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Decrease in fracture toughness of chert by heat treatment

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The fracture toughness of Ocala chert, as measured with short rod specimens and with the microhardness indenter, decreases to 60% of its original value as a result of heat treatment to 500° C while the elastic modulus increases 22%. The change in fracture toughness is associated with a transition from crack propagation around particles in the porous boundaries of densely packed zones in the chert to propagation through the zones. The transition is related to an increase in particle/particle bonding within the porous boundaries. Consolidation of a silica gel in the boundary regions, which resulted in a loss of water of 1.12% by weight, is apparently responsible for the increased bonding.

1. Introduction

Cherts and other similar minerals comprised a large portion of the materials from which prehistoric man made weapons and cutting tools. It has been concluded, from a comparison of the colour and texture of many of the tools with that of the native materials, that the cherts were often heat-treated to make them easier to chip and to obtain smooth fracture surfaces and sharp edges. Anthropologists have empirically determined heat treatments for the native minerals which reproduce the changes in colour and fracture surface texture found in the tools [1]. Purdy [2] measured the weight and specific surface area decrease of chert subjected to such heat treatments and compared the microstructure and resistance to flaking of thermally modified chert with that of the original mineral. To quantify resistance to flaking, she used a "point tensile test" in which a 1.0 inch diameter cylinder of the chert was loaded between two 0.25 inch diameter hardened steel rods oriented perpendicular to the sample cylinder axis. She observed a decrease in failure load from 12.5×10^3 to 7.0×10^3 N as a result of heat treatment to 400° C.

The mineral chert (often referred to as "flint") is a crypto-crystalline assemblage, primarily silica, with crystallites of the order of 0.1 μm. The similarity of its structure to that of glass–ceramics and, in some respects, to that of consolidated gels makes its behaviour of interest to the glass technologist. The current study examines the relationship of the fracture behaviour of this material to changes in the microstructure of the material which are produced by heat treatment.

2. Experimental procedures and results

2.1. Materials description

The Ocala chert used in this study was part of the same nodule used by Purdy [2] in the earlier study. The heat treatment used to modify the structure is the one determined by Purdy to give the optimum improvement in workability as measured by the "point tensile" test. That treatment consisted of an initial 4 h hold at 100° C followed by 1 h holds at 50° C intervals up to 400° C. Heating rates between holds were $100^\circ \mathrm{C\,h^{-1}}$. For the current study, we also heated specimens to 500° C. Measurements were made on samples extracted after 300, 400 and 500° C holds. Dilatometer measurements over the temperature range 25 to 500° C showed a thermal expansion of $14.9 \times 10^{-6}\,{}^\circ\mathrm{C}$ (0 to 300° C) and, on cooling, no net dimensional change in the 17.5 mm long sample within the accuracy of the measurement (3 μm). Purdy found no change in crystal structure (primarily α-quartz) due to heat treatment.

2.2. Mechanical properties

Fracture toughness values for chert heat-treated to 400° C and for untreated chert were obtained with short rod specimens. The short rod sample is a cylinder with a chevron notch on a diametral plane which permits a stable crack to grow until a critical load is reached. Details of sample configuration and test procedure for the short rod are described by Barker [3]. A crack opening displacement gauge mounted in the loading slot of the short rod permitted determination of elastic modulus during sample loading. Elastic modulus values were also obtained from ultrasonic velocity measurements. Fused silica rods (Suprasil W) were used as reference samples. All testing of short rod samples was done with samples immersed in freon to reduce possible static fatigue effects.

An indentation hardness tester was used to obtain hardness values on samples extracted after heating at 300, 400 and 500° C. The procedure described by

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TABLE I Fracture toughness and modulus change*

	Fracture toughness (MPa m$^{1/2}$)	Young's modulus (GPa)
Untreated chert	1.55 + 0.07	72 + 2
Heat-treated chert (400° C)	1.05 + 0.09	88 + 2

*Obtained with short rod specimens.

Lawn *et al.* [4] was used to estimate fracture toughness from measurements of the length of cracks extending from the hardness indents.

