STRUCTURAL AND MECHNICAL RESPONSE TO A THERMO-RHEOLOGIC HISTORY OF SPINEL SLUDGE IN HIGH-LEVEL WASTE GLASS

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The composition and structure of a sludge sample from a high-level waste glass melter were studied using optical and scanning electron microscopy, and x-ray diffraction. At isothermal heat treatments between 1050°C and 1350°C, spinel crystals partly dissolved to form on cooling tiny (~ 10 μm) star-like crystals or dendrites. The shear stress in sludge was measured at a constant shear rate (from 0.005 s^{-1} to 1.0 s^{-1}) and temperature (from 1050°C to 1350°C) during repeated deformation and after idling. The initial thixotropic character of the loose structure of the settled sludge turned on subsequent deformation (and idling) to rheopectic behavior. As the spinel concentration in the sludge decreased from 28 mass% (sludge as received) to 15 mass% at 1300°C, the sludge turned into a Newtonian suspension.

Keywords: Glass, Spinel, Rheology

INTRODUCTION

Little attention has been paid to the mechanical behavior of sludges of solid particles in molten glass. Yet solid phases, mainly spinel, can precipitate and accumulate in high-level waste (HLW) melters, potentially shortening the melter's lifetime and hindering, even jeopardizing, process operation. Plodinec [1] and Mika et al. [2] reported that spinel sludge is a rheopectic pseudoplastic liquid. The viscosity of such a liquid decreases with increasing deformation rate and increases with the time of deformation. This type of behavior is encountered in suspensions in which solid particles form loosely bounded aggregates or alignment groupings that break down with continuing deformation and increasing shear rate [3]. This study investigates the response of spinel sludge to a complex temperature and deformation history as a preliminary attempt to assess the potential for removing the sludge from the melter.

EXPERIMENTAL

A small (~300-g) sample of spinel sludge from a pilot-scale HLW glass melter was characterized using optical microscopy, scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS), *x-ray* diffraction (XRD), and an inductively coupled argon plasma spectrometer (ICP). Pure spinel crystals were obtained from a portion the sludge sample by dissolving the amorphous and metallic phases in 18 % HNO_3 for 24 h, adding HF for 48 h, and then separating spinel from amorphous gel with a magnet.

Brookfield digital rotating viscometer with a disk spindle was used to study the response of the sample (which was large enough to fill the viscometer crucible) to repeated shear deformation at different temperatures. Thus, all measurements were performed consecutively on a single sample during 3 days as shown in figure 1. For simplicity, each experiment run is represented in figure 1 as the end values of temperature, shear stress, and spindle speed, not as a time interval. As seen in figure 1, the temperature ranged from 1050°C to 1350°C, and the spindle speed varied from 0.005 to 1 RPS. The sludge in the platinum crucible was allowed to cool in air between measurements. With a few exceptions, measurements ran for 15 min. Before each measurement, the sample was held for 90 min at measuring temperature. The idle time for spindle-speed change was 5 min and for temperature change 30 min.

The shear stress (τ) and the shear rate (∇v) were calculated using the formulas*

$$\tau = \frac{M}{2\pi R_d L} \tag{1}$$

$$\nabla v = \frac{2\varpi\, R_c^2\, R_d^2}{x^2\,(R_c^2 - R_d^2)} \tag{2}$$

* Brookfield Viscometer Guide, Brookfield Engineering Laboratories, Brookfield, Massachusetts, USA

where M is the torque, ϖ is the angular velocity, x is the radial distance from spindle axis, R_d is the spindle radius, R_c is the crucible radius, and L is the spindle height (in this study, R_d = 7.3 mm, L = 2.0 mm, and R_c = 33 mm). The lower surface of the spindle was 13 mm above the crucible bottom. The sludge height in the crucible was approximately 30 mm. Equations (1) and (2) are valid for a uniform material. As discussed below, this may not be the case in sludge deformation.

