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**Amphibole Ceramics:
Conceptual Development and
Preliminary Experiments**

R. J. Lauf

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METALS AND CERAMICS DIVISION

AMPHIBOLE CERAMICS: CONCEPTUAL DEVELOPMENT AND
PRELIMINARY EXPERIMENTS

R. J. Lauf

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AMPHIBOLE CERAMICS: CONCEPTUAL DEVELOPMENT AND
PRELIMINARY EXPERIMENTS*

R. J. Lauf

ABSTRACT

Certain natural silicate minerals, commonly called jade, are well known for their resistance to brittle fracture. One type of jade, nephrite, is a compacted form of the amphibole mineral series tremolite-actinolite. Nephrite is tough because the naturally acicular crystal habit of these amphibole minerals produces an interwoven fibrous microstructure that impedes crack propagation. The object of this work was to duplicate the fibrous microstructure of nephrite by pulverizing natural tremolite or actinolite and then compacting it by hot pressing to form a dense body. Two other materials were also investigated, namely, clinochrysotile (serpentine asbestos) and synthetic fluor-tremolite.

For each material, the milling characteristics and densification were studied. The resulting microstructures were characterized, and fracture toughness was measured for a limited number of samples. The most "fibrous" microstructure was obtained by hot pressing clinochrysotile 15 min at 1000°C. Actinolite, hot pressed 15 min at 1100°C, had a critical fracture toughness $K_{Ic} = 4.5 \text{ MPa}\cdot\text{m}^{1/2}$, which compares favorably with the toughness of nephrite jade ($K_{Ic} = 3.6$). Decomposition of tremolite and actinolite to more stable phases occurred to some degree during hot pressing. The results suggest that hot isostatic pressing at high water vapor pressure should yield a dense product without causing amphibole decomposition.

INTRODUCTION

The use of ceramics in structural applications has increased rapidly as designers strive to exploit their desirable properties of high-temperature strength, hardness, and corrosion resistance. Unfortunately, many potential applications are limited by the characteristic tendency of ceramics to fail suddenly by brittle fracture. For this reason, much of

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the current ceramic research is directed toward developing ceramics with improved fracture toughness. Development of toughened ceramics can take any of several approaches. Partially-stabilized zirconia, for example, derives toughness from a controlled solid-state phase transformation that causes local volume changes within the stress field of an advancing crack.¹ A variation of this principle involves dispersion of metastable zirconia particles in a ceramic matrix such as alumina; again, toughness is achieved by volume changes in the zirconia particles close to a crack tip.² The toughness of alumina can also be improved by the addition of dispersed metal particles³ or dispersed silicon carbide whiskers.⁴ Fiber-reinforced glass-matrix composites have also been reported.⁵

The present work takes a new approach to the problem of developing fracture-resistant ceramics, namely, to mimic the structure of jade, whose resistance to brittle fracture is well documented.^{6,7} Early man recognized the exceptional mechanical properties of jade and used it, when it was available, to make tools.⁶ Today, jade is a widely used semiprecious gemstone; its toughness allows artisans to fashion intricate carvings without fracture.

PHASE RELATIONS

The name jade is used for two unrelated chain silicate minerals, jadeite and nephrite.

Jadeite, $\text{NaAlSi}_2\text{O}_6$, has a simple pyroxene chain structure and is typically formed at high pressure from nepheline and albite according to the reaction

for which the reduction in volume for the formation of jadeite is $34.9 \text{ cm}^3/\text{mole}$.⁸ The pressure-temperature equilibrium diagram for this system⁹ is shown in Fig. 1. Jadeite is formed only in metamorphic rocks; its common mineralogical associates generally indicate formation in environments of relatively low metamorphic grade.⁸

Fig. 1. Temperature-pressure relations for jadeite composition.
 Source: P. M. Bell and E. H. Roseboom, Jr., "Melting Relations of Jadeite and Albite to 45 Kilobars with Comments on Melting Diagrams of Binary Systems at High Pressures," *Mineral. Soc. Am., Spec. Pap. 2*, 151-61 (1969).

The term nephrite refers to compacted forms of double-chain amphiboles in the tremolite-actinolite series, $\text{Ca}_2(\text{Mg}, \text{Fe}^{+2})_5(\text{Si}_8\text{O}_{22})(\text{OH})_2$. The series is divided as follows, according to the amount of divalent iron in substitution for magnesium:

<u>Mineral</u>	<u>Mg/(Mg+Fe)</u>
tremolite	>80%
actinolite	80-20%
ferroactinolite	<20%

Members of the series in which the replacement of magnesium by iron exceeds 50% are uncommon in nature and are not of interest to the present study. Tremolite and actinolite are typically formed in lower grade metamorphic conditions [$\sim 500^\circ\text{C}$, 500 MPa (5 kbar)]. On heating at normal pressures, tremolite decomposes according to the following reaction:¹⁰

Equilibrium curves for tremolite^{11,12} and ferroactinolite¹³ are shown in Fig. 2. From this diagram, several observations can be made:

1. The maximum thermal stability of tremolite is about 915°C, at 1570 MPa (15.5 kbar). Above this temperature, tremolite is not the equilibrium phase at any pressure.

