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Abstract

A variety of useful silicate materials can be synthesized from lunar rocks and soils. The simplest to manufacture are glasses and glass-ceramics. Glass fibers can be drawn from a variety of basaltic glasses. Glass articles formed from titania-rich basalts are capable of fine-grained internal crystallization, with resulting strength and abrasion resistance allowing their wide application in construction.

Specialty glass-ceramics and fiber-reinforced composites would rely on chemical separation of magnesium silicates and aluminosilicates as well as oxides titania and alumina. Polycrystalline enstatite with induced lamellar twinning has high fracture toughness, while cordierite glass-ceramics combine excellent thermal shock resistance with high flexural strengths. If sapphire or rutile whiskers can be made, composites of even better mechanical properties are envisioned.

Glasses, Ceramics, and Composites from Lunar Materials

1. Introduction

The Moon is composed primarily of a suite of basic igneous rocks of largely basaltic, gabbroic, and anorthositic types. Because of the lack of weathering and erosion, the lunar soil or regolith reflects the composition of the underlying rocks as resulting from eons of meteoritic bombardment. Both the soils and rock can be used in a chemical extraction, melting, and sintering process to manufacture a variety of glass and ceramic materials.^(1,2) This paper will be concerned with the production of glass and glass-ceramic materials from lunar basalts as well as refined glass-ceramics based on the minerals enstatite and cordierite. It will also explore the possibility of producing fiber-reinforced glass-ceramics using oxide fibers and whiskers from refined lunar materials.

2. Glass and ceramic materials based on basalt

Glasses are easily made from terrestrial basaltic compositions containing >40 wt % silica.³ Typical lunar mare soils such as high titania A11 and low titania A12 (Table 1), analyzing between 42 and 47 wt. % silica, are easily melted and quenched to form glass.

Considerable materials research and pilot scale product development was carried out at Corning Incorporated on the terrestrial tholeiitic basalt from Westfield, Massachusetts. Although this material is somewhat higher in silica and alkalis and lower in titania and iron oxides, as compared to the lunar materials, it is nevertheless generally similar in crystalline constitution and melting characteristics. Glass articles, glass fibers, and foams were all made from the Westfield basalt. High quality glass fibers of 10 mm diameter were continuously drawn from platinum spinnerets and showed good strength and chemical durability, particularly in alkaline environments. In fact, the elastic modulus of Westfield basalt glass was 90 GPa, about 10% higher than standard commercial E fiber-glass, accounting for its higher strength.

It was found that partial recrystallization of basaltic glasses could improve many properties including abrasion resistance, strength, thermal stability, and chemical durability.³ Controlled crystallization of basaltic glass requires internal nucleation. Internal nucleation can be achieved in iron-rich silicate glasses, including basalt, through the thermal precipitation of spinels of composition along the join Fe_3O_4 (magnetite)- Fe_2TiO_4 (ilvospinel). In terrestrial basalts, such as the Westfield material, fine internal precipitation of spinel close to magnetite in composition is observed when the glass made from this basalt is sufficiently oxidized. If chunks of basalt are melted in a neutral atmosphere, the resulting glass will not precipitate sufficient magnetite for efficient nucleation because the $\text{FeO}:\text{Fe}_2\text{O}_3$ ratio is too low, reflecting that of the original rock, about 2.5:1. If melted in a reducing atmosphere, no internal nucleation is achieved because FeO (wustite) is never precipitated. Instead, only surface oriented crystallization develops accompanied by pits, voids, and deformation, and useful glass-ceramics cannot be formed.

If, however, the glass is melted in an oxidizing atmosphere, or an oxidizing agent such as ammonium nitrate is added to the melt, the redox ratio in the glass is reversed with Fe_2O_3 the predominant oxide (see Table 2). Under these conditions, efficient nucleation of spinel is achieved upon reheating above the glass transition ($\sim 650^\circ\text{C}$), and, as the glass is further heated to 880°C , clinopyroxene forms on the magnetite spinel nuclei (*Figure 1*). The final percent crystallinity at this point is roughly 55.

