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MICROSTRUCTURAL CHARACTERIZATION OF GLASS AND CERAMIC SIMULATED WASTE FORMS*

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INTRODUCTION

Glass is currently the primary waste form candidate for immobilization of Hanford high level radioactive wastes from three generations of nuclear fuel reprocessing. Several chemically varied waste types must be immobilized, including slurries and highly concentrated liquids, and each may require a chemically different but optimum glass composition to fix the appropriate set of radio-nuclides. Efforts are also underway to evaluate the application of ceramic forms as an alternative to glass for the fixation of Hanford defense waste. Results of laboratory scale studies for fixation of these wastes into glass¹ and ceramic² forms have been reported and the studies are continuing.

The microstructures of three nonradioactive glass samples, which simulate three Hanford process waste forms, were characterized in this study. In addition, two samples of iodine sodalite which simulate the fixation of radioactive iodine were characterized. These five samples were intended only to demonstrate the potential for fixation of waste in a high integrity solid form and are not necessarily representative of the final products to be used in the immobilization of Hanford defense waste.

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DISCLAIMER

The samples were analyzed at Sandia Laboratories utilizing the techniques of x-ray diffraction, scanning electron microscopy (SEM) coupled with x-ray energy dispersive spectrometry (EDS), transmission electron microscopy (TEM) coupled with EDS, and electron microprobe analysis (EMP). Thorough microstructural analysis is considered essential to understanding isolation mechanisms and to interpret leach rate and other test data on such solid waste forms. A similar microstructural characterization study was reported at the first symposium last year.³

One of the three glass samples, Class 1, demonstrates the potential fixation of sludge generated from the Hanford bismuth phosphate (BiPO_4) process which is a first generation process for separating plutonium and uranium from other radionuclides. This sludge typically consists of a mixture of insoluble BiPO_4 and other hydrated metal oxides and hydroxides. The principal radionuclides in sludge are ^{90}Sr and ^{239}Pu .

Alkaline salt solutions stored in large underground tanks at Hanford are presently being evaporated to salt cake using large evaporator-crystallizer units. A highly alkaline solution called residual liquid remains when the salt solution cannot be further evaporated. The principal radionuclides in residual liquid are ^{137}Cs , ^{90}Sr , and ^{99}Tc . This residual liquid could be treated to remove the radionuclides resulting in a small volume of highly radioactive waste suitable for conversion to glass and a large volume of "decontaminated" solid salt which need not be converted to a high integrity high cost solid such as glass. Glass samples 2 and 3 demonstrate the potential for fixation of the concentrated residual liquids.

The two ceramic iodine sodalite ($\text{Na}_4\text{Al}_3\text{Si}_2\text{O}_{12}\text{I}$) samples demonstrate the potential for fixing radioactive iodine which volatilizes during fuel reprocessing and is removed from the process off-gas. Sodalite is a naturally occurring halide containing mineral. Iodine sodalite is being investigated at Rockwell Hanford to determine its acceptability as a material for the long-term storage of ^{129}I .

SAMPLE PREPARATION

The final compositions of the three glasses, calculated from initial batch mixtures, are given in Table I expressed as wt. % oxides. Glass formation temperatures were 1573K for Glass 1 and 1473K for Glasses 2 and 3. The melts were held for one hour in air atmosphere and then air-quenched. Glass 1 and 2 were then reheated to 1273K and cooled at 3K/h to 673K to determine the devitrification behavior.

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Table I. Calculated Compositions of Glass Samples (Wt. %)

Oxide	Bi-phos. Glass 1	Res. Liq. Glass 2	Res. Liq. Glass 3
SiO ₂	58.1	63.0	63.0
B ₂ O ₃	10.5	10.0	10.0
Na ₂ O	7.1	17.3	11.1
Li ₂ O	2.0	2.0	2.0
Fe ₂ O ₃	7.5		
Cr ₂ O ₃	1.1		
ZrO ₂	0.1		
Bi ₂ O ₅	10.4		
CeO ₂	0.1		
P ₂ O ₅	3.0		1.4
SO ₃	0.05		
F	0.05		
Al ₂ O ₃		5.8	5.5
TiO ₂		0.9	0.6
SrO		0.5	6.0
Cs ₂ O		0.5	0.4

The two iodine sodalite samples were prepared by mixing 19M NaOH, NaI, and a kaolinite clay (nominally Al₂Si₂O₅(OH)₄ with several percent impurities) in a mass ratio of 1.0:1.25:3.22, based on the dry solids. After drying, one sample was hot pressed in graphite dies at 14 MPa and 1253K. A portion of this sample was then reground and hot pressed in graphite dies at 14 MPa and 1353K. (See reference 4 for a more complete discussion on iodine sodalite preparation.)