2. At high pressures, the tremolite field is terminated by the reaction

The maximum pressure stability of tremolite is about 2600 MPa (26 kbar) at 835°C.

3. The maximum thermal stability of the iron-rich end member (ferroactinolite) is significantly lower (~550°C) than that of pure tremolite. Stability curves for intermediate members of the series fall between the two curves shown.

Equilibrium diagrams for these systems must be used with caution, for two reasons. First, stability is influenced by oxygen fugacity, particularly for the iron-rich members.¹³ Second, attainment of equilibrium is often sluggish, sometimes requiring 24 h or more even in a small sample. Consequently, the interplay of thermodynamics and kinetics provides broad opportunities to develop strategies for processing these silicate minerals into dense ceramic bodies.

MECHANICAL PROPERTIES

Quantitative measurements of the fracture parameters of natural jade are summarized in Table 1. Reported fracture toughness (K_{IC}) ranges from 2.0 to 7.7 MPa·m^{1/2} for nephrite and is 7.1 MPa·m^{1/2} for jadeite. Rowcliffe⁷ has questioned the validity of the calculated K_{IC} values reported by Bradt et al.;⁶ nevertheless, the fracture toughness values

Fig. 2. Temperature-pressure stability curves for tremolite and ferroactinolite. Sources: F. R. Boyd, "Hydrothermal Investigations of the Amphiboles," pp. 377-96 in *Researches in Geochemistry*, P. H. Abelson, ed., John Wiley & Sons, New York, 1959; M. C. Gilbert and G. Troll, "A Comparison of the Stabilities of OH- and F-tremolite," *International Mineralogical Association 9th General Meeting, Berlin and Regensburg, Germany, Collected Abstracts*, 84, International Mineralogical Association, Silver Spring, Md., 1974; W. G. Ernst, "Synthesis and Stability Relations of Ferrotremolite," *Am. J. Sci.* **264**, 37-65 (1966).

compare favorably with those for typical engineering ceramics (e.g., K_{IC} is 3-4 for alumina). The bend strength of jade (~ 70 MPa) is not particularly high compared with that of high-performance ceramics, but one must remember that the strength of a ceramic body is determined by the size and distribution of flaws. Jade, like any other natural rock, contains many flaws, which one would expect to control in a synthetic material by careful processing.

Reported fracture energies are perhaps more interesting, because that parameter describes the ability of a material to divert and stop cracks after they have formed. The measured fracture energy (G) values of jade approach 1000 J/m^2 , roughly a factor of 10 higher than G for most ceramics.

Table 1. Fracture properties of jade

Type	Source	Fracture toughness, K_{Ic} (MPa·m ^{1/2})	Fracture energy, G (J/m ²)	Reference
Nephrite	Alpa di Selva, Switzerland	3.6 ± 1.0 ^a	562 ± 128	7
		2.5 ± 0.6 ^b	586 ± 130	
		2.0 ± 0.5 ^c	986 ± 161	
Nephrite	Frazer River, British Columbia	5.5 ± 1.0 ^a	619 ± 127	7
Nephrite	USSR	2.9 ± 0.4 ^a	269 ± 30	7
Nephrite	Unknown, probably USSR	7.7	226 ± 155 ^d	6
Jadeite	Burma	7.1	121 ± 32 ^d	6
Nephrite	New Zealand	3.6 ± 0.3 ^e		This work

^aFour-point bending, 50 mm × 5 mm × 2.5 mm.

^bFour-point bending, 150 mm × 15 mm × 7.5 mm.

^cFour-point bending, 150 mm × 30 mm × 15 mm.

^dThree-point bending, 3 mm × 3 mm cross section, 10 mm span. (G measured on notched beam, E measured by flexural resonance. K_{Ic} calculated from G and E).

^eIndentation technique, Vickers indenter, 4.4-kg load.

It is interesting to note that although both types of jade are quite tough, their toughness results from two distinct mechanisms. Jadeite has a blocky, equiaxed grain structure with crystallites typically in the 50 to 100 μ m size range. Fracture of jadeite displays extensive transgranular cleavage on selected planes (probably parallel to the pyroxene chains). Because the grains are oriented randomly, a crack must change direction frequently as it passes from one grain to the next.⁶ Nephrite, on the other hand, has a fibrous structure (Fig. 3) owing to the naturally acicular habit of tremolite-actinolite. The matted or interwoven bundles

Fig. 3. Microstructure of nephrite jade, showing intergrown bundles of acicular tremolite crystals.

of fibers promote crack diversion and branching. The difficulty in propagating a crack in this structure is demonstrated by comparing its hackled fracture surface [Fig. 4(a)] with the much smoother (predominantly intergranular) fracture surface of polycrystalline alumina [Fig. 4(b)].

