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Comparison of Mechanical Properties of Glass-Bonded Sodalite and Borosilicate Glass High-Level Waste Forms

By:

T.P. O'Holleran, T. DiSanto, S.G. Johnson, and K.M.Goff

Nuclear Technology Division
Argonne National Laboratory
P. O. Box 2528
Idaho Falls, ID 83403-2528

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DISCLAIMER

COMPARISON OF MECHANICAL PROPERTIES OF GLASS-BONDED SODALITE AND BOROSILICATE GLASS HIGH-LEVEL WASTE FORMS

T. P. O'Holleran*, T. DiSanto, S. G. Johnson, and K. M. Goff
Argonne National Laboratory
P. O. Box 2528
Idaho Falls, ID 83236-2528

ABSTRACT

Argonne National Laboratory has developed a glass-bonded sodalite waste form to immobilize the salt waste stream from electrometallurgical treatment of spent nuclear fuel. The waste form consists of 75 vol.% crystalline sodalite and 25 vol.% glass. Microindentation fracture toughness measurements were performed on this material and borosilicate glass from the Defense Waste Processing Facility using a Vickers indenter. Palmqvist cracking was confirmed for the glass-bonded sodalite waste form, while median-radial cracking occurred in the borosilicate glass. The elastic modulus was measured by an acoustic technique. Fracture toughness, microhardness, and elastic modulus values are reported for both waste forms.

INTRODUCTION

Argonne National Laboratory (ANL) will use an electrometallurgical treatment process to condition spent nuclear fuel for repository disposal. Two high-level waste (HLW) streams emerge from the electrometallurgical treatment process. One HLW stream consists almost entirely of chloride salts that are unsuitable for immobilization using conventional borosilicate HLW glass technology. A glass-bonded sodalite ceramic waste form has been developed to immobilize the halide waste stream. The ceramic waste form is fabricated at elevated temperatures (1123 K) and pressures (100 MPa) in a hot isostatic press (HIP). Fission product and actinide bearing salt used as the electrolyte in the electrometallurgical treatment process is absorbed by a granular zeolite (Linde Type A). The salt occluded zeolite is mixed with a powdered glass binder in a 3/1 ratio by weight, and sealed in an evacuated stainless steel (type 304L) can. In the HIP, high pressures and temperatures convert the Linde Type A zeolite to sodalite, and consolidate the ceramic powders into a multi-phase ceramic body.

Waste forms may be subjected to impacts as a result of handling or transportation accidents. Fracture toughness measurements were performed on representative samples of non-radioactive ceramic waste form to provide a basis for postulating the behavior of the waste form in an impact event. Fracture toughness was measured by the microindentation method[1], which also necessitated measurements of hardness and Young's modulus.

Borosilicate glass is currently the only waste form qualified for disposal of high-level waste in the proposed Yucca Mountain repository. Two representative samples of non-radioactive high-level waste (HLW) borosilicate glass from the Defense Waste Processing Facility (DWPF) were obtained. These simulated HLW glasses were poured into full-scale HLW glass canisters during the DWPF Startup Test Program. The canisters were subsequently cut open to obtain samples of the glass product. Fracture toughness, hardness, and Young's Modulus were measured on these samples for comparison purposes.

EXPERIMENTAL

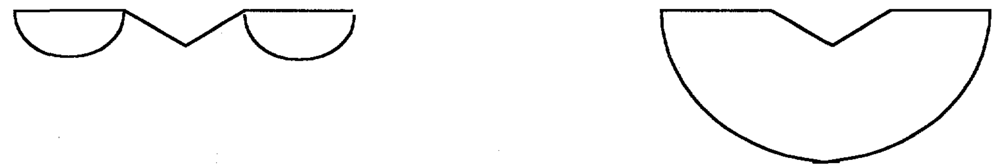
Experiments were initially conducted to provide background data and define an effective method for measuring the fracture toughness, or Mode I critical stress intensity factor (K_{Ic}) of the two materials. Fracture toughness was subsequently measured using techniques refined during the initial experiments. The microindentation method[1] using a Vickers diamond indenter (Leitz-Wetzlar Miniload Hardness Tester) was used to measure fracture toughness and hardness. In this method, a pyramidal-shaped diamond indenter with an apex angle of 136° is lowered onto a flat surface of the material to be measured, and a known load is applied to the material. After the indenter is removed, brittle materials exhibit an impression of the indenter where the material has undergone plastic deformation, with so-called radial cracks ideally extending from the points of the indentation. Knowing the applied load and Young's modulus, the hardness of the material can be determined by measuring the size (diagonals) of the indentation. Fracture toughness is related to either the –1/2 or –3/2 power of the length of the radial cracks, depending on the type of cracking that occurs. Palmqvist cracks are semi-elliptical cracks that extend below the surface of the material beyond the corners of the indentation. Median (or half penny) cracks are semi-circular cracks that extend below the surface of the material, underneath the indentation, and beyond opposite corners of the indentation (see Figure 1).

