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Whisker Reinforced Glass Ceramic

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Prepared by

D. A. Hirschfeld and J.J. Brown, Jr.

Materials Technologies of Virginia

1872 Pratt Drive

Blacksburg, Virginia 24060

(540) 231-5082 (f) 231-3327

Prepared for

U.S. Department of Energy

1000 Independence Ave., SW

Washington, D.C 20585

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Introduction

The process for making an in-situ whisker reinforced glass-ceramic that is up to 1.5 times as strong as conventional glass-ceramics was developed at Virginia Tech and patented in 1993. This technology has been identified as having commercial potential for use in high temperature heat exchanger applications for the electric power generation field by the National Center for Appropriate Technology (NCAT). This technology was licensed by MATVA, Inc., a small Virginia business, for further development. In particular, the goal of this project was to develop a property database and conduct initial testing of heat exchanger prototypes to demonstrate its potential application.

This final report describes how the glass precursor was formed, physical properties of the glass-ceramic, techniques for making heat exchanger prototypes.

I. Glass Powder Formation

The traditional production of glass-ceramics begins by forming a glass of suitable composition and shape which is then heat treated to form a primarily crystalline ceramic. A similar procedure was followed for the production of in-situ whisker reinforced glass-ceramics by first making a modified β -eucryptite glass. It was decided to make a glass powder which could be cast or pressed into the appropriate shape then

The preparation of glass powder for this research was originally subcontracted to Ferro Corporation. Test melts were conducted by Ferro to determine the optimum glass melting/processing conditions. Ferro was contracted to prepare a 50-pound batch of single phase $\text{Li}_{0.41}\text{Mg}_{0.035}\text{AlSi}_{0.48}\text{P}_{0.52}\text{O}_4$. This was to be accomplished by homogenizing appropriate amounts of the raw materials--aluminum hydroxide hydrate, silicic acid, ammonium dihydrogen phosphate, magnesium sulfate, and lithium carbonate. This mixture was then to be fired up to 1050°C to produce the single phase material. This material was to be mixed with 8 wt% TiO_2 and melted at 1620°C for an appropriate period of time to produce a homogenous glass melt. After heating, the glass was to be water quenched and milled to produce glass powder with an average particle size of approximately 10 μm .

Due to the configuration of the small quantity melting operation at Ferro, it was not possible for Ferro to melt this glass. The problems encountered were centered around the fact that the batch had to be heated in one furnace up to around 1000°C and then transferred to the high temperature furnace which was idled at or above this temperature. It was initially anticipated that a platinum crucible could be used for the melting vessel. However, the aluminum metaphosphate used in the batch reportedly reacted and penetrated the platinum crucible. Other crucible materials were tested, but none reportedly possessed both the thermal shock resistance and the corrosion resistance required. Therefore, after many attempts to melt this batch, Ferro determined

that they could not provide this glass to MATVA in the 50-pound quantity requested.

Melting of small quantities of this glass was accomplished in a DelTech box furnace under the Virginia Tech contract. Appropriate amounts of the reagents (lithium carbonate, magnesium carbonate, ammonium phosphate-monobasic, silicic acid, titania, and aluminum hydroxide) were mixed and ball milled for several hours. The resulting mixture was placed in a refractory crucible and heated to 1620°C for 3 hours. The resulting glass melt was next either furnace cooled to form a partially crystallized, opaque material or quenched into a water bath forming a translucent, glassy material.

In order to compare samples made from translucent material with that made from opaque, samples formed by each method were ball milled to -325 mesh and then dry pressed and heat treated under the same conditions. The SEM micrographs of the fracture surfaces of the two types of samples mentioned above are shown in Figure 1. As can be seen in these micrographs, the morphologies of the fracture surfaces appear to be quite similar. Density measurements (using Archimedes method) reveal that the densities of these two types of samples are also very similar. The average densities were 2.20 g/cc for the bars made from the quenched glass powder and 2.30 g/cc for the bars made from the slow cooled (opaque) material. These values were obtained on pieces broken from the two different types of bars.

Since there were no significant differences between the morphology, density, or phases present between the bars made from the glass melt quenched into water and the glass melt which was slow cooled, the slow cooled glass melt powder was chosen to prepare the bar samples for the mechanical property characterization.