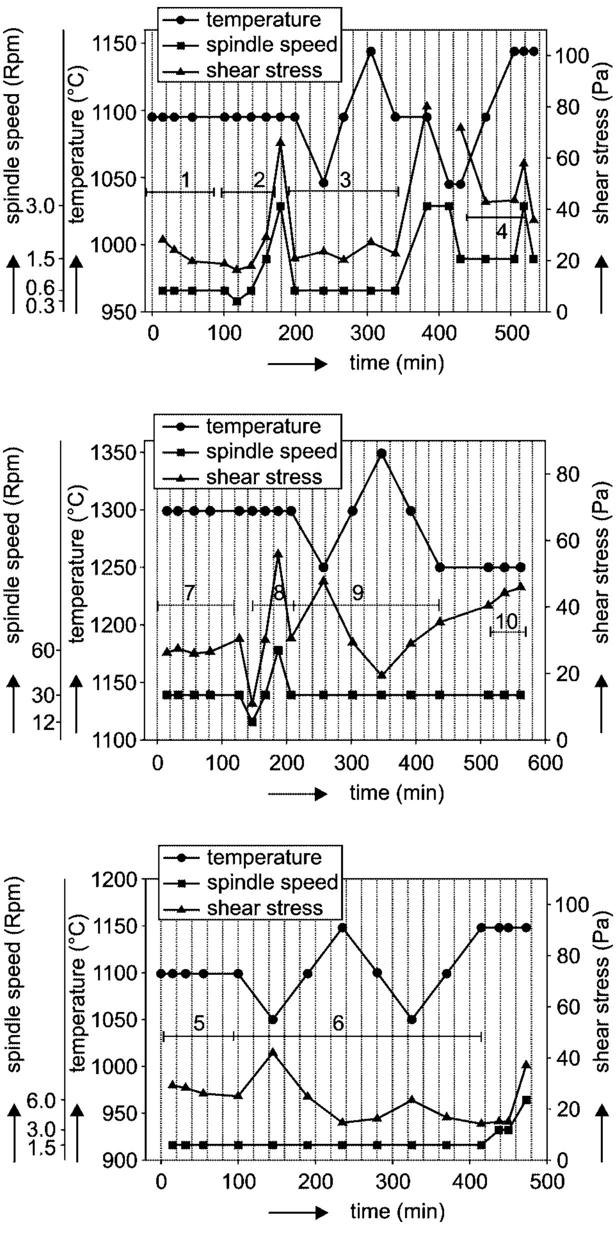

Figure 1. The thermo-mechanical history.
The numbers of the time intervals denote experimental runs; the figures associated with these runs are listed above.
1 - figure 8, 2 - figure 10, 3 - figure 12, 4 - figure 13, 5 -figure 8, 6 - figure 14, 7 - figure 9, 8 - figure 11, 9 - figure 9, 10 - figure 15

RESULTS AND DISCUSSION

Sludge characterization

Figure 2 shows a micrograph of the sludge as received. The major crystalline phase in the sludge was identified by XRD as spinel. Spinel content in the as-received sample was 27.55 mass%. Spinel crystals, 20 to 100 μm in size, formed a loose structure with large (several hundred μm) areas of crystal-free melt. The agglomerates of fine needles in the middle of the micrograph are crystals of silver. Figure 3 shows a micrograph of the sludge quenched from 1250°C at the end of the study. The crystals appear somewhat smaller than in the original sludge, their edges are rounded, and crystals are surrounded with layers of clear glass that are approximately 20 mm thin. Beyond these concentration-boundary layers, the bulk of the amorphous phase is dark brown in color and filled with small (10 μm) star-shaped crystals of spinel as seen in figure 4. The star-shaped crystals probably formed during cooling.

Figure 2. Sludge as-received (27.55 mass% spinel).

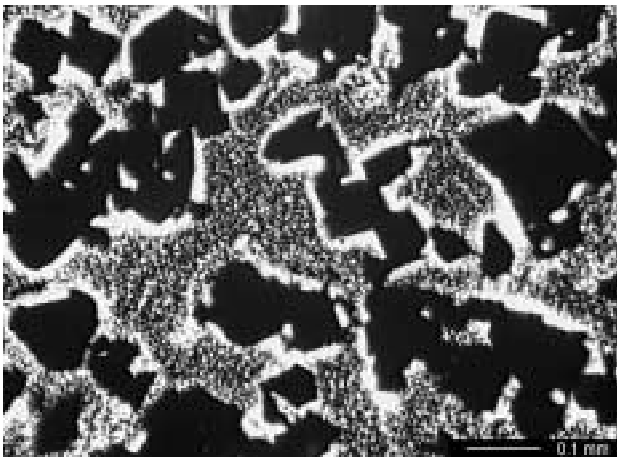

Figure 3. Sludge heat-treated at 1250°C (16.36 mass% spinel).

