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WASTE GLASS MELTING STAGES

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Three different simulated nuclear waste glass feeds, consisting of dried waste and glass frit, were heat treated for 1 hour in a gradient furnace at temperatures ranging from approximately 600°C - 1000°C. Simulated melter feeds from the Hanford Waste Vitrification Plant (HWVP), the Defense Waste Processing Facility (DWPF), and Kernforschungszentrum Karlsruhe (KfK) in Germany were used. The samples were thin-sectioned and examined by optical microscopy to investigate the stages of the conversion from feed to glass. Various phenomena were seen, such as frit softening, bubble formation, foaming, bubble motion and removal, convective mixing, and homogenization. Behavior of different feeds was similar, although the degree of gas generation and melt homogenization varied.

INTRODUCTION

The reprocessing of nuclear fuel generates a form of high-level radioactive waste. In many countries, including the United States, current plans call for vitrification of the high-level and transuranic fraction of these wastes to form a borosilicate glass that is resistant to radioactive damage and leaching. At Hanford, wastes have been generated over the span of 45 years from fuel reprocessing and other operations. These wastes, like other nuclear fuel reprocessing wastes, contain platinum group metals, also known as noble metals. The solubility of noble metals (e.g., palladium, rhodium, and ruthenium) in glass-forming melts is typically extremely low. Undissolved noble metal particles can agglomerate and settle to the floor of the glass melter. Many of the noble metal oxides and alloys are excellent electrical conductors. If a sufficient quantity of noble metals settles to the melter floor, the lower electrodes could be electrically shorted. If this occurs, then the noble metal accumulation would need to be removed or the melter would have to be replaced.

As part of an effort to understand how noble metal particles are formed and how they can agglomerate in a melter, it was necessary to examine how the transition from feed to glass occurs in the cold cap of a melter. In this way, information concerning noble metal particle characteristics could be correlated with the knowledge of the various reaction layers in the melter's cold

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cap. Mechanisms of noble metal agglomeration in this region can then be postulated. This paper is primarily concerned with the various stages that occur during the transition from feed to glass.

BACKGROUND

In a liquid-fed ceramic melter, wastes are fed to the melter as a liquid slurry feed, containing waste and glass-forming frit. If continuous feeding is used, a layer of feed will be present above the glass pool, consisting of slurry in various stages of drying and conversion to glass. A temperature gradient will exist from the temperature of the boiling liquid on top to the temperature of the melt pool below.

In order to simulate the cold cap at laboratory-scale, the Gradient Furnace Testing (GFT) apparatus was used, in which simulated dried feed was placed in a long boat-like crucible and then subjected to a linear temperature gradient horizontally along its length. The gradient produced conditions similar to those in a melter cold cap. However, the gradient furnace cannot completely simulate the cold cap behavior in a melter due to the differing geometries and temperature histories. In an actual melter, the feed in the cold cap is exposed to an atmosphere produced by the gases evolved. Different gases are produced in different strata of the cold cap, according to the local temperature and the nature of the gas-generating reactions occurring at that temperature[1,2]. Gases evolved at lower layers, where the temperature is higher, leave the cold cap through the upper layers, where they mix with gases generated locally. This complex situation cannot be easily reproduced in a laboratory crucible or boat. Gases from crucibles or boats are those generated locally within the crucible volume, which has a nearly uniform temperature in contrast to the temperature layers of a full-scale melter. Moreover, atmospheric gases can diffuse into the sample and affect the reactions, especially when the sample volume is small.

In addition, feed in a melter will experience heating at some rate as the feed proceeds from the top of the cold cap to the bottom and then into the bulk of the melt. In the gradient furnace, the temperature gradient of the sample is established almost immediately upon placing the crucible into the furnace. Therefore, the material reaches the specified temperature quickly, without experiencing the same heating rate and temperature history it would experience in a melter. Despite these limitations, the stages occurring during the conversion of feed to glass as a function of temperature can be observed using the gradient furnace.

The laboratory-scale testing was done using simulated melter feeds for the Hanford Waste Vitrification Plant (HWVP), the Defense Waste Processing Facility (DWPF), and Kernforschungszentrum Karlsruhe (KfK) in Germany. The feeds differed somewhat in composition, but were prepared in generally the same way. A slurry was prepared, from hydroxides and nitrates of the waste constituents. For the HWVP and the DWPF feeds, formic acid was then added. Finally, glass frit was added to the slurry. The frit size varies between feeds. For the HWVP

and DWPF feeds, the frit size was -80/+200 mesh. For the KfK feed, the frit size was -80 mesh.

During drying and melting, gases such as CO_2, NO_x, and H_2O are generated by the feed as the waste decomposes to oxides.

EXPERIMENTAL PROCEDURE

Each of the feeds studied was subjected to heat treatment in the gradient furnace and analyzed using optical and scanning electron microscopy (SEM).