Comparing the two jade types, jadeite has a higher elastic modulus and is harder, whereas nephrite is somewhat tougher. To synthesize jadeite, very high pressures are needed (Fig. 1), whereas to make nephrite one can start with a fibrous amphibole (tremolite-actinolite) that is readily available. The problem then is to compact the amphibole fibers into a dense solid body while minimizing decomposition. Equilibrium pressures for tremolite (Fig. 2) are within the capabilities of modern hot

(a)

L405

(b)

10 μm

Fig. 4. (a) Fracture surface of nephrite jade (New Zealand) showing fibrous grains and tortuous fracture path. (b) Fracture surface of alumina (Coors AD-998); the relatively smooth fracture is mostly intergranular.

isostatic presses, and nonequilibrium processing (e.g., simple hot pressing) is another possibility. In light of those considerations, the present work deals exclusively with the amphibole system (nephrite) rather than the pyroxene system (jadeite).

The goal of this project was to determine whether or not ceramics having an inherently tough, fibrous microstructure could be made from natural or synthetic amphiboles, whose crystals have a predominantly acicular habit. The work included: (1) studying how those candidate minerals respond to mechanical milling operations and characterizing the resulting powders; (2) fabricating dense bodies and determining the stability of the amphiboles during processing; and (3) characterizing the microstructures and, to a limited degree, the fracture properties of these unique materials. Because of the limited scope of this project, it was not possible to obtain strength measurements; fracture toughness was measured by the indentation cracking technique.

This work was supported by the Exploratory Studies Program of Oak Ridge National Laboratory.

POWDER PREPARATION

Four silicates were used in this study; three are natural amphiboles and one is a synthetic fluoramphibole. The characteristics of each material will be described separately.

TREMOLITE

Natural tremolite from North Carolina was obtained in as-mined chunks of approximately 200 g each. The samples had no visible inhomogeneities and consisted of white needle-like crystals ranging in size to about 1 by 5 mm (Fig. 5). Energy-dispersive X-ray analysis (EDX) indicated that the sample is relatively pure tremolite, i.e., no iron is present. X-ray diffraction gave good agreement with the pattern for tremolite (JCPDS Card No. 13-437). Fluorine is not detected by EDX, but small amounts are often observed in tremolite, substituting for the (OH)⁻ group.

(a)

100 μ m

(b)

Fig. 5. Acicular tremolite from North Carolina. (a) Scanning electron micrograph. (b) Characteristic X-ray spectrum. Unlabeled peaks at 8 to 9 keV are copper and zinc from the specimen holder.

Tremolite was crushed in a laboratory jaw crusher and ball-milled in ethanol for three days. We discovered some small (~1 cm) white masses that were not pulverized by milling. These masses, believed to be silica-rich inclusions, were removed from the milled powder before further processing. The natural cleavage is reflected in the platy to acicular habit of the powder particles (Fig. 6). The aspect ratio of the particles is not nearly as high as that of the starting tremolite crystals because of some fracture normal to the fiber axis. It is possible that the aspect ratio could be increased by the use of a more active milling aid, such as butylammonium chloride¹⁴ that could selectively break the bonds between the amphibole chains.

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Fig. 6. Tremolite powder ball milled in ethanol for three days.

ACTINOLITE

Natural actinolite from North Carolina was obtained as mined chunks of 150 to 200 g each. Some of the chunks were visibly inhomogeneous, containing dark platelets of mica (probably biotite). The actinolite crystals [Fig. 7(a)] were comparable in size and shape to the tremolite crystals. An EDX analysis [Fig. 7(b)] showed iron replacing roughly 20 to 25% of the magnesium. [Note that in Figs. 5(b) and 7(b) the magnesium peak should be higher than it is shown, by about a factor of 2. It is low because of diminished sensitivity for lighter elements, demonstrating that caution must be used when interpreting raw EDX spectra.] The presence of sodium and aluminum is not surprising. A virtually continuous solid solution series exists between the tremolite-actinolite and the hornblende series, with an arbitrary division at a Si $\leftrightarrow$ Al replacement of 0.5 atoms per formula unit. Actinolites with compositions bordering on the hornblende field are observed as products of the retrograde metamorphism of basic rocks. The presence of biotite noted above is consistent with this paragenesis.¹⁰

X-ray diffraction confirmed the deviation from ideal actinolite composition; however, because the exact composition is unknown and the total alkali content is quite low, for purposes of this work the material will be treated as actinolite. Figure 7 shows an acicular habit more characteristic of actinolite than of hornblende.

Actinolite was crushed and ball milled in the same way as the tremolite. (Mica flakes were manually removed by sieving before ball milling.) Milled actinolite powder (Fig. 8) contains some acicular material and many platy particles. As with the tremolite, ball milling alone does not yield a predominantly acicular product.