Table I shows the values of fracture toughness (K_{Ic}) and modulus obtained with the short rod specimens. The value of 1.55 ± 0.07 MPa m$^{1/2}$ for untreated chert is the mean for six measurements while the value of 1.05 ± 0.09 for the heat-treated chert is the mean of four measurements. Fused silica specimens under the same conditions gave values of 0.75 ± 0.01 MPa m$^{1/2}$ for K_{Ic}. Although the elastic modulus shows an increase from 72 to 88 GPa in the short rod specimens as a result of the heat treatment, the ultrasonic modulus showed no change within the accuracy of measurement (5%).

Values of hardness and fracture toughness determined from indentation tests are plotted as a function of maximum heat treatment temperature in Fig. 1. Values are the mean of 10 to 14 indentation measurements. The bars indicate standard deviation. There was essentially no change in hardness as a result of the heat treatment. However, the fracture toughness decreased monotonically with increasing treatment temperature. Although the absolute values for K_{Ic} from the hardness tests differ from those obtained with the short rod tests, the ratios of the values for the untreated specimens to those for the heat-treated samples are similar.

2.3. Fracture surface morphology

Optically, at low magnification, the fracture surfaces of the untreated chert had a dull, matt finish. In contrast, the surface of the heat-treated material displayed highly specular reflection. At the macroscopic level, the fracture surface of the untreated short rod specimens was flatter than that of the heated specimens. In the heat-treated chert, deviations out of the central plane of the short rod were more frequent and of greater magnitude and hackle features extending from inclusions were common.

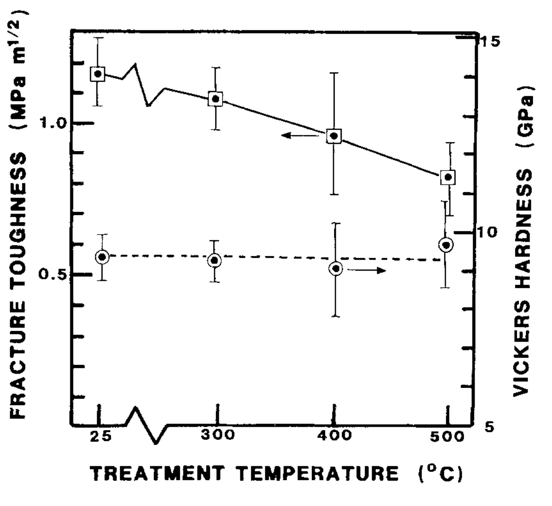

Figure 1 Fracture toughness, ⊡, and Vickers hardness, ⊙, as a function of maximum heat treatment temperature.

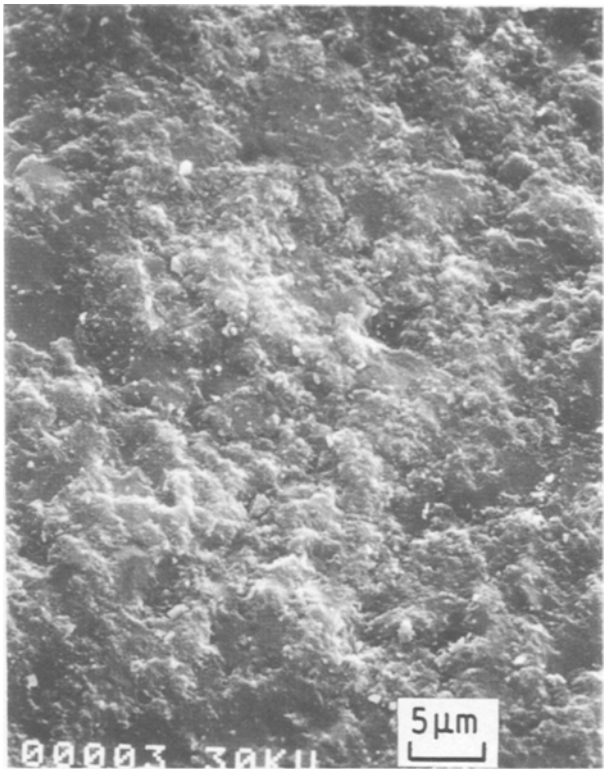

Figure 2 Fracture surface of untreated Ocala chert (× 1780).