For each sample, the feed was loaded into a 30.5-cm-long boat-shaped quartz crucible and held at a specified temperature gradient for 1 hour in the gradient furnace. The furnace produces an adjustable linear temperature gradient. For the DWPF sample, the range used was 579°C to 928°C. For the HWVP and KfK samples, the range was 593°C to 936°C. These gradients approximate the gradient found in a melter cold cap. Most cold caps are only 2-10 cm thick. A longer boat was chosen in order to get more distinct temperature zones. A schematic of the crucible and temperature gradient is shown in Figure 1.

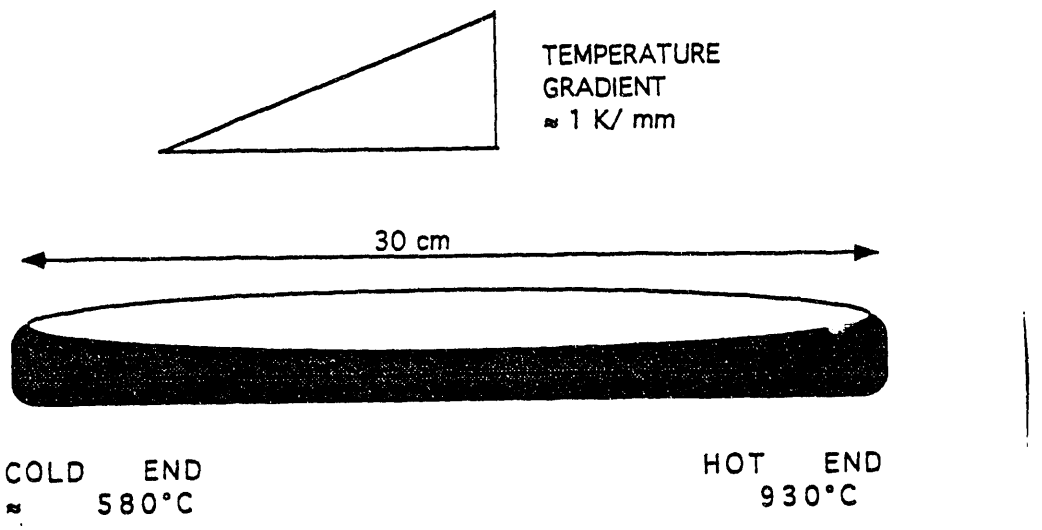

Figure 1. Schematic of Temperature Gradient and Crucible

After removal from the gradient furnace, the samples were annealed for 1 hour at 500°C and cooled slowly overnight. The crucibles were then fixed in an epoxy resin mold and cut in half lengthwise. Six 5-cm segments were made from each sample. Each segment was mounted on a slide, thin-sectioned, and polished for analysis by microscopy. Any given position on the sample could be matched with a corresponding temperature.

Each thin section was examined with an optical microscope so that observations could be made regarding mixing and melting behavior, gas generation, foaming, etc. Selected areas were photographed.

RESULTS

In the four feeds studied, seven separate melting stages could be identified. These stages occurred at slightly different temperatures in each feed, but can be described, with approximate temperature ranges, as follows:

1) Drying of feed (up to 600°C)

This stage corresponds to the upper layer of the cold cap. An example of HWVP feed during this stage is shown in Figure 2. During this stage, water is removed from the feed, and the feed forms a dry, loosely bonded mass. The dry feed remains visibly unchanged throughout this region, although gases are generated at these temperatures due to decomposition of the waste.

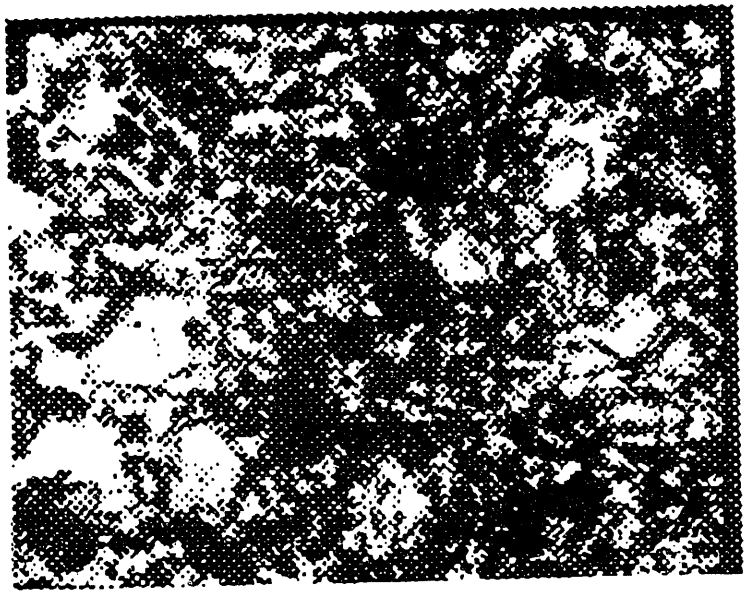

Figure 2. HWVP Feed at 599°C (Optical Microscopy, 100X). Right side of picture corresponds to downward direction of sample.