In the case of the lunar basalts, Fe_2O_3 is not present and normal melting would occur under reducing conditions. Therefore, low titania compositions such as the A12 mare soil would not

Table 1. Composition of Typical Tholeiitic Basalt vs. Some Lunar Mare Soils

	THOLEIITIC BASALT WESTFIELD, MASS.	MARE SOILS	
		HIGH Ti (A-11)	LOW Ti (A-12)
SiO ₂	52.6	42.5	46.2
Al ₂ O ₃	14.1	13.8	13.7
TiO ₂	1.0	7.7	3.1
MgO	6.4	8.2	9.9
CaO	9.3	12.1	10.6
FeO	8.6	15.8	15.4
Fe ₂ O ₃	3.4	-	-
Na ₂ O	3.2	0.4	0.5
K ₂ O	1.2	0.2	0.3
P ₂ O ₅	0.2	0.1	0.3
Cr ₂ O ₃	<0.1	0.3	0.4
MnO	<0.1	0.2	0.2

Table 2. Oxidation State in Westfield Basalt
(1450°C-4 hrs: Electric furnace air atmosphere, covered crucible)

Form	Additions	% FeO Anal.	% Fe ₂ O ₃ Calc.	Total Iron as Fe ₂ O ₃ Anal.	Fe ₂ O ₃ to Total Iron Oxide Ratio	Grain* Size (μm) Anal.	Normative Fe ₃ O ₄ Calc.
Chunks	None	8.4	4.1	13.3	0.31	1.0	6.0
"	"	8.0	4.0	12.8	0.31	1.0	5.8
Powder	None	8.3	5.1	14.2	0.36	0.5	7.4
"	2% NH ₄ NO ₃	7.9	6.2	14.9	0.42	0.2	9.0
"	4% NH ₄ NO ₃	4.8	10.0	15.3	0.65	0.1	14.5
Powder	1% sugar	8.6	3.4	13.0	0.26	2.0	4.9
"	2% "	-	-	-	-	>100.0	-
"	4% " , 4% TiO ₂	11.4	0.7	13.3	-	~1.0	1.0

* Ceram secedule: 4hrs 650°C, 1 hr 880°C

- For effective internal nucleation, at least 5% Fe₃O₄ spinel required

- For Fe₂TiO₄ spinel nucleation in reduced basalt, at least 4% TiO₂ is required



Figure 1



Figure 2

provide sufficient nucleation to achieve a fine-grained glass-ceramic. High titania compositions such as A11, however, with 7.7 wt. % TiO_2 , do not require oxidation to form good internal nucleation because Fe_2TiO_4 (ülvospinel) precipitates on heating glasses of this composition. In fact, an experiment was recently made at Corning with reduced Westfield basalt containing 4% dextrose added to the melt. In this case, only scattered magnetite was precipitated and the grain size of the glass-ceramic when heated to 850°C was in excess of 100 μm . The resulting material was not only coarse grained but severely deformed on crystallization because of the low viscosity of the glass and longer time required to crystallize it in the absence of densely concentrated nuclei. When 4% titania was added to the Westfield basalt and it was melted under the same reducing conditions, fine internal nucleation and crystallization was achieved. The final glass-ceramic had a grain size of approximately 1 μm , did not deform and contained no voids. In this case, a solid solution of ülvospinel and magnetite (primarily the former) produced abundant spinel precipitation and internal nucleation. This result confirmed our belief that at least 4% titania is required in a reduced basalt glass to achieve fine-grained internal crystallization analogous to an oxidized glass. Table 2 shows the results of the effective oxidation state on the grain size of crystallized Westfield basalt. From these experiments with this basalt, it can be inferred that the lunar high titania soils or basalts such as A11 contain more than sufficient titania for spinel nucleation and fine-grained internal crystallization to be achieved in the glass-ceramic process. The resulting materials should have good abrasion resistance and chemical durability, abraded flexural strength at least 100 MPa, thermal expansion coefficients in the $75 \times 10^{-7}/^\circ\text{C}$ range, and thermal stability above 800°C (Table 3). These inexpensive materials could be used as construction materials, e.g., piping, tile, etc., chemically resistant ware and fibers for use in various hostile thermal and chemical environments. Figure 2 shows some glass-ceramic articles made from oxidized Westfield basalt.

Whereas the crystallization of the high titania lunar basalts is expected to be similar to that of either oxidized basalt or reduced basalt with titania additions, the glass-forming characteristics may be significantly different. Figure 3 shows the viscosity temperature curve for the Westfield basalt. This glass can be worked down to temperatures of about 1100° where the viscosity is >1000 poise. Thus, rolling and pressing as well as spinning and casting can be considered viable glass-forming techniques. Because of the lower silica content of the lunar basalt, however, the viscosity curve may be lower and perhaps rolling and gob pressing may not be feasible. Certainly casting or spinning of pipe, tableware, tiles, or spun sheet would be practical, however.