CLINOCHRYSOTILE

Natural clinochrysotile (serpentine asbestos) from Thetford, Quebec, was obtained as vein sections about 2 to 3 cm thick. The fibers run mainly across the vein. They are thin, flexible, and easily separated

(a)

100 μm

(b)

Fig. 7. Acicular actinolite from North Carolina. (a) Scanning electron micrograph. (b) Characteristic X-ray spectrum. The small peak at 8.04 keV (unlabeled) is copper from the sample holder.

Fig. 8. Actinolite powder ball milled in ethanol for three days.

(Fig. 9). An EDX analysis indicated a small amount of iron (a few atom percent) and some chlorine. Published analyses of chrysotile¹⁵ do not mention chlorine, but one can assume that a small amount of it could substitute for $(OH)^-$ in the structure.

Figure 10 is an optical micrograph taken normal to the axis of the fibers. The easy separation of the fibers is clearly shown in this cross section. (The highly reflective phase is probably magnetite; the Thetford deposit was derived from the alteration of peridotite, and iron from the original olivine would mostly be partitioned to magnetite or hematite owing to its low solubility in serpentine.¹⁵)

Clinochrysotile was ball milled in water with a small amount of milling aid (Darvan C). The fibers separated easily (Fig. 11), forming large matted aggregates, rather than grinding into powder. Of the materials studied, this one seems most likely to produce a fibrous ceramic if the tendency to decompose could be suppressed.

(a)

100 μ m

(b)

Fig. 9. Clinochrysotile from Thetford, Quebec. (a) Scanning electron micrograph of fibers. (b) Characteristic X-ray spectrum.

Fig. 10. Cross section of clinochrysotile vein, normal to fiber axes, showing easy separation of fibers and highly reflective inclusions.

FLUOR-TREMOLITE

The structure and properties of fluor-tremolite, $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}\text{F}_2$, have been extensively studied¹⁶ in an effort to find potential substitutes for asbestos. Early research established that fluor-tremolite will crystallize from the melt (rather than decomposing into pyroxene, as tremolite does) and defined effective methods of synthesis. We followed those procedures, using a powder mixture ("Batch 1") with the following composition: 480.6 g SiO_2 , 201.6 g MgO , 78.1 g CaF_2 , 100.1 g CaCO_3 . The powders were mixed together and wet ball milled overnight. The milled powder was cold pressed into pellets (weighing about 20 g) to remove as much air as

L319

(a)

100 μm

L321

(b)

10 μm

Fig. 11. Scanning electron micrographs of clinochrysotile, ball milled in water and Darvan C. (a) Fiber aggregates beginning to mat together. (b) Fiber bundle, showing easy separation of thin, flexible fibers.

possible, and then the pellets were melted under vacuum in covered graphite crucibles under conditions shown in Table 2. Examination of the solidified melts (Fig. 12) confirmed the acicular crystal habit of the fluor-tremolite.

Table 2. Fluor-tremolite synthesis

Melt	Powder	Maximum temperature (°C)	Time (min)	Starting weight (g)	Final weight (g)
1A	Batch 1	1480	60	100	35
1B	Batch 1	1390	5	200	160
1C ^a	Batch 1 +0.5% Co ₂ O ₃	1400	5	20	11 ^b
1D	Melt 1A	1450	60 ^c	10	9
1E	Batch 1	1450	60 ^c	400	294

^aMelt 1C was made to determine if transition metals could serve as coloring agents in fluor-tremolite. No color was observed in this melt; the cobalt appeared to be reduced to metal.

^bSome loss due to adherence to crucible.

^cHeld 60 min at 1350, 1250, and 1150°C followed by furnace cool. All others furnace cooled directly from indicated temperature.

The synthetic fluor-tremolite was crushed and ball milled. Melt 1B was milled in water with 5% Darvan C; melt 1E was milled with a small amount of ethylene glycol. Ball milling the fluor-tremolite yielded very little acicular material (Fig. 13), consistent with early observations that the synthetic phase is not as flexible as natural asbestos fibers.¹⁶

DENSIFICATION

All four amphiboles were densified by hot pressing under vacuum in graphite dies. Hot pressing runs are summarized in Table 3.

(a)

200 μm

L112

(b)

100 μm

Fig. 12. Fluor-tremolite crystals grown from melts. (a) Optical micrograph, melt 1A. (b) Scanning electron micrograph, melt 1E.

10 μm

Fig. 13. Fluor-tremolite, melt 1E, ball milled in ethylene glycol. Particles are predominantly equiaxed.

A few pressureless sintering runs were done on the fluor-tremolite powder (Table 4). Pressureless sintering of the natural minerals was not attempted because, in the absence of confining pressure, decomposition of the amphibole structure would be severe. The fluor-amphibole, in contrast, is much more stable and could, in principle, be sintered without decomposing. Sintering experiments used fluor-tremolite melt 1B, ball milled in water and Darvan C. Pellets were cold pressed at 200 MPa (30,000 psi) to a green density of 1.83 g/cm^3 (61% theoretical).

Table 3. Hot pressing experiments

Sample	Powder	Temperature (°C)	Pressure		Time (min)	Density (g/cm ³)
			(MPa)	(psi)		
TREM-1	Tremolite	900	55	8000	15	1.82
TREM-2	Tremolite	1300 ^a	55	8000	15	2.99
TREM-3	Tremolite	1200 ^a	55	8000	15	3.07
TREM-4	Tremolite	1100 ^a	55	8000	15	2.59
TREM-5	Tremolite	1200	55	8000	15	2.59
ACT-1	Actinolite	1200	55	8000	15	<i>b</i>
ACT-2	Actinolite	1000	55	8000	15	2.24
ACT-3	Actinolite	1100	55	8000	15	3.06
ACT-4	Actinolite	1050	55	8000	15	2.97
ACT-5	Actinolite	1100	55	8000	15	2.93
ACT-6	Actinolite	1150	55	8000	5	<i>b</i>
ASB-1	Clinochrysotile	900	62	9000	15	1.55
ASB-2	Clinochrysotile	1000	62	9000	15	1.88
ASB-3	Clinochrysotile	1100	62	9000	15	3.16
FT-1	Fluor-tremolite	1100	62	9000	15	2.97
FT-2	Fluor-tremolite	950	62	9000	15	2.00
FT-3	Fluor-tremolite	1000	62	9000	15	2.68
FT-4	Fluor-tremolite	1050	62	9000	15	2.83
FT-5	Fluor-tremolite	1100	62	9000	15	2.95
FT-5HT ^c	Fluor-tremolite	1200			120	2.69

^aTREM-2, -3, -4 were pressed with pieces of TREM-1 (60% theoretical density) as starting material.

^bDecomposed catastrophically.

^cHeat treated 2 h in vacuum after hot pressing.

Table 4. Sintering experiments

Sample	Temperature (°C)	Time (h)	Atmosphere	Density (g/cm ³)	Comments
FTS-1	1300	1	Hydrogen	n.d. ^a	Fused to alumina crucible
FTS-2	1200	1	Hydrogen	2.68	
FTS-3	1250	1	Ar-4% hydrogen	n.d.	Fused in graphite crucible

^aNot determined.

Densities of hot-pressed amphiboles are plotted in Fig. 14. From these data, several observations can be made:

1. Actinolite is less stable than tremolite under hot pressing conditions as expected from their equilibrium behavior. At 1150°C and above, actinolite fused into a mass of porous, glassy material. Tremolite can be pressed to high density at 1200°C, although some breakdown of the amphibole structure no doubt occurs at this temperature. Tremolite completely fused at 1300°C.

2. Fluor-tremolite reaches approximately theoretical density at 1100°C, although density can be misleading if some residual forsterite ($\rho = 3.22 \text{ g/cm}^3$) is present. Within the limits of this experiment, gross decomposition of the fluor-tremolite was not observed, although the density loss of sample FT-5HT suggests some volatilization, which perhaps can be attributed to loss of fluorine.

3. Clinochrysotile appears to decompose at or below about 1050°C. This conclusion is based on the fact that the density of sample ASB-3, hot pressed at 1100°C, is significantly greater than the theoretical density of chrysotile (3.16 versus 2.55 g/cm^3). It is interesting to note that under equilibrium conditions, chrysotile decomposes to form forsterite, silica, and water.¹⁵ Assuming that the water escapes, mass balance predicts a final density of about 3.04 to 3.14 g/cm^3 for the resulting phase assemblage.

4. At 1200°C, tremolite is more dense after hot pressing 15 min than after only 5 min. This density increase could be due in part to decomposition (as discussed above for chrysotile) because the major products are diopside and enstatite, both of which are more dense than tremolite ($3.21\text{--}3.22$ versus 3.02 g/cm^3).

Pressureless sintering of synthetic fluor-tremolite proved to be difficult. The first sample, fired in hydrogen in an alumina crucible at 1300°C, melted and readily wet the alumina. Another sample, FTS-3, was fired to 1250°C in Ar-4% H₂ in a graphite crucible to determine if a reaction with the alumina lowered the melting point in the first run. Sample FTS-3 also fused into a low-viscosity melt, indicating that the crucible material was not involved.

Fig. 14. Density versus temperature for amphiboles hot pressed 15 min in vacuum.

Sample FTS-2, fired to 1200°C, retained its integrity but reached only about 90% of theoretical density. The density, along with microscopic features to be discussed later, suggests that volatile species were evolved at the sintering temperature.

MICROSTRUCTURES AND PROPERTIES

TREMOLITE

Sample TREM-1, hot pressed at 900°C, was very poorly consolidated. Density was 1.82 g/cm³, or about 60% of theoretical. The appearance of the fracture surface (Fig. 15) suggests that the original powder was almost entirely unaltered. The significance of this run is to show the importance of kinetics; thermodynamics alone would have predicted decomposition of tremolite at this temperature.

10 μm

Fig. 15. Natural tremolite hot pressed 15 min at 900°C. Fracture surface shows mostly unaltered powder. Density is 1.82 g/cm³.

In contrast, after 15 min at 1300°C, sample TREM-2 appears to have decomposed completely. The microstructure (Fig. 16) consists of equiaxed pyroxene grains. An intergranular silica phase (probably glass) was removed by etching with hydrofluoric acid.

Tremolite reaches theoretical density in 15 min at 1200°C. The microstructure [Fig. 17(a)] shows some elongated grains remaining, as well as equiaxed grains that are probably pyroxenes. A fracture surface normal to the pressing direction [Fig. 17(b)] confirms the fact that some fibrous material has survived hot pressing. Comparing this fracture surface with that of nephrite jade [Fig. 4(a)] gives support to the concept of achieving a jade-like fracture mode in a synthetic material.

As expected, more amphibole is retained after 15 min at 1100°C (Fig. 18). Unfortunately, sample TREM-4 is only about 86% of theoretical density and would not be expected to have good mechanical properties. The same observation applies to TREM-5, hot pressed 5 min at 1200°C to about 93% of theoretical density.

Fig. 16. Tremolite hot pressed 15 min at 1300°C. Amphibole structure has completely decomposed to equiaxed pyroxene and intergranular silica.

The elastic moduli of sample TREM-3 and TREM-4 were measured by the sonic velocity technique (Table 5). Young's modulus of TREM-3 is comparable to that of nephrite,⁶ whereas TREM-4 has a much lower value consistent with its low density.

Table 5. Elastic properties of hot-pressed tremolite

Sample	Young's modulus (GPa)	Shear modulus (GPa)	Poisson's ratio	Reference
TREM-3	151	63	0.199	This work
TREM-4	91	38	0.183	This work
Nephrite jade	130			Bradt ⁶

(a)

50 μm

L2

(b)

10 μm

Fig. 17. Natural tremolite hot pressed 15 min at 1200°C. (a) Optical micrograph; pressing direction is vertical. (b) Fracture surface normal to pressing direction, showing acicular grains. Density is 3.07 g/cm³.

Y-196533

(a)

100 μm

Y-196532

(b)

50 μm

Fig. 18. Tremolite hot pressed 15 min at 1100°C. Much acicular material is retained. Pressing direction is vertical. Density is 2.59 g/cm³.

ACTINOLITE

Actinolite was much less stable than tremolite during hot pressing. Total decomposition occurred within 5 min at 1150°C. Approximately theoretical density was reached at 1100°C (sample ACT-3), whereas a sample pressed at 1050°C reached about 96% of theoretical density (ACT-4). Microstructures will now be examined in order of increasing temperature.

Elongated, apparently unreacted actinolite grains are present in sample ACT-2, hot pressed 15 min at 1000°C, Fig. 19. The actinolite grains in Fig. 19 appear dark and sharply defined, surrounded by partially decomposed material (gray elongated grains) and decomposition products (equiaxed grains).

Y-196163

100 μm

Fig. 19. Actinolite hot pressed 15 min at 1000°C. Pressing direction is vertical. Some alignment of the actinolite fibers normal to the pressing direction can be seen. (Optical micrograph, polarized light). Density is 2.24 g/cm³.

After 15 min at 1050°C (ACT-4), no unaltered material remains (Fig. 20). Elongated, somewhat convoluted amphibole grains are heavily oriented normal to the pressing direction.

Hot pressing 15 min at 1100°C (ACT-3) causes more amphibole decomposition (Fig. 21). Some elongated grains are present, but decomposition products (gray equiaxed material) make up a larger portion of the structure. A preferred orientation of the elongated grains normal to the pressing direction is still visible in the figure. Fracture of ACT-3 normal to the pressing direction (Fig. 22) shows very little of the desired fibrous character. The smooth platelike defects visible at several points on the surface are possibly small biotite mica crystals originally observed as an

Y-196540

50 μ m

Fig. 20. Actinolite hot pressed 15 min at 1050°C. Pressing direction is vertical. (Optical micrograph, polarized light.)

Y-196166

(a)

100 μm

Y-196167

(b)

50 μm

Fig. 21. Actinolite hot pressed 15 min at 1100°C. Pressing direction is vertical.

Fig. 22. Fracture surface of actinolite hot pressed 15 min at 1100°C. Fracture is normal to pressing direction.

impurity in the raw actinolite. A much larger sample, ACT-5, pressed at the same temperature did not reach as high a density (2.93 versus 3.06 g/cm³), possibly because of increased friction in the die.

Elastic moduli of ACT-2 and ACT-3 (Table 6) are consistent with their respective densities. Young's modulus of ACT-3 is not as high as that of either TREM-3 or nephrite jade (Table 5), consistent with its slightly lower density (with respect to theoretical) and possibly greater amount of decomposition products.