2) Sintering and adhesion of waste to frit (600°- 650°C)

Figure 3 shows an example of HWVP feed during this stage. At the beginning of this stage, the frit is softened, as can be seen by the frit particle edges becoming rounded rather than sharp as in the drying stage. At these softer edges, the waste particles adhere to the frit. The feed is now a more solid and strongly bonded mass. By the end of this stage, the waste has "slumped" together, closing the gaps and channels present at lower temperatures in the dried feed. In some cases, small waste particles have become encapsulated due to frit slumping around them.

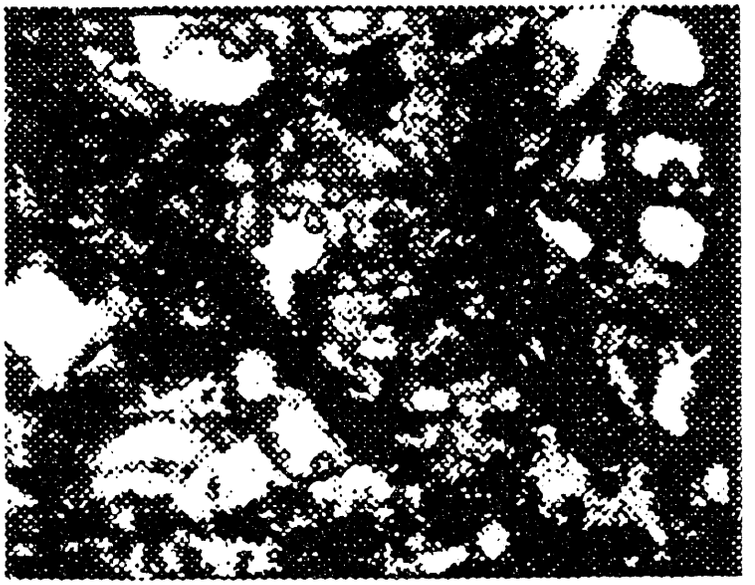

Figure 3. HWVP Feed at 621°C (Optical Microscopy, 100X). Right side of picture corresponds to downward direction of sample.

3) Bubble formation at the waste/frit interfaces (650°C - 700°C).

As a result of the frit softening and filling in voids in the feed, gas generation leads to the formation of bubbles at the interface between the waste chunks and the frit (see Figure 4). Previously, gases generated could escape through channels in between frit particles. Beginning at approximately 650°C, the gases generated cannot escape by this route. As a result, theyform bubbles in the softened frit. During this stage, the bubbles are numerous and relatively small (<0.2 mm).

Figure 4. KfK Feed at 679°C (Optical Microscopy, 100X). Right side of picture corresponds to downward direction of sample.

4) Bubble growth and foaming (690°C - 740°C).

In this temperature region, bubbles have grown in size up to approximately 5 mm (see Figure 5). Severe foaming in some feeds created a melt volume several times as large as its original size, where the bubbles suspended the entire sample volume in thin films. The bubbles are not completely circular due to viscosity differences caused by the uneven dissolution of waste in the frit. The frit pieces are no longer distinct, but have melted together to form one mass with waste chunks dispersed throughout the melt. Though the waste chunks have not dissolved into the frit to a significant extent, there are areas in the frit that have become tinted with color, indicating that some dissolution of the waste elements into the glass matrix has occurred.

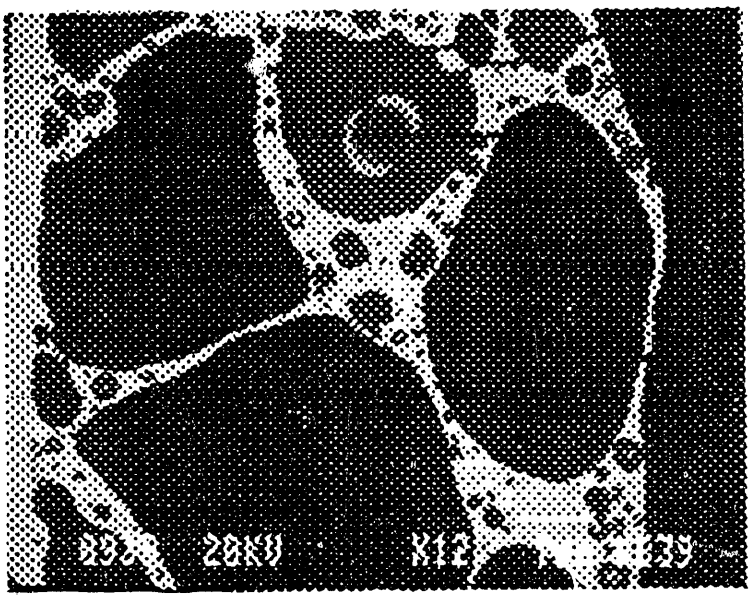

Figure 5. HWVP Feed at 697°C (SEM, 12X). Right side of picture corresponds to downward direction of sample.

