Conf 911202--16

ANL/CP--73611

SHAPING PARTICLES FOR ULTRAMICROTOMY

DE92 005242

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ABSTRACT

A technique for preshaping large particles of reacted glass for ultramicrotomy is described. This technique preserves delicate surface layers and results in more sections per block extending deeper into the sample than other techniques.

INTRODUCTION

The samples of interest in this laboratory are simulated nuclear waste glasses which have been aged either in a water vapor environment like that expected at the potential high level nuclear waste repository or in a liquid water environment. Reaction layers develop on the surface of the glass resulting from the deposition of material from the surrounding solution and/or alteration and in situ restructuring of the glass structure. The layer structure is frequently very complex, usually quite delicate, and may vary in thickness from a few hundred Angstroms to more than 100 μm depending on the glass composition, reaction conditions, and the duration of the experiment (20 hr to 8 yrs). Transverse cross-sections provide information to determine the sequence of reactions that control glass alteration with the goal being to predict glass performance in the future.

The reaction layer material is usually a mixture of clays, zeolites, other mineral phases, and amorphous regions. Chemical thinning methods must be avoided since any chemical strong enough to thin the glass would likely alter material in the reaction layers. One can also expect problems with ion milling when preparing these sections because the various components of the layers will display significantly different milling rates and can be altered by the ion beam. Microtomy is preferable for several reasons; a wide variety of samples can be prepared with essentially the same technique, many samples can be mounted and sectioned in a short period of time, and only a very small amount of material ($2.5 \times 10^{-7} \text{ cm}^3$) need be embedded in order to prepare a TEM specimen so cross-sectional views of individual particles of a powdered glass sample can be obtained.

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We describe here a technique for dealing with those samples which have extremely thick reaction layers. The method should be applicable wherever a thick delicate layer structure is of interest. Ultramicrotomy has been applied to preparation of reacted waste glass with thin reaction layers by others[1], and we have used a small particle technique which usually produces good results for layers less than about 40 μm . However, when layers are thicker than this, sectioning is usually unsuccessful.

SHAPING LARGE PARTICLES

When reaction layers are very thick there are some special problems. The layers are usually very delicate and the usual manipulations needed to produce a sample do significant damage. A special technique has therefore been developed for such samples. This technique is simple and quite general. A large (3 mm x 1 mm x 0.1 mm) particle of the reaction layer and underlying glass is carefully cut from the glass surface with a small diamond knife and transferred to a half-block of epoxy previously prepared by half filling a silicone mold (Ladd 21775 or equivalent) with epoxy embedding resin and curing for 24 hrs at 60°C. The half-block is wet at the tip with uncured resin just before the particle is put in place (Figure 1) and this assembly is cured in an oven at 60° C for a few hours to tack the particle in place. After the particle has been tacked down the epoxy half-block is returned to the silicone mold and filled with epoxy, embedding the particle (Figure 2). The shape of the particle and size are not important at this stage. Larger particles are actually preferred so as to make subsequent steps in the process easier.

Figure 1 To prepare a glass sample with a very thick reaction layer for microtomy a large (3 mm x 1 mm x 0.1 mm) particle is carefully transferred to an epoxy block which has been wet at the tip by the uncured embedding resin.

Figure 2 After the particle has been tacked in place the half-block is pressed back into the mold, the mold is filled with epoxy, and cured for 24 hrs at 60°C.

When the block has cured, a low speed diamond saw is used to trim away most of the epoxy on one side of the particle and expose the cross-section of interest (Figure 3). This face is then polished (3 μm diamond) by hand, washed with water, and then polished with 0.5 μm diamond paste. After the final polish, the block is washed with water, methanol, and then ethanol and then the remnant of the epoxy block is pressed back into the mold; the mold is filled with epoxy resin and cured at 60 °C for 24 hrs (Figure 4).

The same procedure is now applied to the other side of the particle (Figure 5). The bulk of the epoxy is cut away with a low speed diamond saw, the block face is rough ground with 3 μm polish and then finally polished with 0.5 μm diamond paste. The objective is to produce a slab of glass and reaction layer that is approximately 10 to 20 μm wide. Only crude polishing techniques need be used in this application of preshaping an embedded particle of a hard material for microtomy, since it is not necessary to obtain a slab whose sides are absolutely parallel; a small

Figure 3 A low speed diamond saw is used to trim away most of the epoxy on one side of the particle and expose the cross-section of interest. This side is then polished washed and polished with a finer grit.

taper will still permit many sections to be taken from the thinner portions at the tip of the particle. When this operation is complete the block is again pressed back into the mold filled with epoxy resin and cured for 24 hrs at 60°C. After polymerization the block is trimmed for thin sectioning. Sections ~ 500-1000 Å are taken from the tip of the sample and transferred to a carbon coated grid.

Figure 4 The remnant of the epoxy block is pressed back into the mold; the mold is filled with epoxy resin.

Figure 5 The epoxy on the other side of the embedding block is cut away with a low speed diamond saw and polished.

RESULTS

Using this technique, we have been able to produce electron transparent cross-sections of the reaction layers where the depth from the surface to glass was more than 100 μm (Figure 6). The reaction layers are clearly visible in this section as can be seen in a closer view of the outer portion of the section (Figure 7). The sections produced in this way are superior to sections produced from the same samples by embedding and sectioning small "as broken" particles (Figure 8). Invariably these earlier attempts resulted in a delamination of the reaction layers.

Figure 6 A 100 + μm cross-section produced by this technique. There is a tear, a typical microtomy artifact, near the outer surface. Ample material remains around the edges of this tear for investigation at a higher magnification.

Figure 7 A closer look at layers near the surface of the section shown at low magnification in Figure 6.

Figure 8 A typical result of attempts to produce cross-sections of the layer structure without using this technique. Layers tend to delaminate with handling. The sections produced are therefore individual layers and interfaces between the layers are not preserved.

The particle shape produced by this method is much more uniform than that produced by picking out "as broken" particles. Such particles frequently taper very rapidly from the bulk to a very fine tip. This thin tip sections well but the cross-section expands rapidly as one advances into the particle. Very quickly the particle becomes too large to produce good sections. This rapid expansion of the particle cross-section can easily be avoided by shaping a larger particle to the desired thickness with the result that many more sections can be taken from such a block.

Sectioning of the layer material is best done with the knife edge perpendicular to the layers cutting parallel to the layer structure. With other directions there is a tendency to either delaminate, or compress the delicate reaction layers (Figure 9). This delamination is easily seen in thin reaction layers and is more significant when layers are thicker. Starting with a "bulk" piece of material and shaping it has the advantage that the orientation of the layers is known. When working with fine particles it is sometimes difficult to identify the orientation of the particle in the epoxy block. It may be necessary to section, observe the sections in the TEM, rotate the sample and re-section. Since the number of sections that can be taken from an "as broken" particle is limited; this re-sectioning is frequently not successful.

Figure 9 When the knife edge is parallel to the interface between layers there is a tendency to either delaminate, or compress the delicate reaction layers.

This method of preshaping an embedded particle is very simple to implement, quite general, and maintains most of the advantages of sample preparation by ultramicrotomy. Delicate surface layers are protected from the delamination or disruption associated with a breaking process. The particle shape produced by this method is uniform and more sections can be produced than with "as broken" particles. Furthermore, knowing the orientation of the reacted layers with respect to the cutting direction makes it possible to take better sections without the delamination or compression that often accompany sectioning of very thick layer structures.

ACKNOWLEDGMENTS

Work supported by the U.S. Department of Energy, Office of Environmental Restoration and Waste Management, under Contract W-31-109-ENG-38.

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