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THE EFFECT OF OXIDATION EMBRITTLEMENT ON THE IMPACT BEHAVIOR OF NICALON REINFORCED CAS II CERAMIC MATRIX COMPOSITES

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stress and dynamic fracture toughness of CAS II composites when fractured in impact. It was further demonstrated that specimens reinforced with mica-coated Nicalon fibers are more susceptible to oxidation embrittlement than specimens reinforced with standard Nicalon fibers.

ABSTRACT

The impact behavior of Nicalon reinforced CAS II composites is described. Impact tests of samples loaded to 1.0 micro-cracking yield and heated to 600°C for 10 hours were compared to tests of as received samples to determine the degree of degradation caused by the treatment. In addition, samples which were loaded to 1.0 micro-cracking yield but not heated and samples which were heated to 600°C for 10 hours were compared to isolate the effects of pre-cracking and heating. It was demonstrated that oxidation embrittlement has a negative effect on the maximum stress and dynamic fracture toughness of CAS II composites when fractured in impact. It was further demonstrated that specimens reinforced with mica-coated Nicalon fibers are more susceptible to oxidation embrittlement than specimens reinforced with standard Nicalon fibers.

INTRODUCTION

Structural applications of ceramics have been limited by their low toughness. A ceramic matrix will crack at very low tensile stress levels. In order to improve toughness, ceramic matrix composites (CMC's) have been developed. CMC's gain toughness by means of a fiber pullout mechanism. After matrix cracking, the weak bonds between fiber and matrix allow the fibers to pull out of the matrix. This mechanism allows a CMC to continue to support a load after matrix cracking occurs. The frictional pullout absorbs energy and increases the toughness of the composite. Impact toughness measurements which illustrate this fracture pullout mechanism have been reported for lithium aluminosilicate (LAS) CMC's [1,2].

Essential to the fiber pullout mechanism are carbon based fibers, such as Nicalon, which have a carbon-rich layer at the interface between matrix and fiber. At temperatures above $450^{\circ}C$, however, this layer could be destroyed by oxidation [3]. As a result, the strength and toughness properties of the composite could be degraded. For example, detrimental oxidation embrittlement (OE) effects have been observed in LAS/Hybrid composites that were heated in flowing oxygen [4]. In order to further illustrate the OE phenomena, a process of pre-cracking specimens to specified levels of the micro-cracking yield stress and heating them in air was suggested by Chyung [3]. The micro-cracking yield stress (MCY) is defined as the point at which the matrix first cracks. It is determined from the first point of deviation from linearity on the load vs.

deflection curve. A schematic load vs. deflection curve for a flexure test is given in fig. 1. Pre-cracking may allow more oxygen to reach the fiber-matrix interface and accelerate the OE process.

In order to determine the degree of OE degradation caused by various thermal and/or mechanical treatments, the concept of residual strength in CMC's was suggested. Residual strength is defined as the ratio of the fracture strength of a treated specimen to an untreated specimen. Residual strength results for tensile and flexure tests of Nicalon reinforced CAS II CMC's have been reported [3]. The effect of OE on the residual impact fracture toughness, however, has not been reported.

The objective of this study is to determine the effects of pre-cracking and oxidation embrittlement on the residual impact behavior of Nicalon reinforced CAS II composites.

EXPERIMENTAL DETAILS

Materials

The CMC's used in these tests consisted of a Corning calcium aluminosilicate (CAS II) matrix reinforced with Nicalon fibers. Some samples contained standard uncoated Nicalon fibers; others contained potassium fluorophlogopite (KFP) mica coated Nicalon fibers. The intent was to determine whether the KFP coating provided improved resistance to oxidation embrittlement. The CMC's were obtained in the form of subscale Charpy impact specimens, 6mm X 6mm X 55mm. All samples were unidirectional composites fabricated by hot-pressing. Some samples were face notched (L-S) and some were edge notched (L-T). Notch orientations are shown in figure 2. Notch depth ratio, a/W, was 0.2.

For comparison purposes, oxidation embrittlement data from a UTRC hybrid material is included. The material consisted of a ceramed lithium aluminosilicate (LAS) matrix reinforced with SCS-6 monofilament and standard Nicalon fibers. The samples were 0/90° Charpy specimens notched L-T, with a/W=0.2.

Methods

Two CAS II/Nicalon and two CAS II/KFP specimens (one L-S and one L-T of each material) were tested to failure in three point bending in order to determine the MCY of the materials. A schematic load vs. deflection curve is shown in figure 1.