At the end of the study, the sample was transferred to a quartz crucible and stirred with the spindle at 1100°C. A sample of the sludge that adhered on the spindle surface contained 15.69 mass% spinel, while a bulk sample contained 21.47 mass% spinel. Two small samples of the bulk sludge were subsequently heat treated in platinum crucibles for 24 h, one at 1035°C, and the other at 1303°C. The corresponding micrographs are shown in figure 5 and 6. Figure 5 resembles figure 2 except for a small number of tiny crystals that probably precipitated during the heat treatment, indicating that the structure of sludge was similar to that as received. At 1303°C (figure 6), the sludge re-boiled during heat treatment (as it did previously at $T > 1300$°C in the viscometer). The crystals are half of their original size (≤ 50 μm), are rounded, and are surrounded with layers of clear glass. Large volumes of crystal-free bulk glass are dark brown in color. Figure 7 shows an interesting dendritic growth of spinel in a sample of the original sludge that was heat treated for about 1 h at 1400°C and then quenched (small sporadic dendrites were also seen in the sample heat treated at 1303°C).

Table 1 lists the sludge composition, determined with ICP, and the compositions of the amorphous and crystalline phases, determined with SEM-EDS. The amorphous-phase composition was calculated using the mass balance equation

$$a_i = \frac{g_i - \sum_{j=1}^{k} c_{ij} C_j}{1 - \sum_{j=1}^{k} C_j} \qquad (3)$$

where a_i and g_i are the i-th component mass fraction in amorphous phase and sludge, respectively, c_{ij} is the i-th component mass fraction in j-th crystalline phase, and C_j is the j-th crystalline phase mass fraction in sludge. We used spinel composition as measured (in sludge) and assumed that the metallic phase was pure silver, and all the Ag_2O was reduced to a metallic phase. The composition of spinel isolated by dissolving the amorphous phase in acid shows a smaller content of

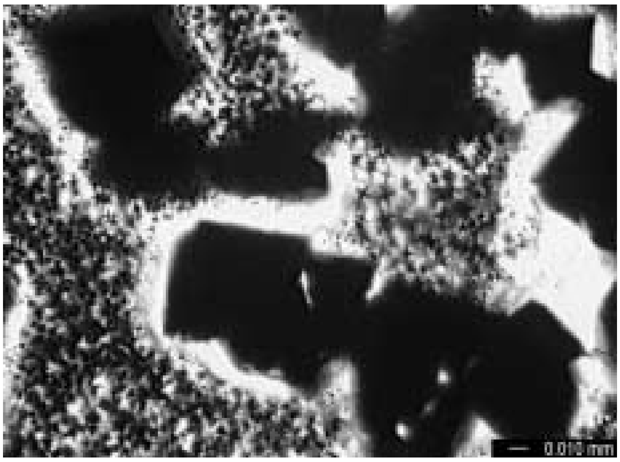

Figure 4. Sludge heat-treated at 1250°C (Detail).

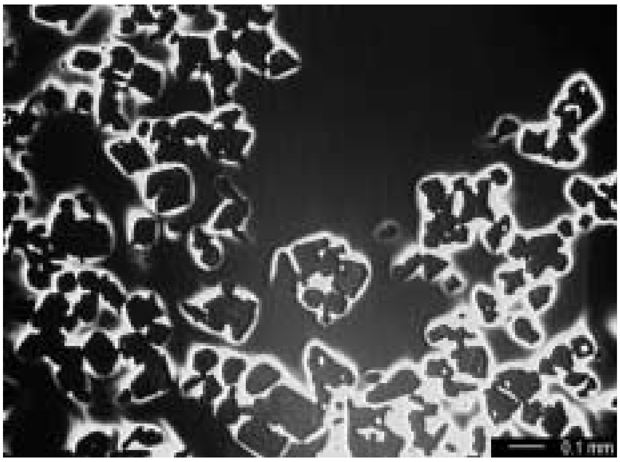

Figure 6. Sludge heat-treated at 1303°C (15.30 mass% spinel).

