INTRODUCTION

Spinel \((\text{Ni,Fe,Mn})(\text{Cr,Fe})_2\text{O}_4\) is a ubiquitous crystallization form that precipitates from high-level waste glasses containing \(\text{Fe}_2\text{O}_3\), \(\text{Cr}_2\text{O}_3\), and \(\text{NiO}\) [1-4]. It nucleates virtually instantaneously and grows rapidly [5]. Spinel is harmless when it precipitates in glass during cooling. It does not cause cracking nor does it reduce glass durability [6]. However, spinel can cause serious problems in glass melters. Formation of spinel sludge at the melter bottom or precipitation of spinel in the melter overflow can obstruct the discharge of glass and shorten the melter lifetime [7]. Economic concerns may require an increase in the loading factor of the waste in glass. At a certain level of waste loading, spinel precipitates in the melter. If some fraction of spinel settles and accumulates at the melter bottom, a periodical removal of spinel sludge may be considered. Construction of melters with inclined bottoms and bottom drains has been proposed [8]. The knowledge of rheological behavior of precipitated spinel sludge is important for an advanced melter design. In this work, we produced spinel sludge in the laboratory and studied its behavior using a rotating spindle viscometer.

EXPERIMENTAL PART

We used three glasses (table 1). The baseline glass (SS-A) had high concentrations of \(\text{Fe}_2\text{O}_3\), \(\text{Cr}_2\text{O}_3\), and \(\text{NiO}\) and a large number of minor components. Most of the minor components were absent in its simplified version (SS-AA) that had an identical composition in terms of major components. While SS-A and SS-AA were designed to precipitate spinel, SS-AB was formulated to produce a similar composition that does not precipitate spinel. It had all minor components deleted, including those that form spinel, and its \(\text{Fe}_2\text{O}_3\) content was reduced to almost one half. The major components, \(\text{SiO}_2\), \(\text{B}_2\text{O}_3\), \(\text{Na}_2\text{O}\), \(\text{Li}_2\text{O}\), \(\text{MgO}\), and \(\text{Al}_2\text{O}_3\), were in identical proportions in all three glasses.

We batched the glasses using analytical-grade chemicals and melted them at 1350 °C. We estimated liquidus temperatures \((T_L)\) using a spinel-based first-
-order model [9] and obtained $T_L = 1520^\circ C$ for SS-A and $1344^\circ C$ for SS-AA. We made spinel sludge by heat treating glasses for 5 days at $1100^\circ C$ in 95%-silica crucibles. Then we smashed the crucibles to pieces and carefully separated the sludge from the spinel-free glass. We measured sludge viscosity using a Brookfield digital rotating spindle viscometer (Model DV-II) in the temperature range from 1094 to 1393 °C starting from lower temperatures.

RESULTS AND DISCUSSION

The sludge consisted of agglomerations of cubic black crystals of spinel (figure 1). In SS-A glass, RuO$_2$ needle-like crystals (figure 1b) reinforced the agglomerates. The fraction of spinel in the sludge estimated by XRD was roughly 12 vol.%. The apparent viscosity of the sludge and the sludge-free glass is shown in table 2. Glass behavior was Newtonian, showing no dependence of apparent viscosity ($\eta_a$) on effective velocity gradient ($\nabla v_{ef}$) and time ($t$). The $\eta_a$ of sludge increased with $t$, but this time-dependence weakened as temperature ($T$) increased until the $\eta_a$ became time-independent. SS-A sludge reached this point at $1350^\circ C$, when $\eta_a$ was $< 6$ Pa s, and SS-AA sludge reached this point at $1300^\circ C$, when $\eta_a$ was $< 5$ Pa s. This behavior was probably caused by spinel dissolution that breaks down spinel agglomerates. The higher $\eta_a$ of SS-A sludge as compared to SS-AA sludge can be attributed to the presence of RuO$_2$ needles in SS-A sludge.

Figure 2 displays effective shear stress ($\tau_{ef}$) versus $\nabla v_{ef}$ for SS-A sludge at different temperatures. The $\eta_a$ decreases as $\nabla v_{ef}$ increases. This behavior is typical for pseudoplastic liquids. The idle time between each subsequent measurement at a higher temperature was 30 min. The second measurement at $1293^\circ C$ was carried out after the series of measurements starting at $1094^\circ C$ and ending at $1393^\circ C$ was completed. The lower $\tau_{ef}$ from the second measurement indicates that the preceding heat treatment and deformation weakened the sludge structure. To separate the effect of spinel dissolution from the structural weakening caused by deformation, the second measurement at $1342^\circ C$ was performed immediately after the first one. The decrease in $\tau_{ef}$ was smaller, but the structural weakening by flow was significant.

