt are reduced to Fe^{2+} ions (see Table 2). Ray et al. [2] reported the same result that the ratio of $Fe^{2+}/(Fe^{3+}+ Fe^{2+})$ increases from 0.19 to 0.26 for an iron phosphate glass ($43Fe_2O_3 \cdot 57P_2O_5$ mass%) which was held at 1200 °C from 1 to 24 h, respectively. Some of the Fe^{3+} ions reduced to Fe^{2+} ions and increased the cross-linking in the glass network, thereby increasing the viscosity of the melt.

Small changes in the composition of the melt during the time the viscosity measurements were being made could also have caused an increase in viscosity, although these changes are considered small. Ray et al. [2] measured the composition of the $43Fe_2O_3 \cdot 57P_2O_5$ mass% glass after being melted in a high density alumina crucible (Coors AD998) at 1300 °C for 1 h and found that the glass contained 1.18 mass% Al_2O_3. Furthermore, a small decrease in the Na_2O, CaF_2 and P_2O_5 content could have occurred due to volatilization of these components, particularly at higher temperature.

The viscosity of the IP70W melt followed an Arrhenius temperature dependence, as shown by the straight lines in Fig. 4. For heating and cooling, the activation energies were 82 and 126 kJ/mol (±5% in error), respectively. The difference in activation energy for heating and cooling is attributed to the change in the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio that occurred in the melt during the heating cycle. Ray et al. [2] reported that the ratio of $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ changed from 0.17 to 0.42 when a $43Fe_2O_3 \cdot 57P_2O_5$ (mass%) melt was heated from 1150 to 1350 °C. In addition to an increase in the viscosity with temperature, which was measured in 50 °C increments (0.5 h at each temperature), the activation energy is also higher during cooling for the melt containing more Fe^{2+} ions (as shown in Table 2, the Fe^{2+} ions increasing with melting time). Although the viscosity of melt changed with time, the value of activation energy for viscous flow was comparable with that (108 kJ/mol) for F40 phosphate glass ($43Fe_2O_3 \cdot 57P_2O_5$ mass%) reported by Kim and Day [5].

4.2. AC electrical conductivity

In iron phosphate glasses, the electric charge migration can be due to electrons transfer between the Fe^{2+}

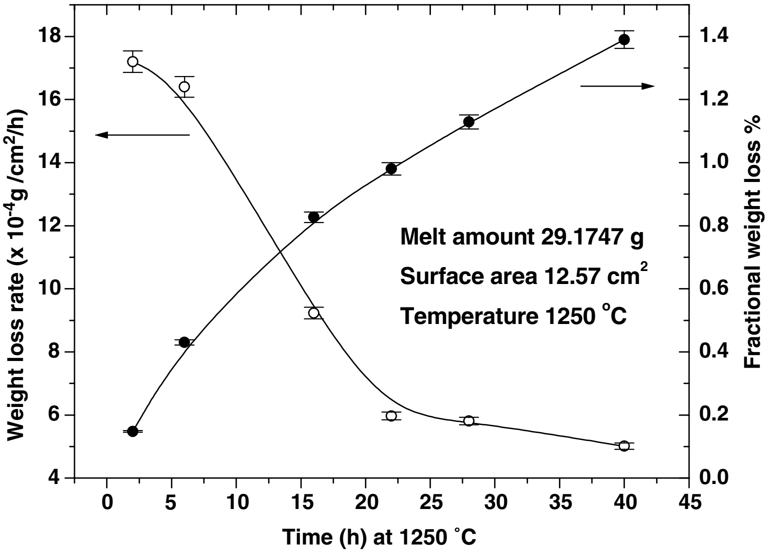


Fig. 7. Weight loss rate and fractional weight loss for the IP70W melt as a function of time at the temperature of 1250 °C. Initial weight and surface area of melt was 29.1747 g and 12.57 cm^2, respectively.

and Fe^{3+} ions, and to the movement of alkali ions, such as Na^+ ions in the glass network. In the IP70W glass melted at 1250 °C for 2 h, Mossbauer data [7] shows that only about 7% of the iron was present as Fe^{2+} ions at room temperature. Since the concentration of Fe^{2+} ions is known to increase with increasing melting temperature or with time at a given melting temperature (see Table 2) while measuring the AC conductivity, electron transfer in the melt would be expected to increase with both time and temperature. Also, the mobility of the Na^+ ions in the melt is expected to increase with increasing temperature. The increase in the AC electrical conductivity with increasing temperature as shown in Fig. 5, therefore, is attributed to the increase in of $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio and to some unknown increase in the Na^+ ion mobility.

The data points in Fig. 6 are close to an Arrhenius behavior, but the fit is not perfect. The slight, but noticeable curvature of the points is attributed to the change in the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio that was certainly changing during the initial heating cycle and was likely to be changing as the melt cooled. Ray et al. [2] reported that the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio for a $43Fe_2O_3 \cdot 57P_2O_5$ mass% iron phosphate glass changed from 0.17 to 0.42, when melt was held for 1 h at temperatures between 1150 and 1350 °C. The activation energy for AC electrical conductivity was calculated as 28 and 18 kJ/mol (±5% in error) from the slope of the straight line (the relationship factor, R, for the fit straight line was −0.97952 and −0.97864, respectively) for the heating and cooling cycle respectively, see Fig. 6. Both values for the activation energy are comparable with the values reported by Kim et al. for other iron phosphate glass [6].

4.3. Weight loss

The ratio of $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ for the IP70W melt increased during the time the melt was held at 1250 °C (Table 2). When Fe_2O_3 converts to FeO, oxygen is released from the melt according to equation:

$$Fe_2O_3 \rightarrow 2FeO + 1/2\,O_2 \tag{1}$$

When the ratio of $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ increased from 7% to 35%, more than 10% of the total weight loss (405.50 mg) can be accounted for by the release of oxygen (51.35 mg) from the melt as calculated from Eq. (1). Furthermore the evaporation of some components from the melt, such as Na_2O, CaF_2 and P_2O_5 could contribute to the small weight loss that occurred at 1250 °C. Overall, the weight loss fraction (only 1.39×10^{-2} after 40 h) and the weight loss rate (only 5.0×10^{-4} g/cm^2/h after 40 h) were very small (see Fig. 7).

5. Conclusion

The viscosity of the IP70W melt between 1150 and 1350 °C varied from 10 to 50 poise, respectively, while the activation energy for viscous flow was 82 and 126 kJ/mol as the melt was heated and cooled, respectively. When the melt was held at 1250 °C, the viscosity increased with time due to an increase in the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio, reduction of Fe^{3+} to Fe^{2+}.

The AC electrical conductivity between 1050 and 1350 °C varied from 45 to 65 S/m, which is similar to the electrical conductivity reported for another iron phosphate melt, F40N15 melt. The activation energy for electrical conductivity was 28 and 18 kJ/mol for heating and cooling the melt, respectively.

A small weight loss rate was observed for melt at 1250 °C, but overall the weight loss was nearly negligible.

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