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APPLICATION OF DRY-POLISHING TECHNIQUES TO WATER-SOLUBLE GLASS CERAMICS*

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ABSTRACT

A dry polishing technique is presented for the preparation of glass ceramics for microstructural characterization. The technique is shown to be applicable to water soluble phosphate based glass ceramics and also to a non-water soluble zinc silicate glass ceramic. Microstructural characterization is performed primarily with composition backscattered electron imaging in the scanning electron microscope. Some relief is observed on the polished surface utilizing topographical backscattered electron imaging.

Some agglomeration and adherence of alumina polishing powders on the polished surface occurs especially during early polishing. This is eliminated by the Freon cleaning procedures described.

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INTRODUCTION

Microstructural analyses of materials by optical microscopy, scanning electron microscopy, energy dispersive x-ray analysis and electron microprobe analysis require flat polished surfaces. For most materials this is accomplished by embedding the sample in a mounting material (for example epoxy), wet grinding the surface with 240 grit through 600 grit SiC abrasive papers, and final polishing with a diamond paste or alumina suspended in water. This procedure cannot be used when portions of the specimens are water soluble. Division 5845 (Ceramic Development) is currently developing a series of phosphate glass ceramics for sealing to metals ranging from aluminum to copper. These glass ceramics encompass a variety of compositions having varying degrees of water solubility. Microstructural analysis of these materials, then, requires development of polishing techniques for partially water soluble materials.

Several techniques have been proposed for obtaining suitably polished samples of water soluble glass ceramics. The use of solvents such as kerosene and alcohols as lubricants has been suggested, but these solvents can still result in dissolution of some of the water soluble phases. In addition, kerosene and even alcohol can act as a contamination source in the scanning electron microscope (Krstic 1980). Simons has developed a dry polishing technique, modified by Jones (1978), for polishing high temperature and salt induced corrosion samples where some of the corrosion products and the salts are water soluble. This report deals with the application of a similar polishing technique to the polishing of water soluble phosphate glass ceramics. This technique is also applicable to other non-water soluble glass ceramic materials as well as to geological samples.

Materials and Methods

Four different phosphate glass ceramic compositions with varying degrees of water solubility were examined in this study. These glass ceramics are labeled samples 1 through 4, and their compositions are given in Table I. All four of these samples received identical ceraming heat treatments of two hours at 400°C followed by two hours at 450°C. Sample 5 is a zinc silicate glass ceramic (non-water soluble) that has been included to compare the results of the dry polishing technique to those obtained using standard polishing techniques. This material received a ceraming heat treatment of 30 minutes at 1050°C, and its composition is also given in Table I.

Samples for microstructural analyses were cut from the heat treated pellets, mounted in Epon 828 epoxy, and cured at 100°C for 16 hours. They were then ground on dry SiC abrasive papers from 240 grit through 600 grit. Final polishing was also done dry utilizing a vibratory polishing unit lined with a 62 durometer neoprene rubber pad. Polishing was performed with 0.3 μm alumina powder covering the rubber pad. The samples were mounted in standard vibratory sample holders and placed on top of the alumina powder in the vibratory polisher. Polishing times ranged from 12 hours to 48 hours, depending on the sample and its surface finish before the start of polishing.

One problem encountered with this technique was that of agglomeration of some of the alumina particles on the surface of the glass ceramic. This agglomeration prevented any further polishing of the sample. As a result, the samples needed to be cleaned approximately every two hours. This was accomplished by placing the samples face down in a beaker of Freon while ultrasonically cleaning for one minute. The low surface tension of the Freon effectively removed all the agglomerated alumina powder from surface of the

sample during ultrasonic agitation. The epoxy mounted samples floated in the Freon, preventing the polished surface from being scratched, and allowing the released powders to sink to the bottom of the beaker.

After completion of the polishing procedure, the samples were again ultrasonically cleaned face down in Freon for several minutes to remove any adherent alumina particles, and were then blown dry with Freon. No etching of the glass ceramics was used; the as-polished glass ceramic surfaces were examined. The scanning electron microscopy was performed with a JEOL-JSM35C electron microscope. This instrument was equipped with a high resolution, annular, split ring backscattered electron detection system. The detector was capable of being ganged and deganged to produce a compositional (ganged) and topographical (deganged) image signal (Kimoto 1964). The analyses were performed at a 15 mm working distance with the electron beam perpendicularly incident to the sample surface (Healey 1980). The compositional backscattered imaging mode was primarily used with the topographical imaging mode being used to determine if any polishing relief had occurred.