The foaming occurring during this phase and remaining after the 1-hour heat treatment was much more significant in the HWVP and KfK feeds than in the DWPF feed.

5) Bubble motion and removal (720°C - 760°C)

In this temperature region, the viscosity of the melt has decreased enough to allow the bubbles to rise through the melt to the surface. Most of the bubbles in the sample were removed in this region, though a few remained after the one-hour heat treatment. Mixing is promoted during this phase by shear created from the motion of the bubbles and the boundary layers adjacent to the bubbles.

6) Convective mixing (760°C - 900°C)

During this stage, convective mixing is evident from streaks of waste particles aligned in convection patterns (see Figure 6).

The mixing in this and the previous stage appears to have broken the waste chunks up into smaller particles. Coloration of the glass increases during this temperatures region due to increased dissolution of the waste into the glass.

Figure 6. HWVP Feed at 879°C (Optical Microscopy, 100X). Right side of picture corresponds to downward direction of sample.

7) Homogenization (above 900°C)

Above approximately 900°C, the process of homogenization is occurring as convection continues (see Figure 7). This temperature region corresponds to the bottom layer of the cold cap or the beginning of the melt pool. During the hour that these samples underwent the heat treatment, complete homogenization did not occur due to the insoluble noble metals present, primarily ruthenium dioxide. SEM analyses revealed that the RuO_2 is generally present as sliver- or needle-shaped crystals approximately 2 μm long, or as agglomerates of these particles.

Discounting the noble metal particles, the melt is still not completely homogeneous, as can be seen from the non-uniform color of the melt. This indicates that the soluble waste constituents have dissolved into the glass matrix, but more time and/or higher temperatures are required for the glass to become uniformly mixed.

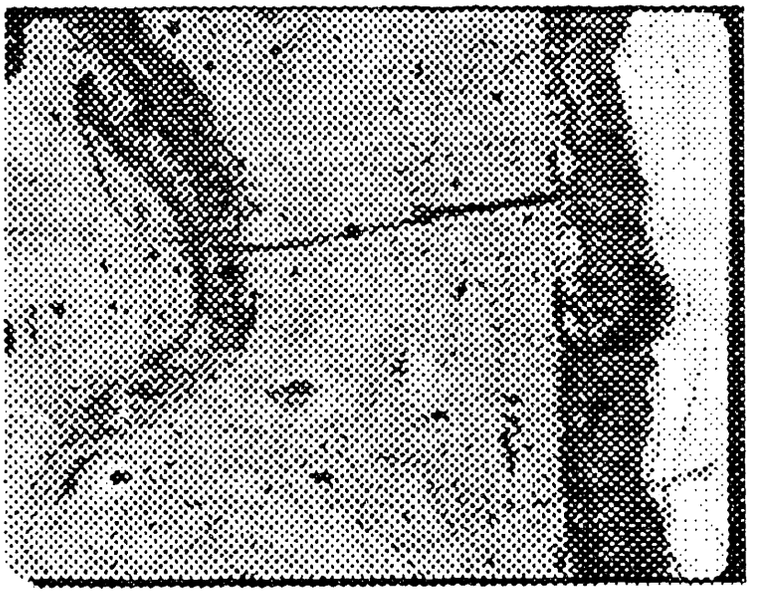

Figure 7. HWVP Feed at 913°C (Optical Microscopy, 100X). Right side of picture corresponds to downward direction of sample.

CONCLUSION

In summary, it was found that simulated HWVP, DWPF, and KfK melter feeds all experienced common stages during the conversion of feed to glass. The temperature ranges these stages occurred at varied due to differences in the frits and the composition of the wastes. However, but were generally within the ranges reported here. The knowledge of these stages aids in formulating agglomeration mechanisms for noble metal particles. Two possible mechanisms are as follows:

1. Concentration during waste dissolution

As the major waste constituents are dissolved into the glass frit, the insoluble noble metal particles become more concentrated in the remaining waste particles. This increased density of noble metals increases the potential for agglomeration.

2. Shear flocculation

The melt is subjected to a substantial amount of shear as bubbles grow, move, and break during the foaming stage. It is postulated that this may give rise to noble metal particles coming into contact with each other and agglomerating.

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