Table 6. Elastic properties of hot-pressed actinolite

Sample	Young's modulus (GPa)	Shear modulus (GPa)	Poisson's ratio
ACT-2	32.3	14.4	0.12
ACT-3	115	44.9	0.28

The fracture toughness of ACT-3 was compared with that of nephrite jade by the indentation crack technique.¹⁷ The results (Table 7) indicate an improvement of about 24% over the natural material, although in the natural material there was more crack diversion and branching. One would expect substantially more improvement with processing optimized to reduce or eliminate decomposition of the amphibole phase.

Table 7. Fracture toughness (K_{IC}) comparison

Material	Indent designation	Load (kg)	Indent length (μm)	Crack length (μm)	K_{IC} ($\text{MPa}\cdot\text{m}^{1/2}$)	Hardness (kg/mm^2)
ACT-3	1	5.3	50	64.7	4.55	3992
	2	5.3	51	61.4	4.79	3809
	3	5.3	53	73.8	4.07	3517
	4	5.3	52	67.9	4.40	3615
Average toughness 4.5 ± 0.3						
Average hardness 3730 ± 211						
Nephrite	B-4	4.4	44	72.6	3.56	4175
	A-4	4.4	53	73.0	3.89	2862
	A-7	4.4	53	83.2	3.32	2930
Average toughness 3.59 ± 0.3						
Average hardness 3320 ± 739						

CLINOCHRYSOTILE

Hot pressing serpentine asbestos for 15 min at 900, 1000, and 1100°C covered the range from very little densification and decomposition to nearly complete decomposition and melting. Sample ASB-1, pressed at 900°C, reached only 61% of theoretical density. It was, accordingly, quite weak and would not be suitable for structural applications. The microstructure (Fig. 23) shows a strong layered texture normal to the pressing direction.

Pressing for 15 min at 1000°C increased the density to about 75% of theoretical. Again, a prominent texture exists [Fig. 24(a)]. The

400 μm

Fig. 23. Clinochrysotile (serpentine asbestos) hot pressed 15 min at 900°C. Pressing direction is vertical. Density is 1.55 g/cm³. (Optical micrograph, polarized light.)

fracture surface of this sample [Fig. 24(b)] is the closest approximation thus far to the fibrous texture that we sought. The density, however, is still inadequate for good mechanical properties.

Virtually complete decomposition occurred during pressing at 1100°C. The sample had a dark, glassy appearance and smooth fracture surface (Fig. 25). The predominance of decomposition products had been deduced from the density of sample ASB-3 (3.16 g/cm³ versus a theoretical density of 2.55 g/cm³ for clinochrysotile).

(a)

400 μm

L410

(b)

10 μm

Fig. 24. Clinochrysotile hot pressed 15 min at 1000°C. (a) Optical micrograph showing layered texture. Pressing direction is vertical. (b) Fracture surface showing fibrous morphology.

Fig. 25. Fracture surface of clinochrysotile hot pressed 15 min at 1100°C. All fibrous character is lost; crystalline material is very fine grained, and much glass is present.

FLUOR-TREMOLITE

As-pressed fluor-tremolite contained very little acicular material. Sample FT-2, hot pressed 15 min at 950°C, is typical. Figure 26 shows a predominantly equiaxed structure with a few elongated grains. X-ray diffraction showed a substantial amount of unreacted forsterite in the synthetic powder, and much of it appears to have been retained.

Further evidence that fluor-tremolite had not formed completely can be seen in Fig. 27. After pressing 15 min at 1100°C, some equiaxed grains (possibly forsterite relics) are surrounded by fine material, a very small amount of which is elongated or acicular. After heat treatment for 2 h at

Fig. 26. Synthetic fluor-tremolite, hot pressed 15 min at 950°C. Much of the equiaxed material probably is retained forsterite. Density is 2.00 g/cm³. (Optical micrograph, bright field.)

1200°C, elongated crystals of fluor-tremolite have grown substantially, although they still do not make up the major phase. This suggests that, to make a fluor-tremolite ceramic, one must either convert the powder more fully to fluor-tremolite or choose a heat treatment schedule that will precipitate fluor-tremolite in the dense body. One can see this process occurring in the sintered sample FTS-2 (Fig. 28).

(a)

50 μm

(b)

50 μm

Fig. 27. Fluor-tremolite hot pressed 15 min at 1100°C. (a) As pressed. Density is 2.95 g/cm³. (b) Heat treated 2 h at 1200°C in vacuum. Density is 2.69 g/cm³. (Optical micrographs, bright field.)

Fig. 28. Needles of fluor-tremolite forming in sample FTS-2, cold pressed and sintered 1 h at 1200°C in hydrogen. Density is 2.68 g/cm³.

CONCLUSIONS

1. Ball milling tremolite or actinolite does not yield a predominantly acicular powder. Chrysotile, on the other hand, separates readily into very thin fibers.
2. Tremolite, actinolite, and chrysotile can be hot pressed at temperatures at which the amphibole phase is thermodynamically unstable. Decomposition to pyroxene and silica or to forsterite and silica is controlled by kinetics. Even when some decomposition occurs, unique microstructures can be developed in these materials.