RESULTS OF MICROSTRUCTURAL CHARACTERIZATION

Glasses

A. Bismuth Phosphate Glass 1: Optical, SEM and TEM microscopy revealed that this glass did undergo devitrification during the slow cool from 1273K to 673K. The resulting microstructure was composed of four separate crystalline phases dispersed in a glassy matrix, as shown in Figure 1. Phase 1 is present as large plate-like crystals which comprise approximately 30-40 vol. % of the sample. Both electron diffraction analysis of these crystals in the TEM and X-ray diffraction analysis of the bulk sample identified this most prevalent crystalline phase as tridymite (SiO₂). Quantitative EMP analysis indicated that the platelets are almost pure SiO₂, but contain about 0.25 wt. % iron oxide.

Fig. 1. SEM Micrographs of bismuth phosphate Glass 1 showing four crystalline phases (1-4) dispersed in glassy matrix.

Phase 2 was present in plane sections as long stringers of small crystallites. This geometry is interpreted in 3-dimensions as cross sections through planar arrays of small crystallites. This phase comprised only about 1-2 vol. % of the total sample. EDS spectra obtained from these crystals in the TEM contained only phosphorous peaks. However, EMP analyses suggested that the particles are not just phosphorous oxide but should also contain some additional component(s). Li and/or B oxide, neither of which is detected by EDS, are likely possibilities. D-spacings which were measured from electron diffraction patterns of this phase did not match any listed oxide of phosphorous with Li and/or B. Therefore, it was concluded that this phase is a Li- and/or B-containing phosphorous oxide not reported in the X-ray Powder Diffraction File.

Phases 3 and 4 were found to be two Cr-Fe oxides with different morphologies. Phase 3 was present as small-blocky shaped particles while Phase 4 had a plate-like morphology. It was determined from electron diffraction analysis that Phase 3 has a spinel structure with $a_0 = 0.812$ nm, but EMP analysis indicated that it has a much higher Cr:Fe ratio than the 1:2 ratio of the normal FeCr_2O_4 spinel. EMP analysis also suggested the presence of a small amount of Li and/or B oxide in solution. The structure of phase 4 was not determined, but morphological characteristics suggested that it is not the Cr-Fe Spinel.

Quantitative EMP analyses of these 4 crystalline phases and

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the glass matrix indicated that all Bi from the BiPO_4 addition went into the glass while P partitioned between the P-rich stringers (phase 2) and the glass. All other elements not found in the 4 crystalline phases were retained in the glass matrix.

B. Residual Liquid Glass 2: Although this glass was subjected to the 1273-673K slow cool test, it did not undergo any devitrification. The glass was found to be completely amorphous when examined by SEM and TEM. Thus all elements of the mix were retained in the glassy matrix.

C. Residual Liquid Glass 3: The increased Sr and P in this glass caused devitrification, even though it was not subjected to the slow cool test. The microstructure, shown in Figure 2, was a two-phase structure composed of approximately 5-10 vol. % of small crystallites dispersed in the glass matrix. Crystallinity was confirmed by the presence of spots in electron diffraction patterns. The particles were highly spherical with an average diameter of about 80 nm. Comparison of EDS spectra obtained from the particles and from the adjacent glass matrix in the TEM indicated that the particles were high in Sr and P and low in Al and Si compared to the matrix. A positive identification of this phase was not obtained from electron diffraction analysis, but it is probably a Sr-phosphate. EDS analysis indicated that Sr partitioned between these crystallites and the glass matrix, while the Cs content, albeit low, was retained in the glass.

Fig. 2. TEM micrograph of small crystallites in residual liquid Glass 3.

Fig. 3. TEM micrograph of the iodine-loaded ceramic which was reground and repressed.