At higher magnification, in the SEM, the reason for the specular reflection from the heated material and for the dull, matt appearance of the untreated material becomes apparent. Fig. 2 shows a representative area from one of the untreated samples at × 1780 magnification. Although there are a number of isolated, relatively smooth areas with dimensions ranging from 1 to 10 μm, most of the surface appears rough. One of these rough areas is shown at × 17 800 magnification in Fig. 3. The surface features are individual particles of the polycrystalline assemblage. The topography of the surface is nodular, i.e. the surfaces of individual grains separated by the fracture are often rounded. In contrast, the contacts between the particles in that surface layer, i.e. the boundaries perpendicular to the plane of the micrograph, are usually high faceted. This micrograph reflects the character of the chert microstructure. It is an assemblage of densely packed zones of the order of 5 μm in diameter, separated by boundaries which are not as densely packed. The fact that failure occurred along this boundary is an indication of the relative strengths of the boundary and the interior of these zones.

In contrast with the generally rough appearance of the untreated material at high magnification, the fracture surface of the heat-treated sample surface (Fig. 4) appears relatively smooth. Except for the hackle features the crack seems to have propagated continuously and coherently. At × 17 800 (Fig. 5) the surface is also very different from that in the untreated sample. There are features which show the particulate character of

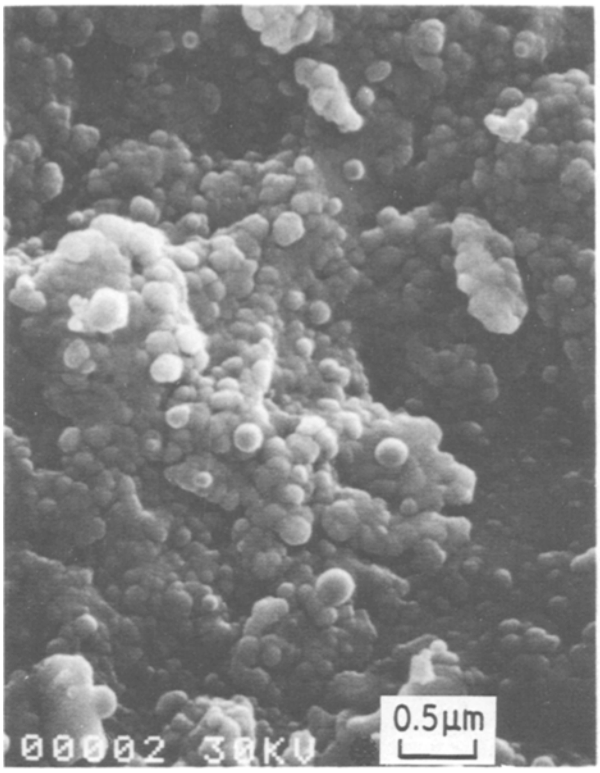

Figure 3 Fracture surface of untreated Ocala chert (× 17 800).

