ANL/NT/CP-99069

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OCT 19 1999
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American Ceramic Society
101st Annual Meeting
Symposium: Waste Management Science and Technology in the Ceramic and Nuclear Industries

Indianapolis, Indiana
April 25 - April 30, 1999

*Work supported by the U. S. Department of Energy, Office of Nuclear Energy, Science and Technology, and the Office of Environmental Management, under contract W-31-109-Eng-38.

FRACTURE TOUGHNESS MEASUREMENTS ON A GLASS BONDED SODALITE HIGH-LEVEL WASTE FORM

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ABSTRACT

The electrometallurgical treatment of metallic spent nuclear fuel produces two high-level waste streams; cladding hulls and chloride salt. Argonne National Laboratory is developing a glass bonded sodalite waste form to immobilize the salt waste stream. The waste form consists of 75 vol.% crystalline sodalite (containing the salt) with 25 vol.% of an "intergranular" glassy phase. Microindentation fracture toughness measurements were performed on representative samples of this material using a Vickers indenter. Palmqvist cracking was confirmed by post-indentation polishing of a test sample. Young's modulus was measured by an acoustic technique. Fracture toughness, microhardness, and Young's modulus values are reported, along with results from scanning electron microscopy studies.

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 will emerge from the electrometallurgical treatment process. One HLW stream consists almost entirely of chloride salts, and therefore cannot be immobilized using conventional borosilicate HLW glass technology. A 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 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.

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 ceramic waste form. 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 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).

In order to determine the type of cracking exhibited by the ceramic waste form, a series of initial indentations was made in a sample of material from HIP can 74 that had initially been polished flat. The indentations proved difficult to see because at moderate magnifications the ceramic waste form appears semi-transparent. This difficulty was overcome by sputtering several hundred angstroms of palladium onto the surface. The thin palladium layer rendered the surface

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.

optically reflective without affecting the mechanical properties of the material. A series of indentations were produced using different applied loads. This experiment defined the practical load range for indentation fracture toughness measurements of the ceramic waste form from >1.96 N to <4.90 N. At 1.96 N and below, radial cracks were not observed. At 4.90 N lateral cracks, sometimes observed forming as delayed crack growth, often caused portions of the material to be ejected from the sample surface, thereby destroying the radial crack pattern.

The indentations and cracks produced in this experiment were examined by scanning electron microscopy using a Zeiss DSM960A digital scanning electron microscope (SEM). This method of examination proved much easier than optical methods for locating and measuring cracks and indentations, particularly in back scattered electron mode. The sample was 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 sample was 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.

In order to calculate the fracture toughness of the ceramic waste form, Young's modulus of the material must also be known. These data were obtained using an acoustic resonance method

(Grindosonic Mk 5 Industrial Instrument). Several samples of a fixed rectangular geometry were cut from HIP cans representing two different sodalite to glass ratios and prepared from different starting materials. The reference ceramic waste formulation uses a 1:3 ratio by weight of glass to salt occluded zeolite. The zeolite is a granular material, about 100 μm in size, containing 10 weight percent clay-based binder. Samples of ceramic waste form made from zeolite powder (about 5 μm in size) at the 1:3 glass to zeolite ratio were also obtained, along with samples made from zeolite powder at a 1:1 glass to zeolite ratio.

RESULTS AND DISCUSSION

In the initial set of experiments, observation of indentations made at 3.78 N and 4.90 N suggested that Palmqvist cracks had formed at least at some of the indentations. Some of the indentations lacked cracks at opposing points of the indentation as shown in Figure 2. The geometry of half penny cracks (see Figure 1) requires cracks at the surface at opposing points of the indent.