II. Sample Preparation Techniques

Bar samples were prepared by filter casting and dry pressing as described below. Samples were prepared from the glass melt which was slow cooled and from the quenched glass (both completely translucent and partly opaque groups). The results of the density and microstructural analysis of each glass melt and bar preparation method is listed below as well.

The ground material from the glass melt which was slow cooled in the furnace was used to make bars using both the filter casting process and by dry pressing. The objective of this segment of the research was to determine if there were any differences in the density and microstructure of samples prepared by these two methods.

a.)

b.)

Figure 1. SEM micrographs of a) bars made from quenched material versus b) bars made from unquenched material

A. Filter Casting Process

A slurry filtration apparatus for preparation of bar samples was constructed. This apparatus was used to prepare rectangular cross-section glass-ceramic bars, 10mm x 10mm x 40mm, to be used for mechanical property testing.

This apparatus is shown schematically in Figure 2. It consists of two parallel and perpendicular glass plates arranged to form a rectangular cavity approximately 11mm x 11mm x 44mm. This will allow the 10% shrinkage expected on drying and firing of the glass-ceramic powder compact to form a 10mm x 10mm x 40mm sintered bar. The glass plates were epoxied at the edges to form the required rectangular cross-section and a stiff wire mesh screen was epoxied at the bottom. This wire mesh screen served as the mechanical support for the filter residing on top of the screen. The acetone/alcohol-glass powder slurry is poured into the top of the apparatus. The fluid portion of the slurry drains through the filter paper depositing the glass particles. The glass side walls were lightly lubricated to allow separation of the sample from the wall during drying. In this fashion, a glass-ceramic bar compact was to be produced.

During the casting process, the particles depositing upon the filter paper plugged off the holes. The result was that after a short period of time, the solution was no longer able to flow through the filter paper and remained above it. The larger particles obviously settled out first as the solvent evaporated from the top of the filter casting setup.

This most likely results in a segregation of the particle size as a function of distance through the bar (a highly undesirable situation). This may have contributed to the cracks which appeared upon drying in some of the samples.

In order to alleviate this problem, a vacuum system was incorporated to try to draw the fluid through the filter paper more efficiently. A roughing pump was connected by a tube to the glass collection vessel which in turn was connected by a tube to the bottom of the filter casting apparatus. This did not produce significantly improved results as the filter paper still became plugged with the fine particles and the removal of fluid ceased. Variations in the solids content and acetone/alcohol ratio did not improve the results significantly.

The samples produced were sintered at 1200°C for 24 h. The resulting bulk density averaged 2.18 g/cc. The resulting microstructure is shown in Figure 3. This SEM micrograph of the fracture surface shows many large pores are present. These are most likely due to the inability of the filter casting process to produce dense and uniformly distributed particle sizes in the cast bars.

Figure 3.3 Slurry filtration process.

Figure 2. Schematic of the slurry filtration apparatus
(after Figure 3.3, ref. 1)

Figure 3. SEM micrograph of fracture surface of samples sintered at 1200°C

B. Dry Pressing Process

For the dry pressed bars, the powder was mixed with approximately 10 wt% methocel and an equal amount of water and pressed under a load of 10,000 lb. The bars were dried and calcined up to 600°C to remove the water and binder and then fired at 1200°C for 24 h (along with the filter cast bars). The resulting bulk density of these bars was 2.18 g/cc. Many small pores were formed due to the burnout of the binder. Additional samples were prepared with 1% binder and an equal amount of water and fired under the same schedule. The measured bulk density for these samples was 2.35 g/cc. The SEM micrograph of the fracture surface for these samples is shown in Figure 4.

C. Comparison of Processes

X-ray diffraction analysis was performed on bars formed by the filter cast and dry pressed processes. Small samples were broken from each of these and ground before x-raying. The x-ray patterns for each of these two were almost identical. The major crystalline phases were β -eucryptite (with the peaks slightly shifted) and rutile. There was also a small amount of an unidentified crystalline phase. A small broad amorphous-like hump also appeared in the patterns for both materials indicating that a significant amount of a glassy phase may still be present in the samples. It is not clear if this is part of the original glassy phase that has remained uncrystallized or if the sintering temperature used was slightly above the solidus in this system. Additional samples were prepared and heat treated for a longer period in the maximum nucleation temperature range which is reportedly around 740°C. These samples were then heat treated at 1040°C (reportedly the maximum crystallization rate temperature) or 1200°C.

Comparison of the bulk densities for the filter cast bars and the dry pressed bars reveals that higher densities can be achieved by dry pressing. Also, since the filter casting process results in particulate sedimentation and solution evaporation after the filter becomes plugged with particulate matter, a large variation in the particle size distribution as a function of depth is expected. The phases formed as determined by x-ray diffraction for bars made from the two methods are identical.

III. Physical Properties of Whisker-Reinforced Glass-Ceramic

A. Mechanical Property Testing

100 bar samples for the mechanical property testing were prepared by heating the glass melt constituents to 1620°C for 3 h, after which the glass melt was cooled at the maximum furnace rate in the refractory crucible. After cooling, the material (which was opaque and was at least partially crystallized) was removed from the fireclay crucible and ball milled to -325 mesh. This powder was mixed with appropriate amounts of binder and water and dry pressed into

Figure 4. SEM micrograph of fracture surface of samples with 1% binder

bars under a load of approximately 10,000 lb. The bars were dried overnight in a drying oven at approximately 90°C. The bars were then calcined slowly up to 600°C to remove the organic binders. After this, the bars were heated to 700°C for 4 h and subsequently at 1040°C for 4 h. A photograph of the resulting 100 bars is shown in Figure 5.

The phases detected by x-ray diffraction were (for representative samples) primarily β -eucryptite and rutile. The measured bulk density was approximately 2.35 g/cc.

The room temperature flexural strength (Modulus of Rupture - MOR) and modulus of elasticity were determined by breaking 48 samples (10mm X 10mm X 40mm) in a 3-point bend fixture with a span of 30mm. The average flexural strength was 27.5 MPa with a range of 14.09 MPa to 43.29 MPa. The Weibull Modulus was 5.49 with a characteristic strength of 29.81 MPa. A Weibull plot of the probability of failure versus strength is shown in Figure 6. The average elastic modulus as calculated from the load and displacement of the 3-point bend tests was 16.7 GPa. Table 1 lists data from the 49 samples. A typical fracture surface is shown in Figure 7.

B. Thermal Properties

The thermal expansion to 775°C was determined using a differential dilatometer. The average coefficient of thermal expansion over this temperature range is $2.44 \times 10^{-6}/^{\circ}\text{C}$. Expansion as a function of temperature is shown in Figure 7 and average coefficient of thermal expansion (α) is shown in Figure 9.

The thermal diffusivity was determined at room temperature using the laser flash technique at the Virginia Thermal Physical Properties Laboratory. The thermal conductivity is calculated using this equation:

$$k = a_t r C_p$$

where k is the thermal conductivity, a_t is the thermal diffusivity, r is the density, and C_p is the heat capacity. The thermal diffusivity for a section of an MOR bar was $0.004 \text{ cm}^2/\text{sec}$, the heat capacity was $0.849 \text{ joules/g}^{\circ}\text{C}$, yielding a thermal conductivity of $0.0102 \text{ w/m}^{\circ}\text{K}$.

Figure 5. β -eucryptite bar sample for mechanical property testing

Figure 6. Weibull plot of probability of failure versus strength

**Table 1 - MOR and Elastic Modulus of Whisker-Reinforced
Glass-Ceramic**

Bar #	Load (kN)	Displacement (mm)	MOR (MPa)	Elastic Modulus (GPa)
1	0.91	0.27	41.00	1.57
2	0.45	0.12	20.34	1.75
3	0.53	0.15	23.85	1.64
4	0.66	0.16	29.75	1.92
5	0.44	0.11	19.89	1.86
6	0.42	0.17	18.90	1.15
7	0.64	0.23	28.94	1.30
8	0.44	0.18	19.76	1.13
9	0.49	0.16	21.96	1.42
10	0.56	0.21	25.07	1.23
11	0.62	0.18	27.68	1.59
12	0.58	0.17	26.01	1.58
13	0.58	0.16	25.97	1.67
14	0.65	0.17	29.12	1.77
15	0.61	0.18	27.41	1.57
16	0.31	0.11	14.09	1.32
17	0.58	0.19	26.10	1.42
18	0.57	0.17	25.56	1.55
19	0.95	0.20	42.57	2.20
20	0.41	0.15	18.63	1.28
21	0.61	0.15	27.45	1.89
22	0.49	0.11	22.01	2.06
23	0.77	0.19	34.70	1.88
24	0.63	0.16	28.53	1.84
25	0.77	0.22	34.74	1.63
26	0.67	0.19	30.06	1.63
27	0.58	0.15	26.06	1.79
28	0.56	0.17	25.16	1.53
29	0.96	0.20	43.29	2.23
30	0.61	0.16	27.50	1.77
31	0.65	0.15	29.34	2.02
32	0.69	0.18	30.96	1.77
33	0.58	0.17	26.10	1.58
34	0.65	0.17	29.39	1.78
35	0.76	0.21	34.07	1.67

Bar #	Load (kN)	Displacement (mm)	MOR (MPa)	Elastic Modulus (GPa)
36	0.73	0.22	32.76	1.54
37	0.68	0.18	30.69	1.76
38	0.60	0.17	26.96	1.64
39	0.61	0.15	27.41	1.88
40	0.70	0.20	31.50	1.62
41	0.66	0.15	29.84	2.05
42	0.50	0.13	22.59	1.79
43	0.57	0.15	25.43	1.75
44	0.58	0.16	26.15	1.69
45	0.53	0.15	24.03	1.65
46	0.58	0.19	25.88	1.40
47	0.58	0.16	25.88	1.67
48	0.83	0.23	37.26	1.67
49	0.46	0.13	20.66	1.64

Figure 7. Typical fracture surface

Figure 8. Expansion as a function of temperature

Figure 9. Average coefficient of thermal expansion (alpha)

IV. Heat Exchanger Prototype Production and Evaluation

A. Glass Casting Technique

An attempt was made to melt the β -eucryptite material in a large fireclay crucible at 1620°C and cast a heat exchanger tube. The casting rig was prepared by mixing a fine grained sand with water and casting into a previously prepared box mold with a 4-inch PVC pipe at the center. After vibrating the thixotropic mixture to remove entrapped air, the sand was allowed to dry for several days. A heating tape was applied and the mold was subsequently heated at approximately 70°C for one week to ensure complete removal of all the water. The PVC pipe was then removed. The inner core was made by sawing, sanding, and fitting refractory bricks into a 3.5-inch diameter by 12-inch high cylinder. A paste was prepared by using -400 mesh ground brick. The paste was applied to this cylinder to seal any pores present in the bricks. After application and drying, the paste was sanded to produce a smooth, pore free surface on this cylinder. In the center of the cylinder a one-quarter inch diameter hole was drilled and an alumina tube was inserted to maintain alignment and structural integrity during the casting process. This cylinder was placed inside the mold described above, producing a hollow cylindrical cavity with a 4-inch O.D. and a 3.5-inch I.D. This rig was then positioned next to the Deltech furnace used for melting the glass. The glass melt was to be heated to 1610°C. After several power interruptions (due to controller intervention) the furnace returned to 1580°C and it was decided that the crucible should be removed and the glass cast at this point. Unfortunately the glass melt penetrated the fireclay crucible before the casting could be attempted. Additional trials were made with limited success. Bar samples for heat exchanger testing were made using this technique.

Several melts of the modified β -eucryptite glass were prepared and cast into stainless steel molds. The glass was melted at 1620°C for 3 h in fireclay crucibles (using an outer crucible lined with alumina powder for protection). After this period of time, the crucible was removed from the furnace and the glass poured into a stainless steel mold with internal cavity dimensions of approximately 0.5" x 4" x 12". The poured glass sample was allowed to cool in the stainless steel mold overnight. During the cooling period, the sample shattered into many large chunks. This process was attempted several times, but without satisfactory results.

Several other methods were attempted to keep the glass bars from shattering, including preheating the molds to approximately 100°C. Unfortunately, none of the methods attempted produced a viable way to prepare the glass bars in the metal mold without significantly modifying the chemical composition.

Examination of the pieces of the glass bars showed that there were a large number of tiny gaseous inclusions. These gaseous inclusions suggested that the fining of the glass had been insufficient. One strategy to help reduce the

number of these gaseous inclusions is to raise the melting temperature or increase the length of the melting time. Unfortunately, the fireclay crucibles which were used softened significantly during the 1620°C/3 hr firing as shown in Figure 10. The crucible on the right became oval shaped when grabbed by the glass tongs during removal. All crucibles had to be removed by grasping the outer porcelain crucible. Therefore, increasing the melting temperature or length of heating time was not a viable option.

Another method to reduce the number of these gaseous inclusions is to add a small amount of a fining agent to the melt. Arsenic, sodium sulfate, sodium nitrate, sodium chloride, etc., are common addition to help control seeds in commercial glass melting operations. Sodium chloride was added to the β -eucryptite glass melt to try to aid fining. The glass bars made with this salt still shattered but had a much lower number of seeds present (almost seed free).

The shattering problem was presumed to be caused by the residual stresses which were developed during the rapid cooling of the glass in the metal molds. Preheating the metal molds to 100°C was not enough to reduce the thermal shock sufficiently. In an attempt to alleviate this problem, a refractory mold was prepared. This was accomplished by making a cavity in a refractory brick approximately 1" x 1" x 6". The glass was melted according to the same schedule listed above and poured into the refractory mold. Some outgassing of the refractory occurred, producing large inclusions in the bottom surface of the bars. Also the glass penetrated to a small extent into the large pores present in the refractory. This made removal of the bar impossible without destroying the refractory mold.

In order to alleviate these problems, the refractory was lined with a fine alumina powder such that it filled all of the large pores in the refractory and formed a relatively flat surface. This was accomplished by mixing the alumina powder with acetone and forming a paste. The paste was then applied to the refractory in a fashion similar to puttying walls. The paste was allowed to air dry (in some cases the bricks were placed in a drying oven). After air drying, the alumina powder coating remained adherent to the sides of the refractory brick well enough to allow pouring of the glass melt into the mold. Zirconia powder was also used in a similar fashion to the alumina powder. Both seemed to perform equally well. Several bars were poured using this procedure.

B. Casting of Heat Exchanger Tubes

Experiments were conducted to determine if the 12" x 4" diameter heat exchanger tubes could be made by casting the β -eucryptite material in plaster of paris molds. Small cylindrical test molds were prepared and used to slip cast small cylinders and tubes. This will allow determination of whether it is feasible to prepare the larger diameter tubes by this method. Initial results on small tubes were not encouraging so this procedure was discontinued.

Figure 10. Refractory crucibles after glass melting

An alternative method of preparing the heat exchanger tubes was attempted by casting a thixotropic paste. A casting rig was prepared by fixing an inner and outer PVC tube such that a three-eighths inch cylindrical cavity existed between the two. The glass melt powder was ground for several days to -400 mesh. This material was mixed with the appropriate amount of binder and water to form a thixotropic paste. The material was added to the casting rig and vibrated for approximately one hour to remove entrapped air. A second casting rig was prepared and the procedure repeated. The cylinders were allowed to dry for one week at room temperature. After this period of time a heating tape was applied to the outside of the PVC pipe and the rig heated to approximately 70°C for one week. The heat was then raised to approximately 100°C for one month. The heating tape was moved further towards the bottom of the tube and will be left there for a month. At this point, one cylinder was dried and crumbled apart as the PVC pipe was removed. The second cylinder was not completely dry after 3 months. This technique has also been abandoned.

C. Heat Exchanger Testing

Two coupons were prepared by casting the molten beta-eucryptite glass into refractory molds as described previously. The bars prepared in this fashion were cut on a diamond saw and polished. The as-cast and polished bars are shown in Figure 11. The polished bar was then cut into 3 sections. Two of these sections were sent to EERC to be included in their heat exchanger testing.

Figure 11. Glass melt cast into refractory bar molds

References

1. *Synthesis and Characterization of In-Situ Whisker Reinforced Glass Ceramic*, Kyoung-ho Lee, Ph.D. Dissertation, Virginia Polytechnic Institute and State University, 1993.

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