Next, several specimens were subjected to thermal and/or mechanical treatments. Using the information from the flexure tests, two Nicalon and two KFP samples (one of each orientation) were loaded to 1.0 MCY in three point bending. After pre-cracking, the specimens were optically examined at 20X and no surface damage was visible. The specimens were then heated to 600°C in a furnace in lab air for 10 hours. The purpose of this treatment was to expose the micro-cracked composite to an oxidizing environment. To separate the effects of pre-cracking and heating, two KFP L-S specimens were loaded to 1.0 MCY in three point bending and not heated. In addition, one Nicalon L-S and one KFP L-S sample were not pre-cracked and were heated to 600°C in lab air for 10 hours.

The final step of the procedure was to impact test the specimens. Two as received Nicalon (L-S and L-T) and two as received KFP (L-S and L-T) samples were tested to provide a standard with which the treated specimens could be compared. The thermal and/or mechanically treated specimens were then tested. All impact tests were conducted at room temperature using an instrumented tup impact drop tower. Impact test velocity was 1.5 m/s.

To determine oxidation embrittlement effects in the LAS hybrid material, one specimen was impact tested as received. The other specimen was heated to 800°C for 64 hours in flowing oxygen, then impact tested at room temperature.

Macrofractography was performed utilizing a low-magnification (20X) stereo optical microscope. Also, microfractography was performed using a scanning electron microscope (SEM).

DATA REDUCTION

The instrumented tup impact tests produced load vs. time curves. Computer software integrated these curves utilizing instantaneous velocities to produce energy vs. time curves. From these curves, the maximum load and maximum energy were determined. These values, were then used to calculate maximum stress (σ_{max}), estimated plane strain fracture toughness (K_q), and maximum dynamic energy absorbed per cross-sectional area (U_d) for each specimen. The equations used to calculate these values are:

$$\sigma\,max = \frac{3P_{max}L}{2B(W-a)^2} \qquad (1)$$

$$U_d = \frac{\text{Total energy absorbed}}{B(W-a)} \qquad (2)$$

$$K_q = \frac{P_{max}L}{BW^{(3/2)}} * f(a/W) \qquad (3)$$

where:

$$f(a/W) = \frac{3(a/W)^{(1/2)}[1.99-(a/W)(1-a/W) X(2.15-3.93a/W+2.7a^2/W^2)]}{2(1+2a/W)(1-a/W)^{(3/2)}} \qquad (4)$$

Equations (3) and (4) are taken from reference 5.

RESULTS AND DISCUSSION

The results from the flexure tests are given in table 1. In both the Nicalon and KFP materials, the L-T orientation had a slightly higher MCY stress than the L-S orientation, as would be expected. With the exception of the KFP L-S sample, σ_{max} is essentially the same for uncoated fiber (Nicalon) and coated fiber (KFP) specimens.

The results from the impact tests of as received specimens are given in table 2. This data shows that, when tested in impact, KFP specimens have a higher U_d than Nicalon specimens. A comparison of the load vs. time and energy vs. time curves for a Nicalon and a KFP sample is shown in figure 3. It can be seen that the increase in U_d for the KFP sample results from higher loads in the tail of the curve. This indicates that the as received KFP specimens experience greater fiber pullout than the as received Nicalon specimens. The slight difference in K_q values between Nicalon and KFP is due to the fact that the K_q calculation is based on the maximum load absorbed by the specimen.

Due to the availability of KFP L-S samples, this material and orientation was used to thoroughly examine the effects of mechanical and thermal treatments. Table 3 gives the results of the KFP L-S impact tests. The data shows that pre-cracking alone has essentially no significant effect on the U_d of the material. In fact, the pre-cracked specimens have a slightly higher U_d than the as received specimens. There is no apparent explanation for this result. The data further shows that thermal treatment does have a significant effect on the U_d of the material. The thermal treated KFP L-S specimen experienced a 75% decrease in U_d compared to the as received specimens. This indicates that thermal exposure (which can be assumed to cause OE) severely degrades the fiber pullout mechanism in specimens with KFP-coated fibers, thus decreasing U_d. The pre-cracked and thermal treated KFP L-S sample experienced a 55% decrease in U_d compared to as received. It was intuitively expected that the pre-cracked and thermal treated sample would yield a lower U_d than the sample which was thermal treated only. However, the opposite was true. There is no apparent explanation for the difference.

In contrast to the behavior of the KFP specimens, pre-cracking and thermal treatments had essentially negligible effects on the U_d of Nicalon L-S samples, as given in table 4. This implies that the energy-absorbing fracture mechanism in Nicalon specimens is not significantly degraded by pre-cracking or thermal exposure. The load vs. time curves given in figure 4 show the effects of thermal treatment of KFP specimens compared to Nicalon specimens, clearly indicating that CAS II/KFP composites are more susceptible to oxidation embrittlement damage than are CAS II/Nicalon composites.