Palmqvist cracking was previously shown to be the dominant cracking mode in the ceramic waste form[2]. The same procedure used to determine the type of cracking in the ceramic waste form was used to determine the type of cracking in DWPF glass. The DWPF glass samples were obtained from Sharon Marra at the Savannah River Technology Center. The nominal compositions of the two glass samples are given in Table 1. These compositions are considered representative of the DWPF product based on the expected range of melter feed compositions.

Table 1: Nominal compositions of the DWPF glass comparison samples used in this study (as weight percent).

Compound	S00194	S00412
Al_2O_3	6.25	4.55
B_2O_3	7.89	7.95
CaO	0.69	0.99
CuO	0.45	0.40
Fe_2O_3	9.71	12.12
K_2O	2.75	2.47
Li_2O	4.46	4.74
MgO	1.48	1.54
MnO	2.21	2.16
Na_2O	10.18	9.90
Nd_2O_3	1.37	0.44
NiO	0.60	0.81
SiO_2	51.98	52.73
TiO_2	0.36	0.33
ZrO_2	0.91	1.20

Samples were polished flat to a 1200 grit finish using silicon carbide paper, and a series of initial indentations was made in each specimen. The indentations proved difficult to see because of the optical properties of the material. The instrument used to make the indentations was intended for making hardness measurements on reflective metal samples. DWPF glass absorbs strongly at optical wavelengths, but is sufficiently transparent to make reflected light microscopy very difficult. These difficulties were overcome by sputtering several hundred angstroms of palladium onto the surface of the samples. The thin palladium layer rendered the surface optically reflective without affecting the mechanical properties of the material.



A. Palmqvist cracks B. half-penny cracks

Figure 1: Schematic section through a diagonal of a Vickers indentation in a brittle material showing the subsurface extension of A. Palmqvist cracks, and B. half-penny cracks.

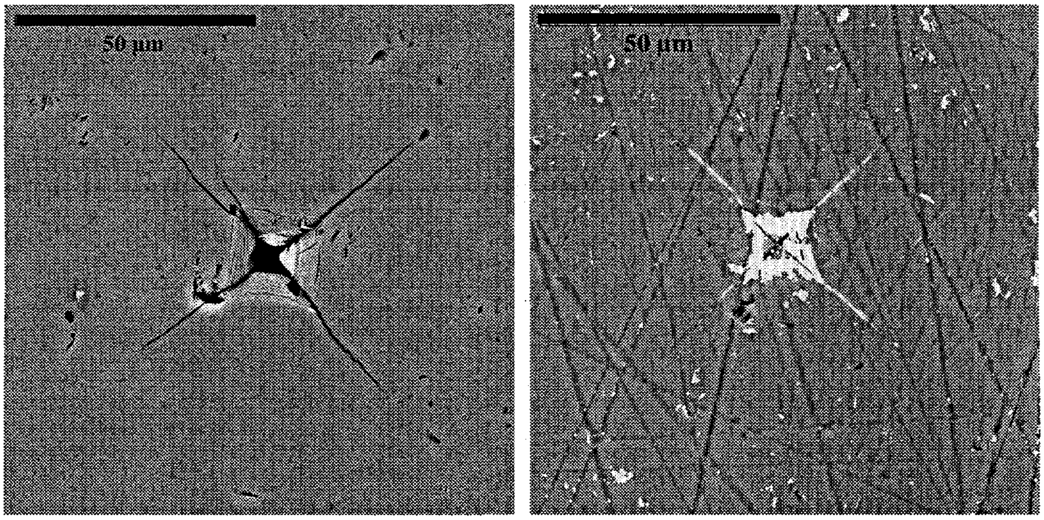
A series of indentations were produced using different applied loads to define the practical load range for indentation fracture toughness measurements. The ideal load for the DWPF glass samples was found to be 1.96 N.

The indentations and cracks produced in these experiments were examined by scanning electron microscopy using a Zeiss DSM960A digital scanning electron microscope (SEM) to determine the cracking mode. This method of examination proved much easier than optical methods for locating and measuring cracks and indentations, particularly in back scattered electron mode. After the initial examination, the samples were removed from the SEM, and a portion of the surface was polished away with silicon carbide paper. The polished surface (re-polished to a 1200 grit finish) was re-coated with palladium to provide electrical conductivity, and the samples were returned to the SEM. Individual indentations were re-located, and measurements indicated that the sample surface had been ground away to approximately half the depth of the indentations made in DWPF glass sample S00412, and approximately 20% of the depth of the indentations made in DWPF glass sample S00194. This approach effectively provided a sectioned view of the indentations and the cracks emanating from them.