Cast basalt ceramics have been made from very fluid and rapidly crystallizing materials.⁴ Cast basalt does not require glass formation, but since the crystallization occurs directly on cooling at low viscosities, the grain size is coarse and surface pits and internal voids form from rapid shrinkage on densification. Large forms can be made with strengths somewhat better than concrete, but the materials are weak in comparison to the basalt glass-ceramics (40 MPa vs. 100 MPa in flexural strength).

3. Refined glass-ceramics

Glass-ceramics based on enstatite and cordierite can be manufactured from high magnesia glasses in the systems $\text{SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-CaO-TiO}_2$ and $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-TiO}_2$, respectively. The processing of lunar materials to produce various oxides or purified minerals necessary to serve as raw materials for these glasses have been described by Waldron.²

3.1 Enstatite glass-ceramics

Refractory, tough, and fine-grained glass-ceramics based on enstatite have been produced in the $\text{SiO}_2\text{-MgO-ZrO}_2$ and $\text{SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-Li}_2\text{O-ZrO}_2$ systems.⁵ These materials contain from 50-85 weight percent enstatite with auxiliary phases zircon, β -spodumene solid solution, minor tetragonal zirconia, and small amounts of glass. A representative composition from each system is listed in Table 4,

Table 3. Properties of Oxidized Basalt Glass-Ceramics

Mechanical

M.O.R. (abraded)	115 MPa
Young's Modulus	105 GPa
Shear Modulus	45 GPa
Poisson's Ratio	0.21
Hardness (Knoop)	850

Thermal

C.T.E. (0-300°C)	73 x 10 ⁻⁷ /°C
Annealing Temperature	850°C
Strain Point	800°C

Table 4. Enstatite glass-ceramics: compositions and properties

	E-1	E-2
SiO ₂	58.0	54.0
Al ₂ O ₃	5.4	-
MgO	25.0	33.0
Li ₂ O	0.9	-
ZrO ₂	10.7	13.0
Glass crystallization treatment	800°C/2 h 1200°C/4 h	800°C/2 h 1400°C/4 h
Phase assemblage	Enstatite (proto, clino), β-spodumene, tet. zirconia	Enstatite (proto, clino), zircon, minor tet. zirconia, cristobalite
Abraded MOR (MPa)	193 ± 15	200 ± 15
Fracture toughness (MPa m ^{1/2})	3.5 ± 0.4	4.6 ± 0.6
Refractoriness (°C)	1250	1500
CTE (0-1000°C) (× 10 ⁻⁷ /°C)	68	80

Table 5. Commercial Cordierite Glass-Ceramic (Corning 9606)

Composition		wt%	mol%	Phases
SiO ₂	} x1	56.1	58.1	Cordierite Cristobalite Rutile
Al ₂ O ₃		19.8	12.1	
MgO		14.7	22.6	
CaO		0.1	0.1	Mg-dititanate
TiO ₂	n	8.9	6.9	
As ₂ O ₃	f	0.3	0.1	
Fe ₂ O ₃		0.1	0.1	
Use: Radomes				

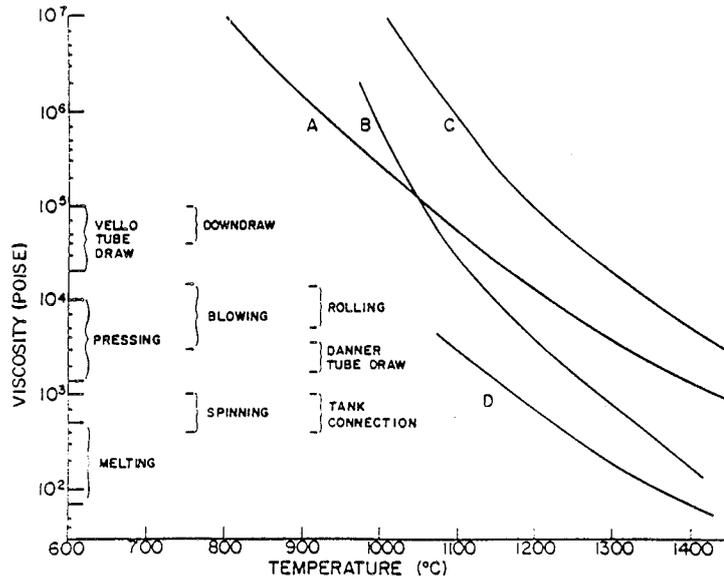


Figure 3. a) Lithium aluminosilicate glass used to make rolled sheet.
 b) Magnesium aluminosilicate glass used to make Code 9606 cordierite radomes.
 c) Lithium aluminosilicate glass used to make CORNING WARE®
 d) Westfield basalt glass.

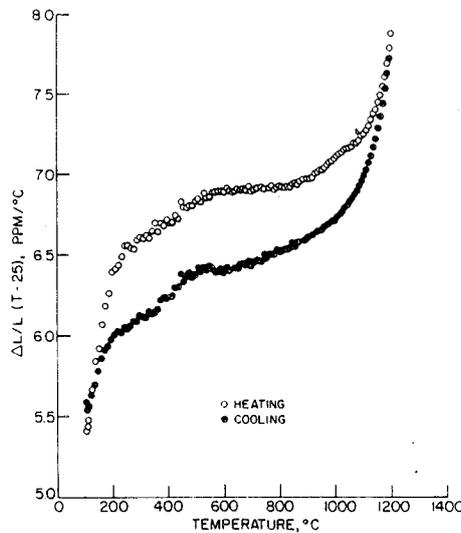


Figure 4. Thermal expansion hysteresis in enstatite glass-ceramic E-1.

along with crystallization schedule, phase assemblage, and key properties.

Enstatite is found in three structural polymorphs: orthorhombic forms protoenstatite and orthoenstatite, and the monoclinic form clinoenstatite. The structure of these polymorphs and the nature of the transformations between them have been extensively studied,^(5,6) but early efforts at applying these transformations to toughening glass-ceramics in poorly nucleated compositions were not very successful.⁶

Protoenstatite is stable above 980°C and converts to either the stable ortho or metastable clino forms on cooling. The former is a relatively slow order-disorder transition, while the latter is rapid and martensitic. Although protoenstatite has been described as nonquenchable in large crystals (≈ 1 cm) such as those found in meteorites, the fine grains typical of well-nucleated glass-ceramics (≈ 1 mm) only partially transform to clinoenstatite and retain much of the protoenstatite x-ray diffraction pattern on normal cooling from above 1000°C. Moreover, the thermal expansion behavior of enstatite glass-ceramics shows considerable hysteresis through the ortho to clino conversion (*Figure 4*). Even on slow cooling, e.g. 50°C per hour, the fine crystals form twinned clino rather than ortho, underscoring the sluggish nature of the proto-to-ortho transformation. The proto-to-clino inversion is accompanied by a 4% volume shrinkage, so toughening is not believed related to the metastable presence of the proto form in simple analogy to toughening from partially stabilized tetragonal zirconia. The actual toughening mechanism appears to involve crack deflection from the fine polysynthetic twinning, resulting from the partial transformation and possible energy absorption from the development of penny-shaped cracks along twin boundaries (see *Figure 5*). Further transformation to clino under the shear stress preceding fracture may be a possible accompanying mechanism, as suggested by hysteresis observed in stress-strain curves from these materials. Splintering due to the intersection of cleavage (110) and twin planes (100) in clinoenstatite is observed in fracture micrographs (*Figure 6*) and is also believed a factor in toughening. Fracture toughness values as high as $5 \text{ MPa m}^{1/2}$ were measured in composition E-2. The flexural strengths of enstatite glass-ceramics are also high ($\approx 200 \text{ MPa}$), in part due to their high elastic modulus ($\approx 140 \text{ GPa}$).

Although zirconia and lithia are rather rare on the Moon, enstatite glass-ceramics similar to E1 (Table 4) can be made by substitution of CaO for Li₂O and TiO₂ for ZrO₂ in roughly equivalent molar proportions. The resulting glass-ceramic has a phase assemblage of enstatite, anorthite, and rutile instead of enstatite, β -spodumene, and tetragonal zirconia. The strength and fracture toughness will be similar, but the refractoriness and the coefficient of thermal expansion will be compromised. The effect of rutile instead of zirconia in the phase assemblage will reduce the high temperature use to below 1200°C. The replacing of β -spodumene solid solution, which has a very low coefficient of thermal expansion, approximately $10 \times 10^{-7}/^\circ\text{C}$, by anorthite with a thermal expansion of $55 \times 10^{-7}/^\circ\text{C}$, will cause the thermal expansion coefficient to be increased from $68 \times 10^{-7}/^\circ\text{C}$ to about $80 \times 10^{-7}/^\circ\text{C}$.

Enstatite glass-ceramics could be pressed or cast and would find application where mechanical toughness, thermal stability, and good dielectric properties are required.

3.2 Cordierite

Glass-ceramics based on the hexagonal form of cordierite, sometimes referred to as indialite, are strong, have excellent dielectric properties, and good thermal stability and shock resistance. Corning Code 9606, whose composition is given in Table 5, is the standard glass-ceramic used for radomes. It is a multiphase material nucleated with titania, but based on a cordierite of composition $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ with some solid solution toward "Mg-beryl" (i.e., $\text{Mg}^{2+} + \text{Si}^{4+} + 2\text{Al}^{3+}$).⁷ This major phase is mixed with cristobalite, rutile, magnesium dititanate, and minor glass, which is isolated at grain-boundary nodes. The mechanical properties of these glass-ceramics have been studied



Figure 5. Replica electron micrograph of the fracture surface of enstatite- β -spodumene-zirconia glass-ceramic E-1. Twinning in the enstatite is seen to influence the fracture path; spodumene grains are smooth.



Figure 6. Fracture surface (REM) of enstatite-zircon glass-ceramic E-2 showing interlocking twinned enstatite grains and nodular zircon. Note the step splintering effect of the intersection of cleavage and twinning.

extensively.⁸ A Weibull plot of flexural strength data on transverse-ground bars hewn from a slab of this commercial composition is shown in *Figure 7*. Other important properties include a coefficient of thermal expansion (0°-700°C) of $45 \times 10^{-7}/^{\circ}\text{C}$, fracture toughness (K_{IC}) 2.2 MPa m^{1/2}, thermal conductivity 0.009 cal/s·cm·°C, Knoop hardness 700, dielectric constant and loss tangent at 8.6 GHz: 5.5, and 0.0003, respectively.

One of the difficulties in crystallization of glass-ceramics involves relieving stresses due to change in density accompanying phase transformation. This is well illustrated by Code 9606. Table 6 shows the phase assemblage and corresponding density when the parent glass is heated to various temperatures for two hours. There is a significant increase in density from glass to dense metastable crystalline assemblage up to 1010°C, followed by a volume expansion to cordierite above this temperature. Clearly, to avoid extreme stresses and cracking, the heat-treatment schedule must be carefully adjusted to minimize extremes in metastable phase density and allow sufficient plastic glassy phase at various stages to prevent cracking. The final desired assemblage developed at 1260°C has good thermal stability toward grain growth and will not revert to other phases when held at lower temperatures.

The choice of composition for Code 9606 was based primarily on glass-forming considerations. To optimize viscosity at the liquidus, the lowest ternary eutectic in the refractory system MgO-Al₂O₃-SiO₂ was approached with little compromise in the key properties of cordierite by maintaining it as the major crystalline phase. Some cristobalite had to be incorporated, which had the adverse effect of raising thermal expansion. This phase, however, allowed a post-ceram surface leaching treatment with hot caustic to be effective in producing a porous silica-deficient skin which tends to prevent mechanical flaw initiation.

The viscosity-temperature curve for the parent glass of Code 9606 appears as curve B in *Figure 4*. Because the liquidus temperature is near 1350°C, close to the ternary eutectic temperature, and the glass is relatively low in silica (58 mol %) and therefore fluid, only such forming processes as spinning or other types of casting can be used. Fortunately, the radome shape is particularly amenable to centrifugal casting, as would piping, flat slabs, and other symmetrical shapes. Cordierite-based materials would be useful on the Moon wherever thermal stability, thermal shock resistant, or dielectric materials are required.

4. Fiber reinforced glass-ceramics

Over the last decade, an intense effort to produce ceramic materials with high strain at rupture, fracture toughness values approaching metals, and graceful failure has developed. The key concept involves continuous fiber of high strength, elastic modulus and thermal stability embedded in a glass or glass-ceramic matrix. One approach which has yielded particularly promising results has been the use of polymer melt spun amorphous silicon oxycarbide fibers (Nicalon, Nippon Carbon Company) as a reinforcing agent in Corning glass-ceramic matrices based on lithium aluminosilicate (LAS) or calcium aluminosilicate (CAS) glass-ceramics.^(9,10) The achievement of high fracture toughness (~20 MPa m^{1/2}) in these brittle composite materials requires both strain tolerance to fracture and fiber pullout at rupture, thus producing a graceful failure. This requires a fiber matrix interface which is characterized both by some inherent resiliency and some inherent strength. The strength criterion is a sensitive one. The interface must be strong enough to allow load transfer from the matrix to the relatively stronger, stiffer fiber and yet not overly strong or the fiber pullout at failure will be prohibited and the composite will display the brittle behavior of normal monolithic ceramic materials.

The highest modulus oxide fibers which could be envisioned as being manufactured from lunar materials are based on alumina and titania. These oxides both have Young's moduli near 30 GPa

Table 6. Phase Assemblages during Crystallization of Glass-Ceramic 9606

Temp. (°C)	Density	Phases
700	2.64	Glass
800	2.67	Glass, MgTi ₂ O ₅
900	2.75	β-quartz ss, MgTi ₂ O ₅ , glass
1010	2.95	α-quartz, sapphirine, enstatite, MgTi ₂ O ₅ , rutile
1260	2.60	Cordierite ss, rutile, MgTi ₂ O ₅

Table 7. Lunar Glass-Ceramic Materials

<u>BASALT</u>	<u>MATERIALS</u>	<u>MANUFACTURING PROCESS</u>	<u>USEFUL PROPERTIES</u>	<u>KEY LIMITATIONS</u>
Glass	Basalt	Melt*, Fiberize	Strong Fibers	-
Glass-Ceramics	HI-Ti Basalt	Melt*, Rapid Forming (Spin, Roll, Press, Cast)	Moderate Strength, Abrasion Resistance	Brittle
Cast Ceramic	Basalt	Melt*, Cast, Slow Cool	Large Forms, Some Toughness	Weak, Pits, Voids
<u>REFINED GLASS-CERAMICS</u>				
Enstatite	Refined Pyroxene	Melt**, Rapid Forming (Press, Spin, Cast)	Strong, Tough, Dielectric	Require Purified Composition
Cordierite	MgO, Al ₂ O ₃ , SiO ₂ , TiO ₂	Melt**, Rapid Forming (Roll, Press, Spin, Cast)	Strong, Thermal Shock Resistant, Dielectric	Require Purified Composition
<u>FIBER REINFORCED GLASS-CERAMICS</u>				
	Coated Al ₂ O ₃ , TiO ₂ Fibers, Whiskers, Aluminosilicate Glass Frit	Fiber Growth, Melt Frit, Pre-Preg, HIP	Strong, Tough, Refractory, Non-Brittle	Complex Manufacturing Process

* In Fe-Cr Alloy, or In-Situ

** High-Al₂O₃ Refractory

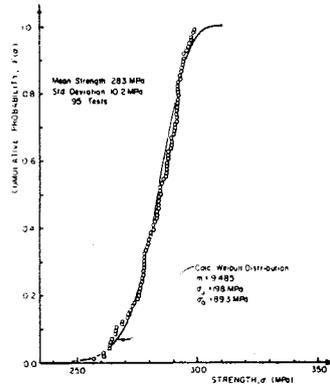


Figure 7. Flexural strength distribution of transverse ground bars of Corning Code 9606 glass-ceramic (after Lewis et al).

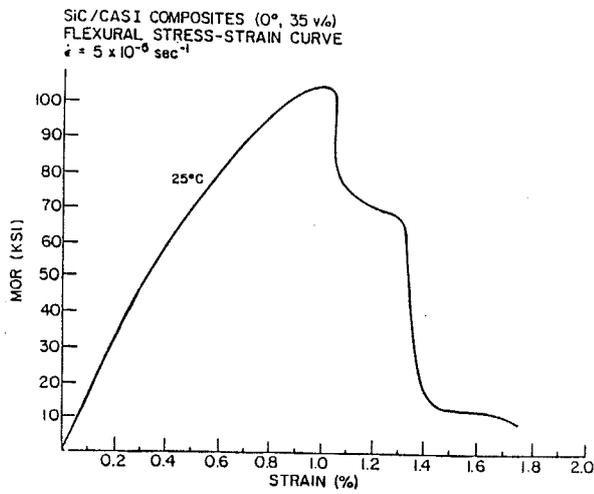


Figure 8.