It was observed that in all CAS II comparisons, the behavior of as received and thermal treated samples was essentially the same up to the point of maximum load. Figure 4 shows that the slopes of the load vs. time curves for as received and thermal treated samples are initially the same. This indicates that the thermal treatment has no effect on the stiffness of the composite. OE degradation in the KFP specimens is shown in fig. 4(a) by the differing loads in the tails of the curves. The as received specimen sustained greater loads for a longer period of time, thus increasing impact fracture toughness. In fig. 4(b), the tails of the curves are nearly identical. Therefore, there is no significant difference in energy absorbed for the Nicalon specimens.

A representative fracture macrograph is shown in figure 5. It was observed that the fracture surfaces of all specimens were characterized by narrow, pointed ridges, or laminae, of intact matrix and fibers running parallel to the sample notch, some extending up to 5mm from the fracture surface. The edges of these laminae were jagged and featured numerous small points or peaks. The pullout of these ridges and peaks could absorb energy similar to the fiber pullout mechanism, but on a lesser scale.

For comparison, fracture macrographs of LAS/Nicalon specimens show fiber pullout of approximately 4mm [6]. In the present tests, both Nicalon and KFP specimens show fiber pullout much less than 1mm.

Additional visual examination of the as received specimens revealed that the KFP samples exhibited slightly more individual fiber pullout than did the Nicalon samples. The Nicalon samples were characterized by high laminar pullout. The KFP samples showed some laminar pullout, but many short individual fiber ends were also visible. This supports the result that the as received KFP specimens displayed a higher U_d than the Nicalon specimens.

Further visual examination of the pre-cracked and thermal treated Nicalon specimens revealed no significant differences from the as received appearance. The fracture surfaces were all characterized by highly laminar pullout. The pre-cracked and thermal treated KFP samples differed from the as received appearance. The treated samples exhibited more laminar pullout than the as received, and very few individual fibers were visible. This supports the result that KFP specimens are more affected by pre-cracking and thermal exposure than Nicalon specimens. It further indicates that the laminar pullout absorbs less energy than individual fiber pullout. Finally, comparison of a thermal treated KFP sample and a pre-cracked and thermal treated KFP sample showed identical fracture appearances. This indicates that the majority of degradation is due to thermal exposure and not pre-cracking.

The SEM micrographs given in figure 6 are representative of both Nicalon and KFP specimens. The fiber pullout illustrated in fig. 6 was not characteristic of the entire fracture surface. Rather, the areas shown were localized regions located within the laminae discussed earlier.

For comparison, Chyung's results [3] showed a 25% decrease in σ_{max} for CAS II/Nicalon specimens pre-cracked and fractured in tension. His specimens were pre-cracked to 0.9 MCY and heated to 600°C for 10 hours [3]. The present impact test results show a 17% decrease in σ_{max} for pre-cracked and thermal treated Nicalon specimens. This indicates that CE has a slightly greater negative effect on Nicalon samples tested in tension than in impact. No previous data from tension tests on CAS II/KFP specimens was available for comparison.

In the LAS hybrid material, heating without pre-cracking resulted in a U_d decrease of 50%, dropping from 8.2 J/cm^2 to 4.1 J/cm^2. This reduction is similar to that observed in CAS II/KFP specimens.

CONCLUSIONS

The following conclusions are made:

1. In static flexure tests, there is no significant difference between the performance of CAS II/Nicalon and CAS II/KFP composites.
2. Impact tests of as received specimens with KFP-coated Nicalon fibers exhibit a higher U_d than specimens with uncoated Nicalon fibers. The KFP coating enhances the fiber pullout mechanism.
3. In impact tests of thermal treated specimens, KFP exhibits a lower U_d than Nicalon. KFP specimens are more susceptible than Nicalon specimens to oxidation embrittlement damage.

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Table 1: Bend Test Results for CAS II Composites

Material	Orientation	MCY Load N	MCY Stress MPa	σ_{max} MPa
CAS II / Nicalon	L-S	890	491	887
CAS II / Nicalon	L-T	1290	671	952
CAS II / KFP	L-S	979	426	562
CAS II / KFP	L-T	1201	572	978

Table 2: Impact Characteristics of As Received CMC's

Material	Orientation	σ_{max} MPa	K_q Mpa-$m^{1/2}$	U_d J/cm^2
CAS II / Nicalon	L-S	887	37.0	9.9
CAS II / Nicalon	L-T	820	29.8	9.0
CAS II / KFP	L-S	758	29.1	13.7
CAS II / KFP	L-S	818	31.9	14.8
CAS II / KFP	L-T	952	37.0	13.3

Table 3: Effect of Pre-cracking and/or Thermal Exposure on the Impact Characteristics of CAS II / KFP Specimens

Material	Orientation	σ_{max} MPa	K_q Mpa-$m^{1/2}$	U_d J/cm^2
Untreated CAS II / KFP	L-S	758	29.1	13.7
Untreated CAS II / KFP	L-S	818	31.9	14.8
Pre-cracked[1] CAS II / KFP	L-S	762	29.1	15.0
Pre-cracked CAS II / KFP	L-S	953	37.2	15.9
Thermal Treated[2] CAS II / KFP	L-S	474	18.4	3.8
Pre-cracked & Thermal Treated[3] CAS II / KFP	L-S	658	24.7	6.6

[1] Specimens were pre-loaded to 1.0 MCY.