In order to calculate fracture toughness, Young's modulus of the material must also be known. These data were obtained using an acoustic resonance method (Grindosonic Mk V Industrial, J. W. Lemmens nv, Belgium). Samples of a fixed rectangular geometry were cut from the two glass specimens, and measured at the Idaho Nuclear Technology and Engineering Center.

RESULTS AND DISCUSSION

Analysis of the indentations and cracks formed in the DWPF glass samples showed half-penny cracking to be the dominant cracking mode (see Figure 4). Secondary radial racks, predominantly lateral cracks, were also observed. The presence of secondary radial cracks at an indentation complicated analysis of the crack pattern, sometimes making unambiguous identification of the cracking mode impossible. Sometimes crack patterns were observed which appeared to be Palmqvist cracks. However, the most common cracking mode that was clearly identified was half-penny cracking, so fracture toughness in the DWPF glasses is proportional to the $-3/2$ power of the crack length. Figure 4 shows a typical indentation and associated crack system observed in the DWPF glass samples before and after polishing away a surface layer. All four of the long cracks are still connected to the corners of the indentation after polishing, indicating half-penny cracking. The short secondary crack in Figure 4 A is still visible in 4 B, but is on the other side of the longer half-penny crack. This indicates that the two cracks crossed before intersecting the original surface in Figure 4 A. Because of the ambiguity identifying the true half-penny crack in cases such as illustrated in the upper left corner of Figure 4 A, such cracks were excluded from the analysis. Only clearly identifiable half-penny cracks such as those eminating from the upper right/lower left corners of the indentation such as in Figure 4 A were used to calculate fracture toughness.



A B

Figure 4: Back scattered electron images from DWPF glass sample S00194. A, Fresh indentation showing a typical crack pattern. B, the same indentation after material constituting the original surface was polished away. Cracks in B still connected to the corners of the remaining indentation indicate half-penny (radial/median) cracks.

Following the analysis of Anstis et al.[3], equation 3 was used to calculate fracture toughness (K_{Ic}) of the DWPF glass samples from the experimental data as:

$$K_{Ic} = 0.016\left(\frac{E}{H}\right)^{1/2} \frac{P}{c^{3/2}} \tag{3}$$

where P is the applied load in Newtons, c is the half-penny crack length in microns, E is Young's modulus in GPa, and H is the hardness in GPa. Hardness (H) is calculated from the length of the indent diagonals as:

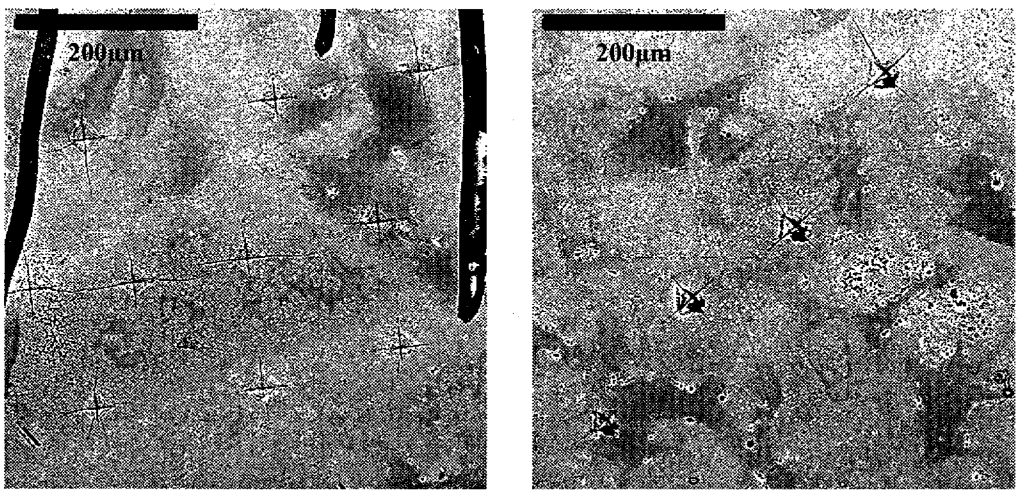
$$H = \frac{1854.4P}{(2a)^2} \tag{2}$$

Young's modulus E was measured on seven ceramic waste form samples prepared from different mixtures and types of starting materials, and on both the DWPF glass samples. There were no statistically significant differences between the seven ceramic waste form samples, so the average Young's modulus (69.10 GPa) was used for all ceramic waste form fracture toughness calculations. With only two samples available, no statistical analysis was performed on the Young's modulus values obtained for the DWPF glasses (85.30 GPa for S00194, and 87.61 GPa for S00412). Measured values were used to calculate fracture toughness for each DWPF glass.