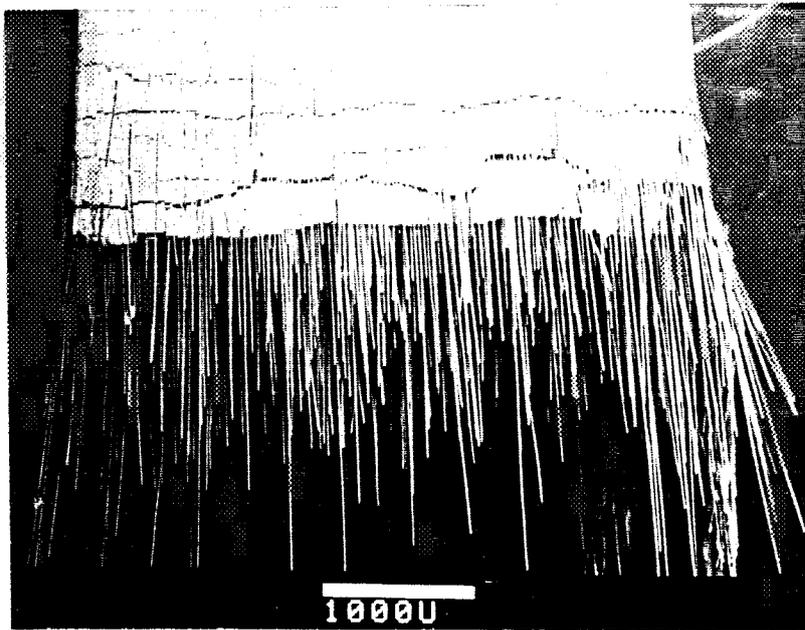


Figure 9. Non-brittle fracture mode of Nicalon®/glass-ceramic matrix composites.

and would, therefore, serve as functional reinforcement agents if the bonding between these fibers and the powdered glass used to make the composite could be intermediate in strength after the matrix is crystallized. The control of the bonding between fibers or whiskers of sapphire or rutile and a calcium aluminosilicate (anorthite: $\text{CaAl}_2\text{Si}_2\text{O}_7$) matrix has not been studied, but if measures could be taken to control the strength of this bond, a refractory and tough composite could certainly be envisioned.

Figure 7 shows a typical stress strain curve for a ceramic matrix composite with a lithium or calcium aluminosilicate matrix using about 50 percent uniaxially oriented silicon oxycarbide fibers. The process here involves coating the continuous fiber with a glass frit slurry, forming a prepreg tape, by hot isostatic pressing. During the hot pressing, the glass frit sinters and crystallizes, yielding the glass-ceramic matrix. The strain at rupture in this case, in the range of 1%, is unique among ceramic materials and reflects the fracture pullout of the fibers as depicted in Figure 8. The maximum stress is in excess of 600 MPa at 25°C and can be almost 500 MPa at 1000°C in the most oxidation resistant composites. These materials may replace superalloys in engine components. Higher use temperatures and lower densities are perceived advantages.

5. Conclusions

It is clear that a wide variety of glass and ceramic materials from simple glass to complex fiber reinforced glass-ceramics could be made using lunar materials. Their advantages and limitations are summarized in Table 7.

Basalt can be melted to a glass and subsequently fiberized or foamed to produce insulating or reinforcing components. Glass-ceramic articles can be made from high titania mare basalts using spinning, pressing, rolling, or casting processes. Useful properties include good strength and abrasion resistance. Cast ceramic forms can be made from basalt, but these would have modest mechanical properties similar to high grade cements or concretes.

Refined glass-ceramics can be made based on enstatite and cordierite, both magnesium-rich minerals, the constituents of which could be developed from lunar soils. After melting and forming, glass-ceramics with good strength, toughness, thermal shock resistance, and dielectric properties can be developed by simple thermal treatment.

At the extreme end of sophistication would be single crystal alumina or titania fibers and whiskers of high mechanical strengths which might be developed from lunar materials. These fibers would then be coated with a glass designed to crystallize with intermediate bonding to the fibers. A hot isostatic pressing process would be required to make shapes. The resulting materials could be strong, tough, refractory, and non-brittle, if the strength of fiber-matrix bond can be controlled.

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