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High temperature rheological study of borosilicate glasses containing platinum group metal particles by means of a mixer-type rheometer

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HIGHLIGHTS

- Rheological behavior of nuclear glass melts is well accounted by the Cross model.
- A first Newtonian plateau has been evidenced at low shear.
- First Newtonian plateau and critical stress values depend on PGM (Platinum Group Metals) content.
- At high shear, Quemada's law well represents the PGM content impact on viscosity.

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ABSTRACT

In this paper, the rheological behavior of six simulated high level waste nuclear glasses containing 0 to 5.2 wt% platinum group metals (PGM) has been studied at a temperature of 1200 °C. By means of a stress imposed rheometer, the shear stress dependence of the viscosity, which was so far assessed only at high shear rates, has been investigated on a wider range. Experimental data have been well fitted by the Cross model and a critical stress corresponding to the rupture of PGM aggregates has been evidenced. At high shear rates, the dependence with the volume fraction in PGM particles is well accounted for by Quemada's law. At low shear rates, the first Newtonian plateau is shown to be strongly dependent on the PGM content, notably above 3 wt% and to follow an exponential dependence due to the existence of more complex structures at the origin of the critical stress.

1. Introduction

High level radioactive wastes originated from reprocessing of the spent nuclear fuel are vitrified into a borosilicate glass at 1100–1200 °C. The vitrification process melts nitrates salts of the waste (converted to oxides at high temperature) and oxides from the glass, forming a complex material which has around 40 different containing glass precursors [1]. Some elements from the Platinum Group Metals (PGM), rhodium, ruthenium and palladium, remain insoluble after the vitrification process in the nuclear glass, both in the Induction Heated Melter with cold or hot crucible or in the Liquid Fed Ceramic Melter with electrodes. These dense compounds settle in the melter and affect physical properties of the glass melt (Fig. 1).

Although it had been proved that the nuclear glass structural characteristics and the leachability properties are not modified by PGM particles [2–4], evolutions of electrical and rheological properties during the vitrification process are not well understood. Glass electrical conductivity, which is a key property for the vitrification process control in cold crucible melter or in ceramic melter, increases strongly when the PGM content is higher than a threshold value, which depends on the particles morphology [5]. Low electrical percolation thresholds have been measured, depending on the synthesis of RuO_2 particles and on the stirring conditions of the melt. The formation of RuO_2 aggregates network and the presence of undissolved ruthenium can explain these low percolation thresholds [5,6]. Moreover, several authors have pointed out the fact that the particular anisotropy of RuO_2 needle-like particles (Fig. 1) has a major effect on the rheological behavior of the glass melt [7–10]. In particular, all these reports indicate a non-newtonian flow behavior, more precisely a shear-thinning

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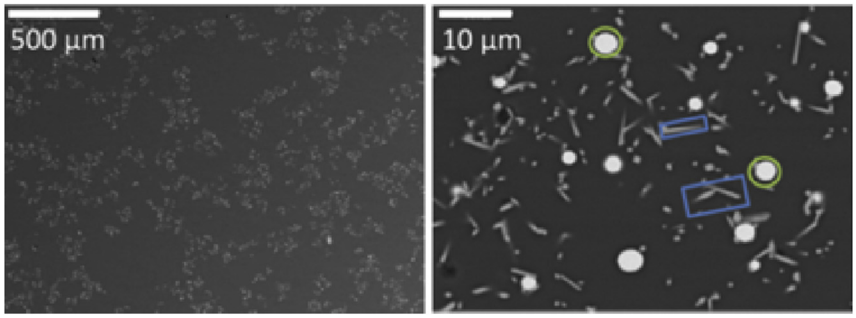

Fig. 1. (Color online) Microscopic snapshots of a nuclear glass containing 3wt% PGM particles after the vitrification process (green circles: Pd–Te spheres, blue rectangles: RuO_2 needle-like). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