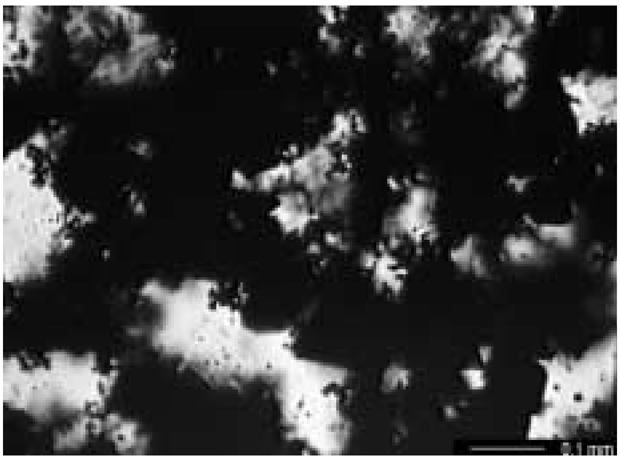

Figure 5. Sludge heat-treated at 1035°C (25.78 mass% spinel).

Figure 7. Sludge heat treated at 1400°C and quenched (28.58 mass% spinel).

Table 1. Composition of sludge, spinel, metallic phase, and amorphous phase (mass fractions).

	Sludge (ICP)	Amorphous phase (Calculated)	Amorphous phase (SEM-EDS)	Metallic phase (SEM-EDS)	Spinel (SEM-EDS)	Isolated spinel (SEM-EDS)
Ag_2O	0.0018	--	--	0.9134	--	--
Al_2O_3	0.0888	0.1933	0.2242	0.0217	0.0162	0.0158
B_2O_3	0.0541	0.0748	--	--	--	--
BaO	0.0004	0.0006	--	--	--	--
CaO	0.0071	0.0067	0.0078	0.0002	--	--
CdO	0.0003	0.0004	--	--	--	--
CoO	0.0001	0.0002	--	--	--	--
Cr_2O_3	0.0081	0.0021	--	--	0.0241	0.0920
Fe_2O_3	0.2533	0.0743	0.0862	0.0179	0.7236	0.6567
K_2O	0.0039	0.0034	0.0039	--	--	--
Li_2O	0.0342	0.0473	--	--	--	--
MgO	0.0040	0.0009	0.0010	0.0024	0.0034	0.0086
MnO_2	0.1016	0.0213	0.0247	0.0035	0.1633	0.1578
Na_2O	0.0691	0.1621	0.1879	0.0168	--	--
NiO	0.0118	0.0064	--	--	0.0259	0.0229
P_2O_5	0.0034	0.0047	--	--	--	--
SiO_2	0.2987	0.3404	0.3947	0.0187	--	--
SrO	0.0388	0.0495	0.0574	0.0037	--	--
TiO_2	0.0008	0.0010	--	--	--	--

Fe_2O_3 (possibly caused by leaching), and a higher content of Cr_2O_3 as compared to spinel in sludge.

Mechanical behavior

Figure 8 shows the shear stress as a function of time at a constant spindle speed (0.01 RPS and 0.025 RPS) and temperature 1100°C. The measurement was repeated several times with increasing idle time between subsequent runs. During the starting run at 0.01 RPS, shear stress of the as-received sludge gradually decreased. This thixotropic behavior can be attributed to the breakdown of the loose structure that formed as spinel crystals settled in the crucible and subsequent motion of the crystals caused by velocity gradient resulting in the formation of a low-concentration zone near the spindle surface. The existence of such a zone was experimentally verified (see previous subsection).

By equation (2), the Newtonian shear rate at the perimeter of the spindle is 20.4 times larger than the shear rate at the crucible wall. For non-Newtonian material, it seems likely that only a limited volume of sludge around the spindle (the deformation zone) moved with the rotating spindle whereas the sludge farther away from the spindle was stagnant. Assuming that the shear was restricted to a sludge layer between R_d and $R_m < R_c$. For $R_m - R_d << R_d$, equation (2) simplifies to

$$\nabla v \approx \frac{\varpi R_d}{R_m - R_d} \qquad (4)$$

Hence, the shear rate decreases as the deformation zone increases. In this paper, we report the value of shear rate (velocity gradient) at the spindle surface, *i.e.*, $x = R_d$.