3. Synthetic fluor-tremolite can be densified by hot pressing. Some residual forsterite is present, which on heat treatment can be converted to elongated crystals of fluor-tremolite.

4. The decomposition of amphiboles during hot pressing is greatly accelerated by the presence of divalent iron, as expected from thermodynamic predictions.

5. Limited mechanical property data suggest that densified tremolite or actinolite can have properties similar to those of nephrite jade. The most "fibrous" fracture mode was observed in hot-pressed chrysotile.

SUGGESTIONS FOR FURTHER WORK

1. Hot isostatic pressing should be used to make dense tremolite or actinolite under equilibrium or near-equilibrium conditions. A slight excess of water could be added to speed the reactions.

2. Larger specimens should be fabricated to get more mechanical property data. Thermal shock resistance should be examined, because theoretical considerations suggest that the combination of relatively low strength and high fracture surface energy can lead to good thermal shock resistance.¹⁸

3. Fluor-tremolite with a large excess of silica should be melted and crystallized as a means of producing a fiber-reinforced glass ceramic.

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REFERENCES

1. R. C. Garvie and P. S. Nicholson, "Structure and Thermo-mechanical Properties of Partially Stabilized Zirconia in the CaO-ZrO_2 System," *J. Am. Ceram. Soc.* **55**(3), 152-57 (1972).
2. N. Claussen and M. Ruhle, "Design of Transformation-Toughened Ceramics," pp. 137-63 in *Advances in Ceramics*, Vol. 3, American Ceramic Society, Columbus, Ohio, 1981.
3. C. S. Morgan, A. J. Moorhead, and R. J. Lauf, "Thermal-Shock Resistant Alumina-Metal Cermet Insulators," *Am. Ceram. Soc. Bull.* **61**(9), 974-81 (1982).
4. T. N. Tiegs and P. F. Becher, "Particulate and Whisker Toughened Alumina Composites," pp. 479-86 in *Proceedings of the 22nd Automotive Technology Development Contractors' Coordination Meeting, Dearborn, Michigan, 1985*, Society of Automotive Engineers, Warrendale, Pa., 1985.
5. K. M. Prevo and J. J. Brennan, "Silicon Carbide Yarn Reinforced Glass Matrix Composites," *J. Mater. Sci.* **17**, 1201-06 (1982).
6. R. C. Bradt, R. E. Newnham, and J. V. Biggers, "The Toughness of Jade," *Am. Min.* **58**, 727-32 (1973).
7. D. J. Rowcliffe and V. Fruhauf, "The Fracture of Jade," *J. Mater. Sci.* **12**, 35-42 (1977).
8. W. A. Deer, R. A. Howie, and J. Zussman, "Rock-Forming Minerals," pp. 461-81 in *Vol. 24: Single-Chain Silicates*, 2d ed., John Wiley & Sons, New York, 1978.
9. P. M. Bell and E. H. Roseboom, Jr., "Melting Relations of Jadeite and Albite to 45 Kilobars with Comments on Melting Diagrams of Binary Systems at High Pressures," *Mineral Soc. Am., Spec. Pap.* **2**, 151-61 (1969).
10. W. A. Deer, R. A. Howie, and J. Zussman, *An Introduction to the Rock Forming Minerals*, Longman Group Ltd., London, 1966, pp. 163-66.
11. F. R. Boyd, "Hydrothermal Investigations of the Amphiboles," pp. 377-96 in *Researches in Geochemistry*, P. H. Abelson, ed., John Wiley & Sons, New York, 1959.

12. M. C. Gilbert and G. Troll, "A Comparison of the Stabilities of OH- and F-tremolite," *International Mineralogical Association 9th General Meeting, Berlin and Regensburg, Germany, Collected Abstracts*, 84, International Mineralogical Association, Silver Spring, Md., 1974.
13. W. G. Ernst, "Synthesis and Stability Relations of Ferrotremolite," *Am. J. Sci.* **264**, 37-65 (1966).
14. D. G. H. Ballard and G. R. Rideal, "Flexible Inorganic Films and Coatings," *J. Mater. Sci.* **18**, 545-61 (1983).
15. W. A. Deer, R. A. Howie, and J. Zussman, *Rock-Forming Minerals*, Vol. 3: *Sheet Silicates*, 1st ed., John Wiley & Sons, New York, 1962, pp. 170-90.
16. J. E. Comeforo and J. A. Kohn, "Synthetic Asbestos Investigations, I: Study of Synthetic Fluor-tremolite," *Am. Min.* **39**, 537-48 (1954).
17. A. G. Evans, "Fracture Toughness: The Role of Indentation Techniques," pp. 112-35 in *Fracture Mechanics Applied to Brittle Materials*, ASTM STP 678, S. W. Freiman, ed., American Society for Testing and Materials, Philadelphia, Pa., 1979.
18. D. P. H. Hasselman, "Elastic Energy at Fracture and Surface Energy as Design Criteria for Thermal Shock," *J. Am. Ceram. Soc.* **46**(11), 535-40 (1963).

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