behavior, i.e., the viscosity decreases as the shear rate increases. Different rheological models have been proposed to describe nuclear melt containing PGM particles [11,12]. Bingham [13], Ostwald [14]-De Waele [15], Herschel–Bulkley [16] or Casson [17] models were in good agreement in the studied shear rates ranges. Uruga et al. [12] successfully fitted their rheological data on Japan nuclear glass containing 1.2 PGM% to 4.5 PGM% with Casson's model [17] indicating the presence of a yield stress varying with the PGM content and the temperature (900–1200 °C). On the other hand, the lack of data at low shear remains a constant problem to accurately describe the rheological properties of nuclear glass melt [11]. Finally, associated to this specific rheological behavior and to the higher particles density regarding the glass density, aggregation mechanism and settling phenomenon of the PGM particles often occur in the melt, which induces pouring and homogeneity problems and could affect the vitrification process efficiency [18]. Recently, we developed a new experimentation which consists of macroscopic rheological observations and density measurements allowing to describe these phenomena under low shear (2 s^{-1}) for few hours in a laboratory Pt–Rh crucible containing inactive nuclear glass with PGM particles [11]. This test proved that the settling phenomenon was accelerated under the application of a low shear, which is the case in the cold crucible melter (calculations demonstrated that 80% of the glass is sheared at shear rates less than 4 s^{-1}).

In the present study, the rheological behavior of six simulated high level waste nuclear glasses containing 0 to 5.2 wt% PGM particles was investigated at 1200 °C using a stress-imposed rheometer. Thanks to this rheometer, it is now possible to extend the rheological measurements over a very wide range of applied shear stress which are representative of the shear sustained by the glass melt. The novel flow curve obtained for a nuclear glass melt with PGM particles displays a shear thinning behavior and a Newtonian viscosity plateau at very low shear rates, which was so far unaccessible. This behavior can be well described by a simplified Cross model, which the fit parameters reveal a strong dependence with the PGM content.

2. Experimental section

The chemical composition of four glass specimens is presented in Table 1. Samples were named with reference to their respective PGM weight content (0wt%, 1.6wt%, 2.1wt%, 3wt%). These borosilicate glasses were made on the full-scale pilot unit installed at CEA Marcoule [1]. The two PGM in simulated glasses were ruthenium and palladium. The glass samples were taken from the middle of a canister, which had been previously cooled at ambient temperature and cut in several pieces. Most of the ruthenium was present as needle-like RuO_2 crystals with a range length from less to 10 μm to up to 50 μm. Spherical particles of Pd–Te alloys with a diameter between 1 and 10 μm were formed during the vitrification process.

In order to obtain two glasses with higher PGM content, some amount of glass containing 3 wt% of PGM particles was put in zirconia crucibles and heated at 1150 °C for 30 h and 60 h. Using this procedure, the PGM particles settled to the bottom and no particles remained in the upper half of the glass. The lower part of glasses was separated from the part without PGM particles. The PGM weight content M(%wt) of these glasses were calculated from density measurements using this formula:

$$M(\%wt) = (\rho_{PGM}/\rho_g) \times (\rho_0 - \rho_g)/(\rho_0 - \rho_{PGM}) \quad (1)$$

where ρ_0 is the density of the nuclear glass without PGM particles ($\rho_0 = 2736$ kg m^{-3}), ρ_{PGM} is the density of the PGM particles ($\rho_{PGM} = 8212$ kg m^{-3}). and ρ_g is the density of the formed glasses. According to microscopic observations by scanning electron microscopy, uniform glasses, i.e. materials in which inhomogeneities were uniformly dispersed, were obtained (Fig. 1). Elemental composition of the glasses samples was checked using X-ray fluorescence. This analysis confirmed that actual chemical composition of glass samples is close to their theoretical chemical composition (standard deviation less than 10%).

A stress-imposed rheometer (Rheometrics Scientific SR5000) was used to perform steady state and transient measurements. In particular, low shear transient experiments were conducted to further investigate rheological phenomena occurring in nuclear glass melts. The rheometer was placed above a vertical tubular furnace heating up to 1500 °C (Fig. 2a). A special tool was designed to ensure a better transmission of the torque from the rheometer to the mobile without perturbing effects. The glass samples were melted at 1200 °C in platinum-rhodium crucible (crucible radius $R_e = 13{,}5$ mm). The crucible was then placed at the center of the furnace. The temperature gradient measured from the top to the bottom of the samples in the crucible is lower than 2 °C. All the rheological measurements were realized at 1200 °C with a multi-blade mobile (Fig. 2b) in order to avoid the settling phenomena and to keep an uniform distribution of the particles in glasses (length of the rotor $L = 27$ mm). Moreover, it had been observed that this rotor allows making measurements at lower stresses than with a simple cylinder with the same diameter as the diameter of the blades.

In order to extract viscosity/shear rate curves from torque/angular rate data with such a non-standard geometrical configuration, the torque C has to be linked to the shear stress τ and the angular rate $\dot{\theta}$ to the shear rate $\dot{\gamma}$, through two geometrical factors, K_τ and $K_{\dot{\gamma}}$, in such a way that: