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Melt-Processing of Lunar Ceramics

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Abstract

The goal of this project is to produce useful ceramics materials from lunar resources using the by-products of lunar oxygen production processes. Emphasis is being placed on both fabrication of a variety of melt-processed ceramics, and on understanding the mechanical properties of these materials. Previously, glass-ceramics were formed by casting large glass monoliths and heating these to grow small crystallites. The strengths of the resulting glass-ceramics were found to vary with the inverse square root of the crystal grain size. The highest strengths (>300 MPa) were obtained with the smallest crystal sizes (<10 μm).

During the past year we continued to examine the kinetics of crystallization in simulated lunar regolith, in an effort to optimize the microstructure and, hence, mechanical properties of glass-ceramics. We also examined the use of solar energy for melt-processing of regolith, and successfully produced strong (> 630 MPa) glass fibers by melt-spinning in a solar furnace. A study of the mechanical properties of simulated lunar glasses was completed during the past year. As on Earth, the presence of moisture was found to weaken simulated lunar glasses, although the effects of surface flaws was shown outweigh the effect of atmospheric moisture on the strength of lunar glasses. The effect of atmospheric moisture on the toughness was also studied. As expected, toughness was found to increase only marginally in an anhydrous atmosphere.

Finally, our efforts to involve undergraduates in the research lab flourished this past year. Four undergraduates worked on various aspects of these projects; and two of them were co-authors on papers which we published.



I. Introduction

While propellant manufacture is one key driving force behind development of indigenous space materials utilization technologies, a variety of solid products - for bricks, pipes, windows, containers, and insulation -- will be needed as well. Since the Moon is composed principally of oxide ceramics, this project is concerned with the development of ceramic processing techniques for making simple, useful materials on the Moon, using indigenous resources. And since it is likely that production of oxygen will provide the main impetus for in-situ materials use on the Moon for some time, a further goal of this research is to develop processes which use the by-products of oxygen production schemes as starting materials.

This project is divided into two main components. In our *processing* effort we are concerned with producing, and then optimizing the mechanical properties of glass-ceramic tiles and bricks. In our *scientific* effort, we are working to understand the relationships between structure, and properties of lunar ceramics. Of course, these activities are not independent, as it is the understanding of the interplay between structure, processing, and final properties which will ultimately allow us to produce a variety of high-quality products on the Moon, using indigenous resources. Our current goal, however, is to produce prototypes of simple, useful products, and to lay the groundwork of scientific knowledge, upon which future, advanced development of lunar ceramics can be based.

In the first two years of this program facilities for melting and casting glasses were set up, the effects of common lunar impurities on the rheological properties of glasses were determined qualitatively, glass-ceramics were fabricated, and the effect of grain size on these materials was investigated. During the past year we examined melting of lunar regolith in a solar furnace, and successfully fabricated glass fibers by melt-spinning in a solar furnace. We also conducted a relatively detailed study of the effect of moisture on the strength and toughness of lunar glasses. These accomplishments are discussed in detail in the following pages. Our success in involving undergraduates in these activities is also described, and our plan for future work is presented in the final section.

II. Processing

A. Monolithic glasses and Glass-Ceramics

In previous reports we discussed the production of monolithic glasses and glass-ceramics by melt casting. These activities continued during the past year, using the compositions shown in Table 1. For examining glass-ceramics, we concentrated on two compositions, A14 and A16, representing the average compositions of the regolith at the Apollo 14 and 16 landing sites. Glass fibers were spun using Minnesota Lunar Simulant (MLS), and monolithic glasses were cast using a composition similar to that of lunar rock sample 14049, returned on Apollo 14.

Table 1. Composition of Lunar Simulants used for Glass and Glass-Ceramic Production (in wt%)

Component	Glass-Ceramics		Glasses	
	A14	A16	Monolithic	Fiber*
SiO ₂	48.1	45.1	49	43.9
Al ₂ O ₃	17.4	26.8	17	13.7
MgO	9.4	5.7	11	6.68
FeO	10.4	5.4	10	13.4
CaO	10.7	15.6	8.9	10.1
TiO ₂	1.7	0.6	1.7	6.32
Na ₂ O	0.7	0.43	0.85	2.12
K ₂ O	0.55	0.14	0.53	2.81
Cr ₂ O ₃	0.23	0.11		
MnO	0.14	0.22		
Fe ₂ O ₃				2.6

*MLS Simulant

B. Solar Heating of Regolith

For materials processing on the Moon solar energy might provide a convenient source of heat, especially if it can be used directly, without conversion to electrical power. While the rate of heating and processing temperature can be difficult to control using direct solar heating, careful control of these parameters is not generally critical for melt processing. Thus, during the past year we began to examine the use of direct solar heating for melt processing of lunar ceramics.

For small samples other researchers have shown that solar heating is a convenient way to melt, and even to volatilize, lunar simulants. For larger samples, necessary for forming useful materials, however, it is difficult to melt an entire charge, since the melt is opaque (as a result of the high concentration of iron in the regolith) and it is, therefore, an effective thermal insulator at the high temperatures necessary for melt processing. As a result, it is not uncommon for the top layer of a glass charge to be completely molten, while the inside of the charge remains relatively unaffected by even an intense solar beam.

To examine this problem we melted samples of MLS in an alumina crucible, using the UA Solar Furnace. We used optical pyrometry to determine the temperature across the surface of a 5 gr charge. The regolith in the center of the crucible, directly under the solar beam, melted readily. As shown in *Figure 1a*, the sample temperature approached 2500 °C in this region. Outside of the direct solar spot, however, the temperature dropped off rapidly, and near the edge of the crucible (only 15 mm from the center) the temperature was well below the solidus temperature of the simulant. By scanning the beam across the sample the entire surface could be melted, but the opaque melt retarded heat transfer into the sample and, as shown in *Figure 1b*, only the top 2 mm was melted.

To melt large samples fully using direct solar heating a crucible with a high thermal conductivity might be used to transport heat to the bottom of the charge. Switching to a graphite crucible, for example, increased the size of the charges which we could melt in the UA Solar Furnace. This approach is likely to provide only minimal improvement for melting extremely large samples, however, as heat transfer to the center would still be difficult. Alternatively, some kind of mechanical mixing might be used, although the mixer itself would have to be stable under the solar beam. After trying several approaches, we found that spinning the melt using an externally driven motor worked well. This allowed us to use any crucible material, as well as providing a convenient way to produce glass fibers, as described in the next section.

C. Melt-Spun Fibers

Thin, short glass fibers have a number of potential uses on the Moon. They could be fused into bricks, or bonded into mats to make materials for thermal insulation; and if polymers are developed on (or transported to) the Moon, glass fibers could be used for reinforcements in polymer matrix composites. Other researchers have shown that individual fibers can be pulled from melts of lunar glass. For practical applications, however, continuous or large batch processes are more attractive. Thus, we examined melt-spinning for making large batches of short, thin fibers during the past year.

Melt-spinning on Earth is a well established technology, wherein molten glass is fed into a hollow "spinner" with holes on the sidewalls. The spinner rotates rapidly, causing the melt to ride up the walls and out, via centripetal force, through the holes. On Earth, jets of hot air blow the glass streams outside of the spinner into even finer fibers, which are then coated with an organic solution to protect the surface from damage.

To adapt this process to the Moon we drilled holes in a graphite crucible, mounted the crucible in a holder attached to a variable speed motor, and placed the entire assembly in a collection can which was set in the UA solar furnace, as shown schematically in *Figure 2*. The crucible was filled with approximately 3 gr of MLS, exposed to the sun, and spun. Once spinning began the entire charge melted rapidly (without spinning only the central portion, directly under the beam, melted, as discussed in the previous section) and fibers were extruded out of the holes into the collection can. As shown in the optical micrograph in *Figure 3*, fibers up to approximately 10 cm long were formed. The diameters of the fibers varied from less than 30 μm to over 100 μm , as shown in the SEM micrographs in *Figure 4*. This variation was probably due to degradation of the holes in the graphite crucible, which oxidized readily, during heating in air.

We are currently characterizing the mechanical properties of the melt-spun fibers. Preliminary indications are that the fibers are extremely strong. As shown in *Figure 5*, a 16 μm diameter fiber could be bent, 180°, with a radius of curvature of less than 3 mm. This corresponds to a stress of over 600 MPa (tension) within the fiber.

III. Mechanical Properties

A. Glass-Ceramics

As in previous years, the mechanical properties of glass-ceramics were studied by cutting disks, approximately 3 cm in diameter by 2 mm in height from larger cast glass pucks, heat treating the disks using different schedules (shown in Table 2) and breaking the resulting glass-ceramics using a ball-on-ring test jig.

Table 2: Heat treatment schedules for fabricating Glass-Ceramics

Schedule	Nucleation		Crystal Growth	
	Temperature	Time	Temperature	Time
A	720 °C	1 hrs	940 °C	3 hrs
B	750 °C	3 hrs	900 °C	1 hrs
C	800 °C	3 hrs	950 °C	2 hrs
D	800 °C	3 hrs	1050 °C	2 hrs
E	800 °C	3 hrs	1000 °C	2 hrs
F	800 °C	4 hrs	1000 °C	2 hrs

The strengths of samples A14 and A16, heated according to the schedules shown in Table 2, are summarized in *Figure 6*. When nucleated at 800 °C, the strength of sample A14 increased with crystallization temperature (schedules C, D, and E) up to 1000 °C. The highest strength (schedule

E) was 315 MPa. Increasing the nucleating time from 3 to 4 hours (schedules E and F) also resulted in an increase in strength. Increasing the crystallization temperature to 1050 °C, however, resulted in a drastic decrease in strength.

In comparison to these results for sample A14, the strengths of sample A16 were lower. We are currently examining the microstructures (using scanning electron microscopy) and phase compositions (using x-ray diffractometry) of these samples to understand the causes of the dramatic differences in strength. Since the concentrations of FeO and TiO₂ are significantly different in the two samples, we expect that both the kinetics of crystallization, as well as the phases that are formed are different. Howard Poisl has therefore fabricated samples and taken them to Johnson Space Center for Mössbauer analysis to ascertain the oxidation state of the iron, potentially a parameter issue in crystal nucleation and growth.

B. Glasses: Effect of Atmospheric Moisture on Strength

It has been suggested in a variety of symposia, conferences, and conversations throughout the ISMU community that bulk glasses might be strong and tough on the Moon. The lack of water in the atmosphere, and concomitant absence of hydrolytic depolymerization (stress corrosion cracking) is cited as the cause of this hopeful effect. While strong, tough glass would have obvious attractions on the Moon, the strength of glass is controlled, generally, by both surface flaws and stress corrosion cracking. Therefore, the relative importance of both of these strength-reducing mechanisms must be understood before structures are made from lunar glasses. Thus, we undertook a detailed study of the effects of water and surface flaws on the strength and toughness of lunar glasses this past year.

1. Theoretical Background

The strength of a glass is generally controlled by surface flaws, which increase the stress felt by a glass at the tip of the flaw. As given by the Griffith/Orowan/Irwin model, the stress, σ_{tip} , that is felt at the tip of a flaw of length c , is given by

$$\sigma_{tip} = 2s \sqrt{R \sqrt{F(c,r)}} \quad (1)$$

where s is the applied tensile stress, and r is the radius of curvature of the flaw. Since glasses are generally quite brittle (i.e., they fracture with little or no plastic deformation) very little blunting of the

crack tip occurs prior to fracture. As a result, r is generally quite small (on the order of atomic dimensions), so that even small flaws cause a dramatic increase in the stress that is transferred to the tip of a flaw. As a result, strength of a glass is reduced markedly by even microscopic imperfections.

Hydrolytic depolymerization - stress corrosion cracking - is a well-documented phenomenon that further decreases the strength of silicate glasses. This weakening is caused by a chemical reaction between the silicon-oxygen bond in the glass and the polar water molecule. It is generally accepted that this reaction occurs through a three-step process. As shown in *Figure 7*, a water molecule first adsorbs to tip of a flaw. The water molecule attaches itself to a bridging Si-O-Si bond, which is strained due to the highly concentrated stress field in the vicinity of the crack tip. Two new bonds are next formed, one between the oxygen atom of the water molecule and the silicon atom and another between a hydrogen atom of the water molecule and the network bridging oxygen atoms. In the third step the original bridging bond is destroyed, leaving two silanol groups at the surface.

This weakening process is practically unavoidable on Earth because of the ubiquitous distribution of water throughout the atmosphere. The lunar environment, however, is anhydrous. Therefore, stress corrosion cracking should not affect silicate glasses when used in engineering applications on the Moon. (An exception to this would be where glass is used within human habitats or other artificial environments that contain moisture on the Moon.)

The effects of water on the strength, s , of a glass in the presence of water can be described by,

$$s = s_0 + \frac{1}{B} \left(\frac{F}{2.3RT, V^*} \right) \log \left(\frac{F(P_0, P)}{P_0} \right) \quad (2)$$

where R is the gas constant, T is temperature, V^* is an "activation volume" (usually determined empirically), and s_0 is the initial strength of the glass under initial partial pressure, P_0 . This equation is based on the thermodynamic increase in the rate of hydrolytic depolymerization (Fig. 7) with applied stress. It predicts, correctly, that strength varies inversely with the partial pressure of water. It is important to realize, however, that water is not *necessary* for rupturing the metal-oxygen bonds that make up the glass network. A high applied stress, especially in the presence of surface flaws which intensify the stress at the crack tip, can cause fracture directly. Thus, in the absence of water, the strength does not increase without bound, as implied by Eq. 2.

2. Experimental Procedure

To examine experimentally the effects of water and flaws on the strength of simulated lunar glasses, a chemical composition similar to that of lunar rock sample 14049, returned by Apollo 14, was used (Table 1). Reagent grade oxides were mixed, melted, quenched, ground, re-melted, and cast into pucks, as described in previous reports. After annealing, the pucks were cut and polished into $3 \pm 0.06 \times 4 \pm 0.06 \times 45 \pm 1.0$ mm bars which were used for 4-point beam-bending. Controlled surface flaws were introduced to one set of bars with a Vickers indenter. The flaw size was controlled by varying the indentation load. By measuring the length of the cracks an average crack length was determined for each indentation load and relative humidity. One set of samples was etched in hydrofluoric acid to eliminate surface flaws. To simulate a glass produced and used on the Moon, some of these samples were then abraded with MLS in a ball mill.

After indentation, the bars were placed in a small oven at approximately 150°C for 45-60 minutes to eliminate any moisture that may have been present in the fresh flaws. To maintain their dry condition until they could be tested, the samples were immediately placed into a desiccator after heating. Samples that were tested under dry conditions were covered liberally with mineral oil immediately after removal from the oven and before placement into the desiccator. The oil did not exclude all moisture from the crack tips, since there was a some small amount of water dissolved in the oil. Studies in the literature indicate, however, that this of moisture has a negligible effect on the strength.

The bars were tested within one hour using a four-point beam-bending fixture in an Instron material testing system at an extension rate of 1 mm/min at room temperature. The dimensions of each specimen were measured after testing in order to increase the accuracy of the strength calculations. At least six samples were tested at each relative humidity and crack size.

3. Results

The effect of humidity on the strength of lunar glass samples, each having an average crack size of $81 \mu\text{m}$, is shown in *Figure 8*. As the humidity decreased, the strength of the lunar glass increased. The error bars on the graph indicate one standard deviation in strength for each relative humidity. The solid line in *Figure 8* is a least-squares fit of Eq.2, using V^* as the adjustable

parameter. (The best-fit of V_c was $2.78 \times 10^{-4} \text{ m}^3$. The physical basis for this value is not well understood, however, so we do not place any significance on this number.)

While the measured strengths increase as the water content decreases, as predicted by Eq. 2, the key feature in *Figure 8* is the lack of extremely high strengths, as predicted by Eq. 2, as the water content approached 0. The highest strength measured (for samples with $81 \mu\text{m}$ flaws) was 125 MPa, which occurred under nominally anhydrous conditions. As mentioned previously, this is not surprising, since fracture can occur without stress corrosion cracking, by direct rupture of the network.

The average strength of sample etched in HF is also plotted in *Figure 8*. The etched samples were much stronger than those that had been indented. The strongest sample broke at over 360 MPa, and the average strength was 205 MPa. This is over twice as strong as those samples which had been indented and tested under dry conditions without HF etching. The average strength of samples which were HF etched but then abraded in lunar simulant is also shown in *Figure 8*. Abrasion weakened the samples substantially, with strengths averaging 103 MPa for this treatment, which is similar to what glasses on the Moon will have to withstand.

Comparing the effects of water and flaws, the difference in strength between the HF etched and indented samples tested under the same (dry) conditions is much larger than the strength difference between samples measured at 0 and 100 percent relative humidity with the same flaw size. State differently, surface flaws affect the strength significantly more than stress corrosion cracking. Moreover, surface flaws are likely to be unavoidable in the lunar environment, where one is likely to find dust from human activity and the bombardment of micrometeorites.

Not surprisingly, extremely high strengths were found with melt-spun fibers, as shown in *Figure 5*. Since the largest flaws in a thin fiber can be no larger than the diameter of the fiber, the surface flaws, and, hence, stress intensification, in fibers are necessarily small. In fact, it is noteworthy that the fiber shown in *Figure 5* withstood more than 600 MPa *in air*; where, stress corrosion cracking can take place. (It should be noted, though, that these fibers must also be protected from surface flaws in order to retain their high strength.)

In summary, if lunar-derived glass is fabricated and utilized on the Moon, it will have imperfections, i.e. surface flaws, as on Earth. Regardless of the specific techniques and methods employed in the

production and handling of lunar-derived glass, surface flaws will be present. Even if flawless glasses were produced on the Moon, surface flaws would be unavoidable due to the dusty environment. Therefore, while the anhydrous conditions of the lunar surface will result in a slight increase in strength in comparison to similar glasses on Earth, the strength of lunar-derived glass will still be limited by small surface flaws, which will reduce the strength well below the theoretical value.

C. Glasses: Effect of Atmospheric moisture on Toughness

In addition to high strength, it has been suggested that the lack of water, glass will be tougher (i.e., less brittle) on the Moon because of the lack of water in the atmosphere. We examined this possibility during the past year both from simple theoretical and experimental standpoints.

The fracture toughness, K_{IC} , is defined as

$$K_{IC} = s_f \sqrt{\pi c} = \sqrt{Eg} \quad (3)$$

where s_f is the fracture strength, c is the flaw size, E is the elastic modulus and g is the surface energy of the glass. Because of the lack of vapor molecules, which adsorb onto and passify the surfaces of freshly fracture glass, it is likely that the surface energy of freshly fractured glass will be higher in an anhydrous environment than in a water-containing environment. While the increase in surface energy may be significant (a factor of two, three, or even ten), the fracture toughness varies with the square root of the surface energy, so that large changes in K_{IC} are unlikely.

To examine this effect quantitatively, we used the Vicker's indenter to produce flaws of three different sizes, and broke the samples under nominally dry, and ambient conditions. The results are shown in *Figure 9*, where the fracture strength is plotted against inverse square root of flaw size. The slope of this plot gives the fracture toughness (Eq. 3). For glass tested in ambient conditions, $K_{IC} \approx 0.7 \text{ MPa}\sqrt{\text{m}}$, which is in the range usually measured for terrestrial glasses. When tested under dry conditions, the fracture toughness increased slightly, to about $1.3 \text{ MPa}\sqrt{\text{m}}$. As demonstrated in *Figure 10*, however, this increase, is insignificant, when compared to the fracture toughness of typical steels, $\approx 50\text{-}90 \text{ MPa}\sqrt{\text{m}}$. In summary, will be brittle in the lunar environment, and tensile stresses will have be avoided in engineering applications of glass on the Moon.

IV. Undergraduate Involvement

In addition to the science and engineering components, as described above, one important goal of this project to involve undergraduates in the laboratory, and make them part of the research effort. Under the supervision of Brian Fabes (PI) and Howard Poisl (graduate student) four undergraduates (Dan Allen, Michelle Minitti, Steve Hawley, and Tony Beck) worked on this project. Their efforts were an integral part of this work. As a result, both Dan and Michelle's participated as co-authors on papers which we published during the past year.

V. Future Work

In the coming year we plan to continue to examine the kinetics and thermodynamics of crystallization in the multi-component lunar glasses, and to optimize the strength of the resulting glass-ceramics in the A14 and A16 systems. Howard Poisl will spend approximately six weeks at Johnson Space Center, where he will use Mössbauer spectroscopy to determine the coordination state of the iron in the various glasses. Dan Allen and Steve Hawley will continue to assist him in measuring crystallization rates, and to measure strengths in the crystallized glasses.

Bob Crockett, from McDonnell Douglas Corporation recently joined our group as a graduate student. Bob's expertise is in space structures. He has been in contact with Wayne Rogers (U of Co SERC) and is finishing a study of the materials issues in fabrication of structures on the Moon. In his initial investigations Bob has identified joining technologies as a critical issue in building large structures. In the coming year, therefore, Bob plans to investigate the effect of composition and processing on the elastic modulus of lunar glasses. Our ultimate goal here will be to design interface materials that can be used to bind and seal bricks, tiles, and other lunar ceramics together for large-scale structures.