Indentation experiments to measure fracture toughness were performed on four different samples of ceramic waste form material composed of starting materials (powdered zeolite vs.

granular zeolite) and formulated with different glass to zeolite ratios. In all cases, the ratio of crack length to indent half diagonal remained within the range expected for Palmqvist cracking[4].

Despite the differences in starting materials and applied loads, there were no statistically significant differences in hardness or fracture toughness for the ceramic waste form materials. This result is probably attributable to the similarity in the microstructures of the two materials, as shown in Figure 4. Apparently, the glass binder, which is relatively fluid at the processing temperature used to produce these materials, readily penetrates into the granules of zeolite starting material used to make HIP can 84. This penetration may be facilitated and accompanied by dissolution of the clay-based binder, but results in a microstructure very similar to the ceramic waste form material fabricated from powdered zeolite starting material (without binder). X-ray spectroscopy does not discern differences in the composition of the intergranular glass in the two materials, so significant differences in mechanical properties are not expected. Similarly, varying the ratio of glass to zeolite between 1/1 and 1/3 had no statistically significant effect on the fracture toughness. The results of all the mechanical property measurements performed on the ceramic waste form materials are summarized in Table III, which also shows results from measurements on the two DWPF glasses for comparison.



A B

Figure 4. Back scattered electron images from: A, sample from HIP can 74, and B, sample from HIP can 84. Lighter contrast areas are sodalite, and darker contrast areas are glass. Several examples of non-Palmqvist cracking (single cracks not clearly radiating from indentation diagonals) that were excluded from the analysis used to produce Table II can be seen in both A and B.

Table III. Summary of averaged mechanical property data for ceramic waste forms. Data for DWPF glasses are shown for comparison.

Material	Fracture Toughness ($MPa\ m^{1/2}$)	Hardness (GPa)	Young's Modulus (GPa)
Ceramic Waste Form	1.13	4.71	69.10
DWPF S00194	0.76	5.89	85.30
DWPF S00412	0.66	5.93	87.61

Comparing the ceramic waste form to DWPF glass, the ceramic waste form exhibits greater fracture toughness (K_{Ic}), while DWPF glass is harder and stiffer. The results for the ceramic waste form compare well with data on other ceramics and glasses published in the literature[3,5,6]. Fracture toughness, for example, is greater than soda-lime or aluminosilicate glasses, but less than a commercial glass-ceramic (Pyroceram)[3], or the cordierite glass-ceramic recently reported by Diaz et al.[6] Hardness of the ceramic waste form is less than silicate glasses[3,5], while Young's modulus is comparable to commercial sheet glass[3]. These observations are largely explained by the microstructure of the ceramic waste form. The heterogeneous microstructure of the ceramic waste form inhibits crack propagation, resulting in greater fracture toughness than soda-lime or aluminosilicate glasses. Coarser grain size and higher intergranular glass content reduces fracture toughness of the ceramic waste form with respect to commercial glass ceramics. Data for DWPF glass also compare well to literature values reported for various glasses, falling very close to data reported for a commercial soda-lime sheet glass[3].

Drop tests have been performed on both DWPF and West Valley canisters containing simulated HLW glass. In those tests, the canisters were required to control dispersal of their contents by remaining leak-tight after a nine meter drop. Both DWPF and West Valley canisters passed the test. Had the canisters ruptured, the dispersal scenario would have required atmospheric transport of aerosol-size particles of glass. In this case, any particles less than 10 μm are considered aerosol-size particles. Unfortunately, the contents of the drop-tested canisters were not examined to determine the effect of the impact on size distribution. However, in the mid-1970s, Battelle Pacific Northwest Labs (now Pacific Northwest National Laboratory) assessed the effect of impacts on simulated high-level waste glass in canisters using similar drop tests[7]. This analysis gave a best estimate for the amount of particles less than 10 μm generated in a nine meter drop test as 0.001% of the contents of the canister. Based on the data reported here, the ceramic waste form would be expected to generate an even smaller fraction of aerosol particles in a nine meter drop test.

CONCLUSIONS

Selected mechanical properties of the ceramic waste form from electrometallurgical treatment of spent nuclear fuel have been measured. No statistically significant variations in properties due to differences in starting materials have been observed in these measurements. Measured values agree well with data published in the literature[5] for a variety of materials measured by different methods. These results suggest that the ceramic waste form would be even more likely to pass transportation drop tests than high-level waste glass.

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