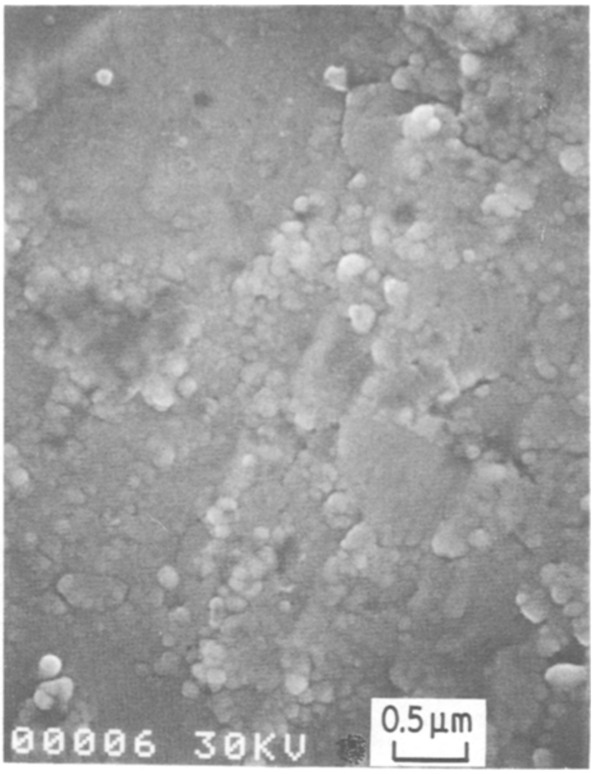

Figure 5 Fracture surface of heat treated Ocala chert (× 17 800).

the microstructure, but much of the surface suggests transgranular fracture. The smooth areas in Fig. 2 have this same appearance. A comparison of the features on the surfaces of untreated and treated materials reveals that the heat treatment had not produced any change in particle size.

3. Discussion

The decrease in fracture toughness of Ocala chert with heat treatment is consistent with observations that heat treated chert is easier to flake than untreated material. The reduced fracture toughness would require smaller loads to initiate fracture under an indenter and to propagate the crack through the material. In a similar study of Pennsylvania jasper, Schindler *et al.* [5] found a reduction of fracture toughness as a result of heat treatment. Their fracture toughness values were obtained with the microindentation technique. They explained the decrease and the accompanying change in colour in terms of a phase change in iron oxide inclusions in the jasper (from $FeO \cdot OH$ to Fe_2O_3). The Ocala chert contains no such inclusions.

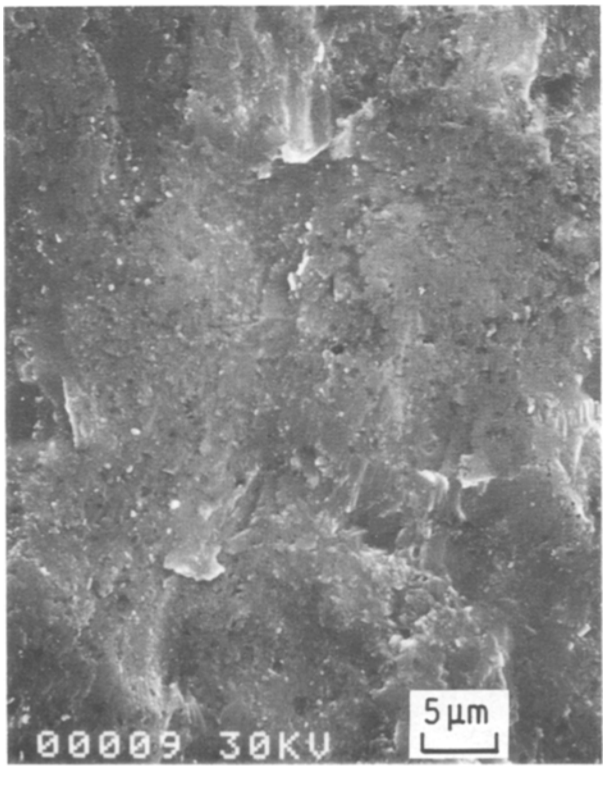

Figure 4 Fracture surface of heat treated Ocala chert (× 1780).

In the current experiment, some of the mechanical data and some of the details of the microstructure seem at odds with the observed decrease in fracture toughness resulting from heat treatment. In particular, the increase in elastic modulus produced by heat treatment would suggest an increase in bonding between particles which, presumably, ought to result in an increase in strength and toughness.