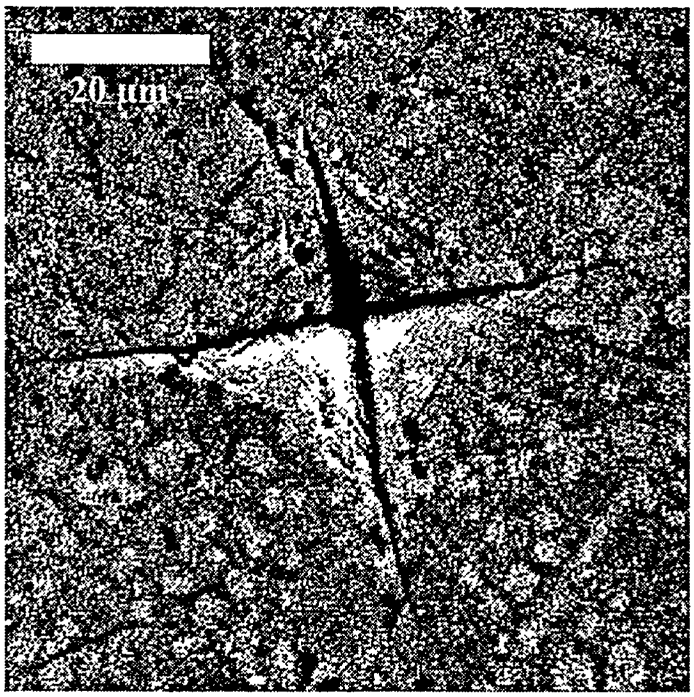


Figure 2. Back scattered electron image of a typical indentation form under a load of 3.78 N in a ceramic waste form specimen. Note that this indent shows radial cracks at only three of the four corners, suggesting Palmqvist cracks. Back scattered electron imaging was determined best for observing cracks.

The average ratio of crack length to half diagonal length also suggested Palmqvist cracks[2]. After removing the top layer of material, radial cracks associated with the indentations no longer appeared connected to the corners of any of the indentations (see Figure 3). This clearly indicated Palmqvist cracking, as half penny cracks would have appeared to be still connected to the corners of the indentations (see Figure 1). Fracture toughness in the ceramic waste form is therefore related to the –1/2 power of the crack length. This result was not unexpected, since other multi-phase materials (such as tungsten carbide-cobalt composites[3]) are known to exhibit Palmqvist cracking.

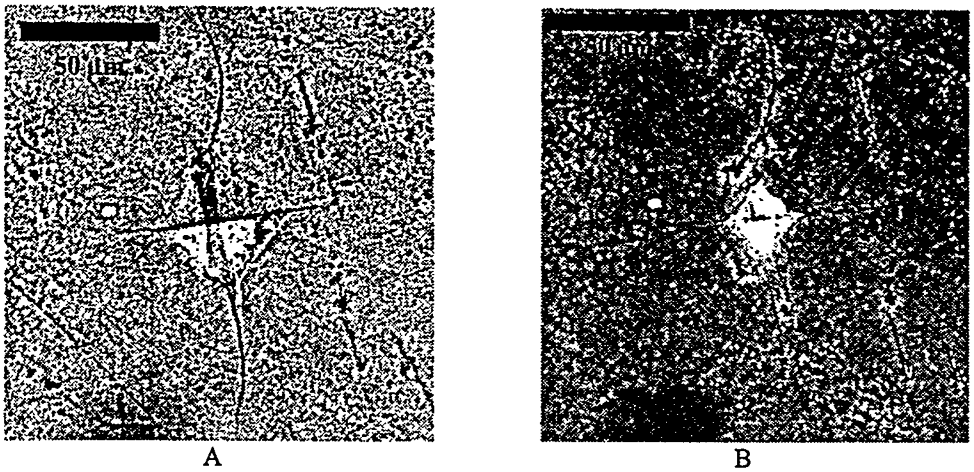


Figure 3. Back scattered electron images of an indentation formed at 4.90 N in a ceramic waste form sample: A is the as-formed indentation, and B is the same indentation after a surface layer equivalent to about half the depth of the indentation was ground away. The radial cracks in B are not connected to the corners of the indentation, clearly indicating Palmqvist cracks.

Following the analysis of Niihara[2,4], equation 1 was used to calculate fracture toughness (K_{Ic}) from the experimental data:

$$K_{Ic} = 0.0084\left(\frac{E}{H}\right)^{0.4}\frac{P}{al^{1/2}} \qquad (1)$$

where P is the applied load in Newtons, a is the length of the indentation half diagonal in microns, l is the crack length in microns, E is Young's modulus in GPa, and H is the hardness in GPa. The load P is determined by weights placed on the indenter. Hardness H is calculated from the length of the indent diagonals as:

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

Young's modulus E was measured on seven samples prepared from different mixtures and types of starting materials. As can be seen from Table I, the results of these measurements showed no statistically significant differences between the seven samples. Therefore, the average Young's modulus (69.10 GPa) was used for all fracture toughness calculations.

Indentation experiments to measure fracture toughness were performed on samples of material from HIP cans 74 and 84. HIP can 74 was a duplicate of HIP can 72 for which Young's modulus is reported in Table I. These two HIP cans were selected to investigate the effect of starting material (powdered zeolite for HIP can 74 vs. granular zeolite for HIP can 84) on waste form properties. Measurements were performed at a loading of 3.78 N on material from HIP can 74, and at loadings ranging from 1.96 N to 3.78 N on material from HIP can 84. In all cases, the ratio of crack length to indent half diagonal remained within the range expected for Palmqvist cracking[2]. Also, crack patterns such as that shown in Figure 2 were frequently observed, lending

Table I. Results of acoustic resonance measurements of Young's modulus performed on samples of ceramic waste form. Samples with the same numerical identification were from the same HIP can.