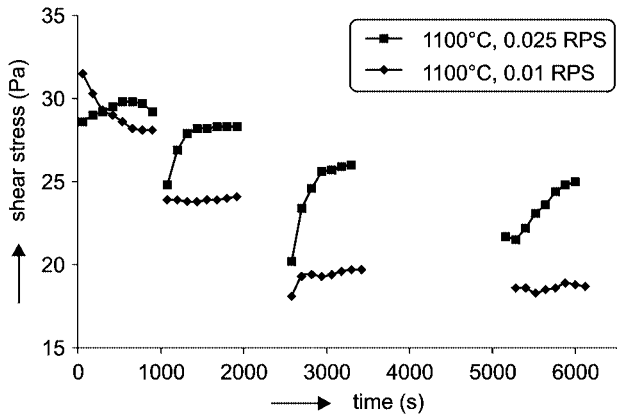

Figure 8. Shear stress versus time at 1100°C.

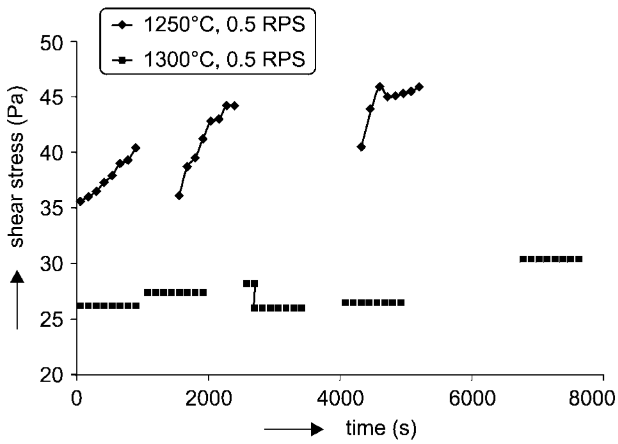

Figure 9. Shear stress versus time at 0.05 RPS.

Within the deformation zone, crystals settle and move in the direction toward lower velocity, creating an area of low concentration in the vicinity of the spindle. The existence of this area may explain the remarkable decrease in the shear stress at 0.01 RPS, seen in figure 8, when the measurement was repeated after a period of idling. This effect was much less pronounced at 0.025 RPS. After the first run at 0.01 RPS, during which the shear stress decreased, the shear stress was nearly constant or increased with time during subsequent runs. This rheopectic behavior, which was more pronounced at a higher spindle speed, could result from stirring settled crystals and their agglomerates into the deformation zone. At both spindle speeds, the first data point (at 60 s) after 1800 s of idling shows a higher shear stress than the corresponding point after 600 s of idling. This indicates that spontaneous strengthening of the structure can occur with extended idling.

As figure 9 shows, the sludge was rheopectic from the start when deformed at a higher temperature (1250°C) and a higher speed (0.5 RPS). Moreover, the shear stress increased during idling. Except for the sharp drop in the shear stress at 1300°C during deformation after 600 s idling, which was probably caused by a breakdown of large agglomerates, the shear stress increased with increasing idle time while the shear stress was constant with time.

Apart from the trends displayed in figure 8, the shear stress exhibited small-scale oscillations of a frequency ~0.025 s^{-1}, and the amplitude ≥ 0.2 Pa. The amplitude decreased with increasing temperature and time. No oscillations occurred at $T \geq 1300$°C.

Figure 10 displays the results of changing spindle speed at a constant temperature after 9 min of constant shear rate (with 5-min intervals between runs). The sludge possessed a yield stress of 16 Pa and approached Newtonian behavior at higher deformation rates. At 1300°C, the pseudoplastic sludge turned to virtually Newtonian (figure 11), but as figure 9 shows, its viscosity increased with idle time. Crystal agglomeration probably occurred while the sludge was at rest.