The effect of $t$, $\nabla v_{ef}$, $T$, and idle time on structural changes is shown in figures 3 and 4. Figure 3 displays $\tau_{ef}$ as a function of time for different values of $\nabla v_{ef}$ and $T$ ($\nabla v_{ef}$ was increased as $\eta_a$ decreased to allow shear-stress reading). The $\tau_{ef}$ values increased with time for all $\nabla v_{ef}$ values, a behavior typical for a rheopectic liquid. Idling to switch spindle velocity was negligible, but it took 20 minutes to increase and stabilize a new temperature. This time probably was not long enough for the agglomerated structure to completely rearrange at $T < 1193^\circ C$ as can be seen from figure 4.

Figure 4 displays the $\tau_{ef}$ increase as a function of time at $1193^\circ C$ and a constant $\nabla v_{ef} = 0.01$ s$^{-1}$. The initial measurement is labeled “start.” In subsequent measurements, the structure was allowed to reassemble from 1 to 30 min. The $\eta_a$ increased with time for each subsequent measurement. This can be attributed to the development of denser agglomeration when the sludge...
was sheared. During idling, when shearing stops, the agglomerates tend to get looser. Therefore, a new measurement started with a lower viscosity. The measured dependence of $\tau$ on $t$ was fitted by the equation:

$$\tau_{ef} = \tau_1 + \tau_2 \left[ 1 - \exp \left( - \frac{t}{t_r} \right) \right]$$

(1)

where $\tau_1$ and $\tau_2$ are constants ($\tau_1, \tau_2 > 0$), and $t_r (t_r > 0)$ is the retardation time. The $\tau_1$ decreases and the $\tau_2$ increases as the idle time ($t_i$) increases (figure 5), while the sum $\tau_1 + \tau_2 (\tau_{ef} \to \tau_1 + \tau_2$ as $t \to \infty$) is nearly constant. The $t_i$ decreases as the $t_r$ decreases (figure 6), resulting in a steeper increase of $\tau_{ef}$ with time.

At $\eta_a$ values higher than 7 Pa s, the apparent viscosity of sludge increased with time at constant $\nabla v_{ef}$.
in the range from 0.005 to 0.05 s⁻¹. This was probably caused by agglomeration of spinel crystals around the spindle. In the range from about 3 to 7 Pa s, viscosity decreased with increasing $\nabla \dot{\gamma}$ in the range from 0.05 to 0.2 s⁻¹, probably because the fast-rotating spindle breaks down the sludge structure formed by crystals with partially dissolved contacts.

CONCLUSIONS

Spinel sludge from high-level waste glass behaves as a rheopectic pseudoplastic liquid. Its $\tau_{ef}$ is an increasing function of $\nabla \dot{\gamma}$ and time. At constant $T$ and $\nabla \dot{\gamma}$, the rotating spindle progressively affects the structure of the surrounding sludge, causing a higher friction and increasing $\tau_{ef}$ with time until a new equilibrium is reached. As $\nabla \dot{\gamma}$ and $T$ increase, the sludge structure rearranges, the $\eta_a$ decreases, and a new equilibrium structure is formed. RuO₂-free sludge approached time-independent behavior above 1300 °C. The sludge containing RuO₂ approached time-independent behavior above 1350 °C. At 1094 °C, $\eta_a$ was roughly 19 times higher than that of sludge-free glass, but only 2 to 4 times higher at temperatures at which it became time-independent.

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REOLOGIE SPINELOVÉ SEDLINY VE SKLOVINĚ

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Spinelová sedlina, která vzniká při vitrifikaci vysoce aktivních odpadů, brání v toku sklovině a ničí tavicí agregát. Efektivnost odstraňování spinelové sedliny z tavicího agregátu pro vysoce aktivní odpady závisí na jejím reologickém chování. V laboratorním kelímku jsme připravili spinelovou sedlinu tak, že jsme nechali spinel usazovat ve sklovině, a za použití rotačního viskozimetru jsme měřili odezvu na smykovou deformaci. Smykové napětí vzrostalo nelineárně s gradientem smykové rychlosti (rychlostí smykové deformace) a s časem při konstantním gradientu smykové rychlosti, jak je to typické pro pseudoplastickou reopeknou kapalinu. Zdánlivá viskozita sedliny podstatně vzrostla, když byly přítomny jehličky krystalů oxidu RuO2.