The change in fracture surface morphology produced by the heat treatment suggests an explanation for the change in fracture toughness. In untreated chert, as noted earlier, much of the fracture involves separation along boundaries of densely packed zones. The fracture surface area is large because the fracture moves around the zones rather than through them, but also, more importantly, because the fracture passes around the submicrometer particles in the interface region. In contrast, the fracture surface in the heat-treated chert, although macroscopically irregular, is smooth at the 1 µm level and shows much more of the character of a uniformly well-bonded material. The decrease in fracture toughness is apparently related to an increase in the bond strength in the interfaces between the dense zones. With stronger bonding at the zone boundaries, the lowest energy path for fracture is through the zones.

It seems at first paradoxical that the *decrease* in fracture toughness of Ocala chert by heat treatment results from *improved* bonding between particles. However, the untreated chert is like a polycrystalline body with grains the size of the dense zones and with very irregular grain boundaries. Although the grain boundaries are weaker than the interior of grains, the increased area of intergranular fracture more than compensates for the decrease in energy per unit area. Consequently, it requires a higher applied stress to propagate a crack through the material. Faber and Evans [6] have described these crack deflection processes for ceramic materials.

Improved bonding is also consistent with the increase in static modulus produced in the short rod specimens by heat treatment. In contrast, the velocity of sound waves is not affected much by the change in bonding at zone boundaries [7] and so the sonic modulus remained essentially constant with heat treatment.

The change in bonding at the zone boundaries is apparently related to the low packing density of the particles and to the presence of a water-rich phase surrounding those loosely packed particles. Cherts usually originated as silica precipitates in marine sediments and are found as nodules in chalk deposits. The individual particles were produced by precipitation from a silicate solution and are essentially dense silica spherulites, usually crystalline. In the chert used in this experiment, the differences in packing between the interior of the dense zones and the zone boundaries suggest that the deposition process may have taken place in several stages, perhaps at different pH levels. In any event, especially for cherts which remain in a moist environment, like the Ocala chert used in this study, it is likely that the porous boundary regions would retain water saturated with silica (perhaps in the form of a gel) essentially indefinitely [8]. The same general structure is found in opals which retain their irridescence because of the stability of the water-rich, low refractive index, interparticle phase. Opals generally contain 4 to 9% water. Only about 1% is lost even at very low humidity; the rest is apparently chemically bound as silanols in a gel phase. This retained water can be removed by sustained exposure to high temperatures (200 to 600° C) [9].

In the prior work, Purdy found that, for Ocala chert, water loss resulted in a decrease in weight of 1.12% with heat treatment to 500° C, more than half of which occurred above 300° C. She also found that heat treatment reduced the specific surface area of the chert from 4.86 to $1.9\,\mathrm{m}^2\,\mathrm{gm}^{-1}$. Those changes are consistent with the consolidation of a gel phase of surface area of $300\,\mathrm{m}^2\,\mathrm{gm}^{-1}$ and amounting to at least 1% by weight of the sample.

Brinker [10] has shown that consolidation of hydroxylated silica gels can take place with associated loss of weight and decrease in surface area at temperatures as low as 200° C. Scherer has observed consolidation of leached borosilicate glasses (in which the residual structure is a hydroxylated silica network) in this same region of temperatures [11]. In those experiments consolidation resulted in shrinkage of specimens. In the chert used in the present experiments, the particles in the porous region were already in contact with each other before the gel phase around them began to consolidate. As a consequence, the consolidation of the gel phase did not produce a change in specimen dimensions. However, it may have produced internal stresses which resulted in perturbations in direction of crack propagation and the macroscopic deviations out of the fracture plane which were observed in heat-treated chert.

It is worth noting that the relatively large changes in mechanical behaviour obtained by heat treating chert involve modest changes in a small fraction of the material. The analogy of the structure of the dense zones separated by relatively weaker interfaces to the structure of a polycrystalline ceramic is also suggestive. The implication is that toughening might be achieved in a ceramic by making the grain boundaries weak and irregular.

4. Conclusions

The changes in fracture toughness, elastic modulus, resistance to chipping and fracture surface texture which are produced by heating Ocala chert to 500° C result from a change in bonding in porous regions within the chert. The change in bonding is obtained through consolidation of a gel phase in these porous regions.

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