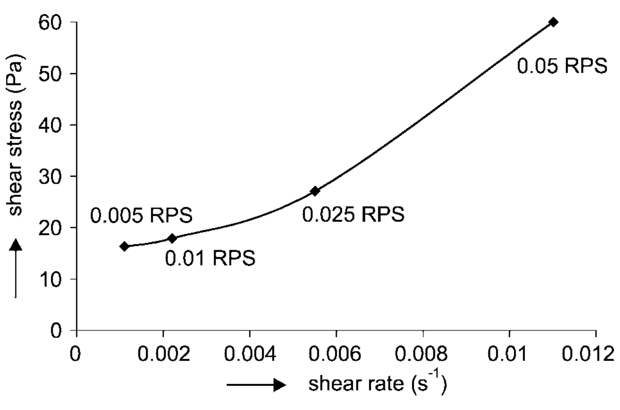

Figure 10. Shear stress versus shear rate at spindle perimeter at 1100°C.

As shown above (see figures 3 and 6), spinel crystals partly dissolved with increasing temperature. The effect of temperature on sludge rheology was tested at two spindle speeds, 0.01 and 0.025 RPS (figures 12 and 13). At 0.01 RPS, the temperatures of the subsequent runs were changed to 1095, 1046, 1095, 1144, and 1095°C. As expected, the shear stress increased when the temperature decreased from 1095°C to 1046°C and returned to the previous value when the

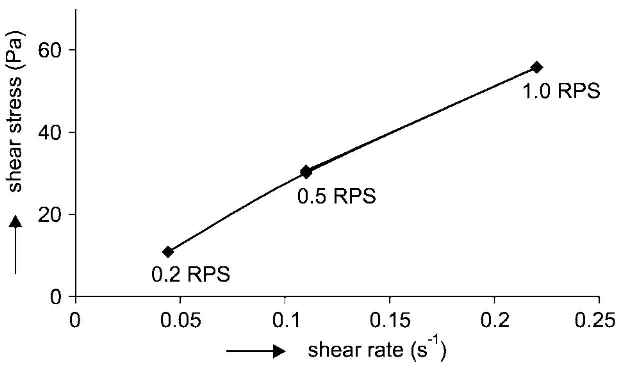

Figure 11. Shear stress versus shear rate at spindle perimeter at 1300°C.

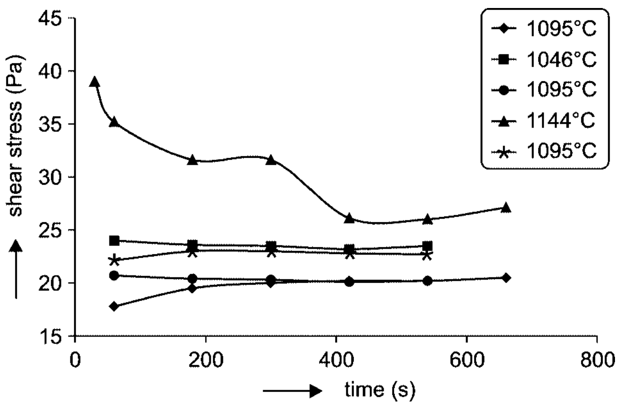

Figure 12. Shear stress versus time at 0.01 RPS.

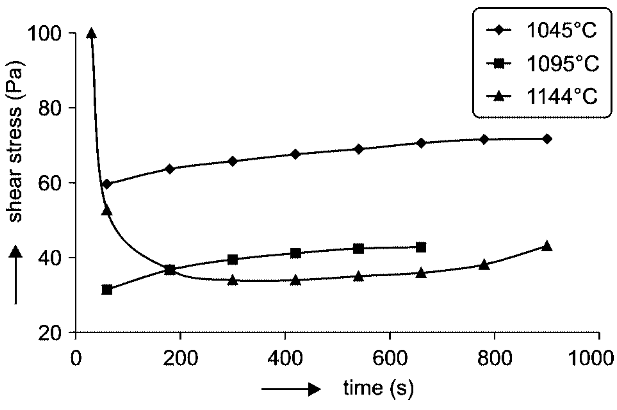

Figure 13. Shear stress versus time at 0.025 RPS.