RESULTS

Figures 1 through 4 are scanning electron micrographs of the four different compositions of the water soluble phosphate glass ceramics. The samples have not been etched. A number of different microstructures are observed in the various compositions when viewed in the compositional backscattered electron mode. Sample 1, (Figure 1) is composed primarily of spherulitic crystalline grains, often containing a bright central region, dispersed in a glassy matrix. Energy dispersive x-ray analysis shows the bright central region to have a high barium and phosphorous concentration and a lower sodium concentration. The remaining spherulitic crystalline

region has a high phosphorous content, an intermediate barium content, and a low sodium content. The glassy matrix is high in phosphorus and sodium, but almost totally region has a high phosphorous content, an intermediate barium content, devoid of barium. Sample 2 (Figure 2) contains a more poorly defined spherulitic crystalline phase which itself contains a second crystalline phase; both of these crystalline phases are again dispersed in a glassy matrix. The second crystals have a high barium and phosphorous concentration with low sodium concentration; the spherulitic crystals have high phosphorus, increased sodium, and virtually no barium. Sample 3 (Figure 3) shows two structures. The first, a pattern of fine acicular crystals, high in barium and phosphorous concentration, dispersed in a high phosphorus and sodium glassy matrix. The second is a pattern of equiaxed crystalline grains in a glassy matrix. The equiaxed grains are high in barium content and the glassy phase is almost devoid of barium with higher sodium content. Sample 4 (Figure 4) shows only isolated crystals present in a glassy matrix. The crystals are high in barium while the glass immediately surrounding the crystals is almost totally depleted of barium. The glass away from the crystals shows intermediate barium concentration.

No polishing scratches or leaching of any of the phases was observed on any of these samples using the dry polishing technique; however, some polishing relief was present. Figure 5 shows a topographical backscattered electron micrograph along with the corresponding compositional backscattered electron micrograph of Sample 3. The crystalline phase is harder than the glassy phase, and as a result is raised slightly with respect to the glassy matrix. For comparison, Sample 3 was also polished by conventional polishing techniques. Figure 6 shows the extensive leaching that results. The glassy

phase, and the equiaxed crystals in the areas between the acicular crystals have been leached out.

The dry polishing technique is applicable to non-water soluble glass ceramics also. Figures 7a and 7b show the microstructure of a non-water soluble zinc silicate glass ceramic prepared with dry polishing (7a) and conventional diamond polishing (7b). The conventionally polished sample has been etched in an HF-H₂SO₄ vapor, while the dry polished sample has not been etched. Some of the definition of the structure has been enhanced in the scanning electron micrographs as a result of polishing (7a) and etching (7b) relief.

As mentioned previously, alumina particles can stick to the surface both individually and as agglomerates. Although ultrasonically cleaning in Freon eliminates most of these particles, any remaining particles can add an artifact aluminum signal to the x-ray energy dispersive spectrum. This signal can be eliminated by utilizing B₄C powders as the polishing agent. The B₄C powders are currently under investigation as to applicability and also to determine polishing parameters. 1000 grit SiC paper is also being evaluated as a possible final grinding step.

CONCLUSIONS

1. The dry polishing technique is an excellent method for preparing metallographic samples of both water soluble and non-water soluble glass ceramics.
2. Care must be taken to remove all the polishing powders from the surface after polishing.
3. Some relief polishing occurs on the glass ceramics; however, this tends to enhance the quality of topographical scanning electron micrographs.

FIGURE CAPTIONS

- Figure 1. Electron micrograph of Sample 1 showing spherulitic grains.
(dry polishing)
- Figure 2. Electron micrograph of Sample 2 showing spherulitic and radial crystallization. (dry polishing)
- Figure 3. Electron micrograph of Sample 3 showing the maltese cross pattern of acicular crystallization. (dry polishing)
- Figure 4. Electron micrograph of Sample 4 showing isolated crystals in the glass matrix. (dry polishing)
- Figure 5. Electron micrograph of Sample 3 utilizing standard polishing techniques resulting in extensive leaching.
- Figure 6. Electron micrograph of Sample 3 showing the topography produced with dry polishing technique.
- Figure 7. Electron micrograph of a non-water soluble sample (Sample 5) polished by the dry technique (7a) and standard polishing technique (7b).

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TABLE I

Composition of Glass Ceramics Investigated

<u>Sample</u>	Na ₂ O	BaO	Al ₂ O ₃	P ₂ O ₅	ZnO	SiO ₂	Mo, MO ₂ *
1	40	10	-	50	-	-	-
2	40	10	1	49	-	-	-
3	34	15	2	49	-	-	-
4	27	20	3	50	-	-	-
5	-	-	9.5	2.5	32.2	46.2	9.4

*Grouped metal and alkaline earth oxides

Figure 1. Electron micrograph of Sample 1 showing spherulitic grains. (dry polishing).

Figure 2. Electron micrograph of Sample 2 showing spherulitic and radial crystallization. (dry polishing).

Figure 3. Electron micrograph of Sample 3 showing the maltese cross pattern of acicular crystallization. (dry polishing)

Figure 4. Electron micrograph of Sample 4 showing isolated crystals in the glass matrix. (dry polishing)

Figure 5a. Topographical backscattered electron micrograph of Sample 3 prepared using the dry polishing technique resulting in slight polishing relief.

Figure 5b. Compositional backscattered electron micrograph of Sample 3 prepared using the dry polishing technique resulting in no leaching of the sample.

Figure 6a. Electron micrograph of Sample 3 prepared using the dry polishing technique with no leaching occurring.

Figure 6b. Electron micrograph of Sample 3 prepared using conventional polishing techniques resulting in extensive leaching of the sample.

Figure 7a. Electron micrograph of non-water soluble sample (Sample 5) prepared using the dry polishing technique.

Figure 7b. Electron micrograph of non-water soluble sample (Sample 5) prepared using the conventional diamond polishing techniques.

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