Sample No.	Glass/Zeolite Weight Ratio	Type of Zeolite	Young's Modulus (GPa)
49	1/1	powder	66.80
72	1/3	powder	67.84
84a	1/3	granular	67.70
84b	1/3	granular	72.18
802a	1/3	granular	67.60
802b	1/3	granular	70.99
802c	1/3	granular	70.59
		Average	69.10
		Standard Deviation	2.10

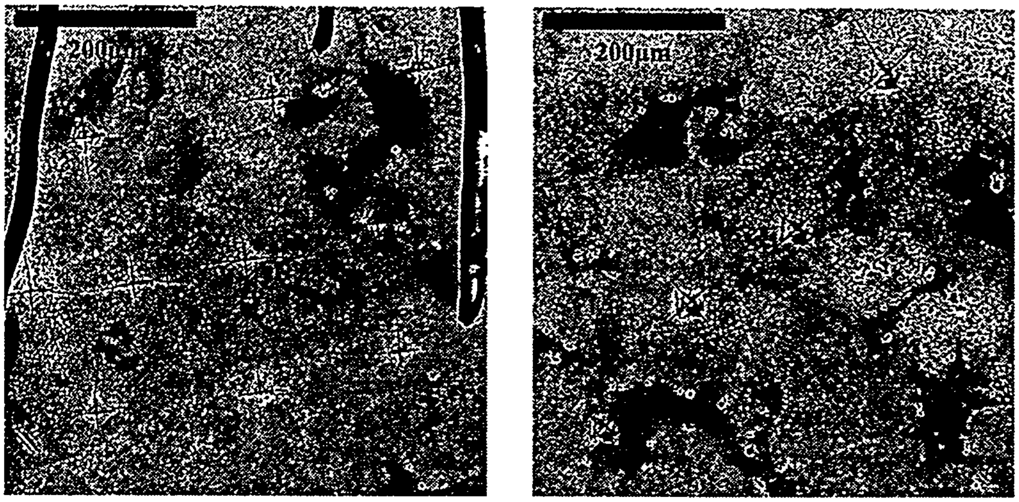
confidence to the use of Equation 1 for the analysis. The results obtained using Equations 1 and 2 to analyze the experimental data are presented in Table II.

Table II. Fracture toughness measured on two different samples of ceramic waste form by the microindentation method assuming Palmqvist cracking. Data reported were calculated using Equations 1 and 2, and are averages of from 9 to 19 indentations, with an average of three cracks per indentation. Cracks that did not clearly radiate from indentation corners were not used for these calculations.

	Fracture Toughness/Standard Deviation (MPa m$^{1/2}$) at:			
Sample no.	Applied Load = 1.96 N	Applied Load = 2.94 N	Applied Load = 3.29 N	Applied Load = 3.78 N
74	n. m.	n. m.	n. m.	1.11/0.25
84	1.14/0.18	1.24/0.24	1.10/0.12	1.10/0.08

n. m. – not measured

Despite the differences in starting materials and applied loads, there were no statistically significant differences between the data reported in Table II. 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. The statistical similarity of the data in Table II implies that the fracture toughness of these two materials is identical. The results of all the mechanical property measurements performed on these two materials are summarized in Table III. Hardness data have also been averaged for the two samples, as these data exhibited even less statistical variation than the fracture toughness data. The heterogeneity of the microstructure and the scale of microstructural features compared to the sizes of indentation initiated cracks (see Figure 4) probably accounts for most of the scatter in the fracture toughness data.



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.

Fracture Toughness ($MPa\ m^{1/2}$)	Hardness (GPa)	Young's Modulus (GPa)
1.13	4.71	69.10

These results compare well with data published in the literature[5,6,7]. Fracture toughness, for example, is greater than soda-lime or aluminosilicate glasses, but less than a commercial glass-ceramic (Pyroceram)[5], or the cordierite glass-ceramic recently reported by Diaz et al[7]. Hardness of the ceramic waste form is less than silicate glasses[5,6], while Young's modulus is comparable to commercial sheet glass[5]. 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.

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.

FUTURE WORK

Future experiments are planned to assess the effects of glass binder content on the mechanical properties of the ceramic waste form. Also, measurements will be performed on representative samples of high-level waste borosilicate glass from the Defense Waste Production Facility to provide a direct comparison of mechanical properties with a material known to pass transportation drop tests.

ACKNOWLEDGEMENTS

Argonne National Laboratory is operated for the US Department of Energy by the University of Chicago. This work was supported by the Department of Energy, Nuclear Energy Research and Development Program, under contract no. W-31-109-ENG-38. The authors wish to thank M. Simpson and K. Bateman for producing the waste forms and providing processing information, and B. Scholes for performing acoustic resonance measurements.

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