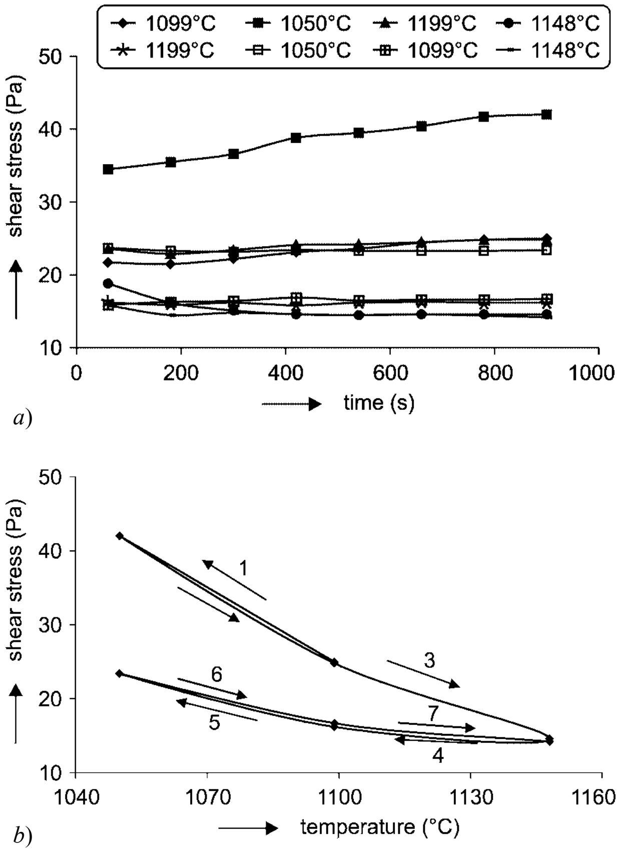

Figure 14. *a*) Shear stress versus time at 0.025 RPS, *b*) Shear stress versus temperature at 0.025 RPS.

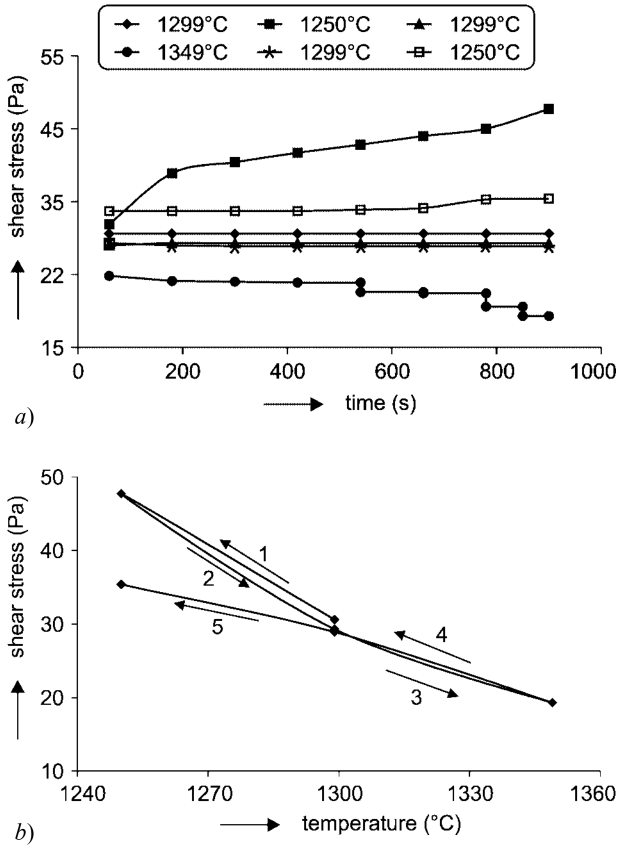

Figure 15. *a*) Shear stress versus time at 0.5 RPS, *b*) Shear stress versus temperature at 0.5 RPS.

temperature was increased back to 1095°C. Contrary to expectation, the stress sharply increased when the temperature increased to 1144°C and then gradually decreased with time. After the return to 1095°C, the shear stress was at a higher level than during the initial run. The unexpected increase in shear stress at 1144°C was probably associated with an increase in the volume of the deformation zone, which resulted in a higher stress resistance by the dense portion of the sludge. The subsequent decrease of the shear stress was similar to that of the initial run in figure 8. A similar sequence of events was observed at the higher spindle speed except that the stress decrease was much sharper.

Figure 14 shows the outcome of a similar experiment as in figure 13, performed at a later date (in between the two experiments, the sludge cooled down to room temperature). The quiescent sludge was heat treated at 1099°C for approximately 90 min, and then the shear stress was repeatedly measured at 1100°C with 0.025 RPS as shown in figure 10. The last of the runs is represented by the starting line (1099°C) in figure 14*a*. When the temperature was subsequently increased to 1148°C, the shear stress did not increase as much as in the previous measurement (figure 13). The final shear-stress values at each temperature are displayed in figure 14*b*. Figure 14*b* shows that the response of the shear stress to a temperature decrease was reversible, but a temperature increase caused an irreversible decrease in the shear stress.

At higher temperatures (1250°C to 1349°C), the shear stress increased with decreasing temperature (figure 15). As in the previous experiment (figure 14), the shear stress increased with time at the minimum temperature of this interval. At 1349°C, discontinuous decreases in the shear stress occurred, probably because of dissolving crystal agglomerates. The irreversible response of the shear stress to a temperature increase was less pronounced as compared to the experiment conducted at temperatures below 1200°C (figure 14).

Potential for sludge removal

Sludge can accumulate during a melter's lifetime to a certain level without unacceptable risk. Sludge removal may be considered if an unacceptable level of sludge accumulates in the melter before the end of the campaign. Advanced melters may allow sludge to be regularly removed. Spinel sludge can be removed either chemically or mechanically. Chemical removal can be accomplished by dissolving sludge in a borosilicate melt, but this is a slow process that may take several weeks and generate additional waste. The effectiveness of mechanical removal by gravity-driven flow through a bottom drain depends on the inclination of the wall, the flow rate, the yield stress of the sludge, and sludge viscosity. The yield stress of the sludge is low (16 Pa at 1100°C), but may increase with densification and aging. Because of the pseudoplastic nature of spinel sludge, a faster flow-rate would facilitate its removal. Sludge, once subjected to deformation, is likely to change its structure from loosely bounded to consolidated. Denser sludge will have different mechanical properties.

CONCLUSIONS

Spinel sludge is a material with memory, and thus its behavior depends on its thermo-mechanical history. Undisturbed sludge has a loose structure formed by slowly settling crystals. Mechanical disturbance by sheer deformation breaks down the original structure. Structural changes continue after deformation when the sludge is at rest. The response of the sludge to shear may vary from thixotropic to rheopectic dependent on the degree of structural alteration. Below 1300°C, the sludge is pseudoplastic. At $T \geq 1300$°C, the spinel content in the sludge drops to 15 mass% from the as-received value of 28 mass%, and the sludge becomes Newtonian.

Acknowledgments

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STRUKTURNÍ A MECHANICKÁ ODEZVA NA TERMO-REOLOGICKOU HISTORII SPINELOVÉ USAZENINY VE SKLE S VITRIFIKOVANÝMI VYSOCE AKTIVNÍMI ODPADY

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Pro studium struktury a složení spinelové usazeniny získané po výhasu experimentální tavící pece pro sklo se simulovanými vysoce aktivními odpady bylo použito optického a skenovacího elektronového mikroskopu a rentgenové difrakční analýzy. Při tepelných expozicích za isotermních podmínek v teplotním intervalu od 1050°C do 1350°C se krystaly v matečné tavenině částečně rozpouštěly a při ochlazení se v tavenině tvořily malé (~ 10 μm) krystaly hvězdicovitého nebo dendritického uskupení. Usazenina byla opakovaně podrobena působení konstantní smykové rychlosti od 0,005 s^{-1} do 1,0 s^{-1} při konstantní teplotě od 1050°C do 1350°C. Průběh smykového napětí usazeniny byl sledován v závislosti na čase při různých teplotách a rychlostech smyku a po různých časových prodlevách. Počáteční thixotropní charakter volné struktury usazeniny se vlivem opakované deformace a časové prodlevy změnil na rheopektický. Snížením koncentrace spinelu v usazenině z původních 28 hmot.% na 15 hmot.% za teploty 1300°C, se chovaní usazeniny přiblížilo k chování Newtonské suspenze.