[2] Specimen was heated to 600°C for 10 hours in laboratory air.

[3] Specimen was pre-loaded to 1.0 MCY and heated to 600°C for 10 hours.

Table 4: Effect of Pre-cracking and/or Thermal Exposure on the Impact Characteristics of CAS II / Nicalon Specimens

Material	Orientation	σ_{max} MPa	K_q Mpa-$m^{1/2}$	U_d J/cm^2
Untreated CAS II / Nicalon	L-S	887	37.0	9.9
Thermal Treated[1] CAS II / Nicalon	L-S	717	27.8	9.7
Pre-cracked & Thermal Treated[2] CAS II / Nicalon	L-S	740	28.5	9.1

[1] Specimen was heated to 600°C for 10 hours in laboratory air.

[2] Specimen was pre-loaded to 1.0 MCY and heated to 600°C for 10 hours.

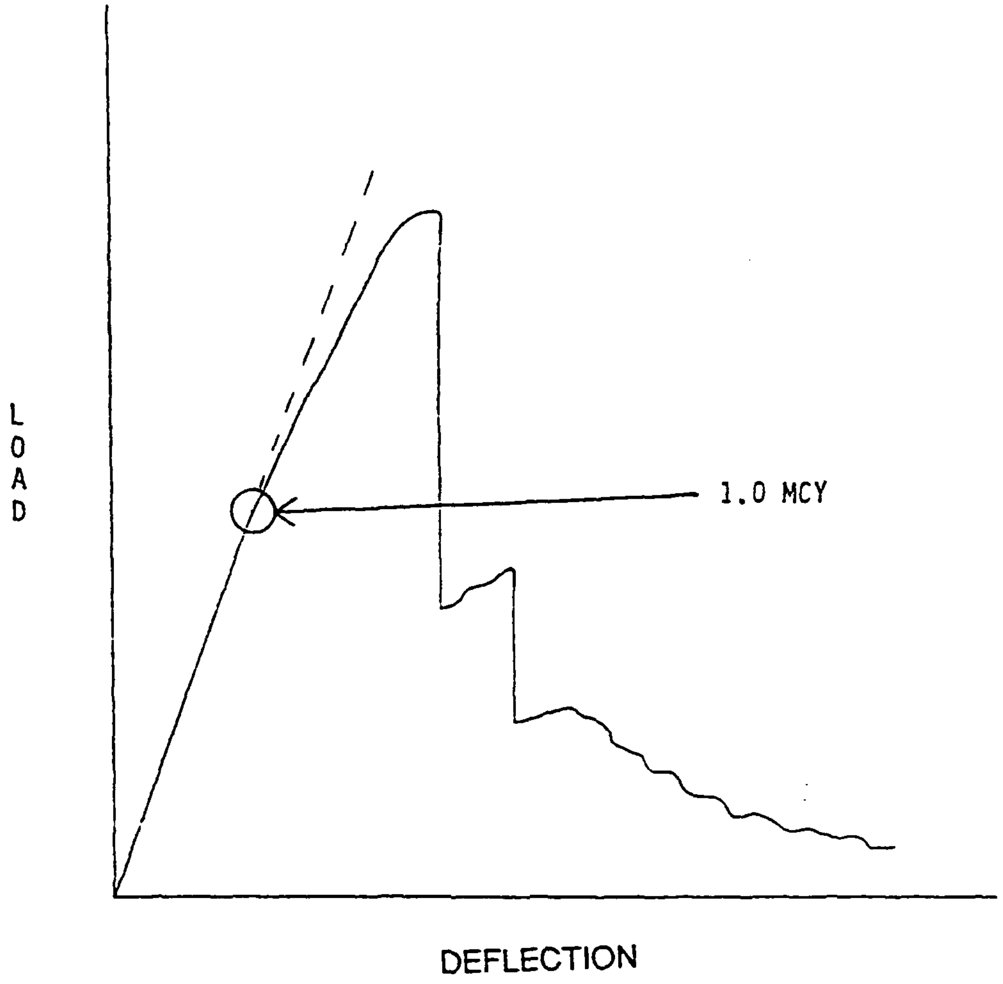
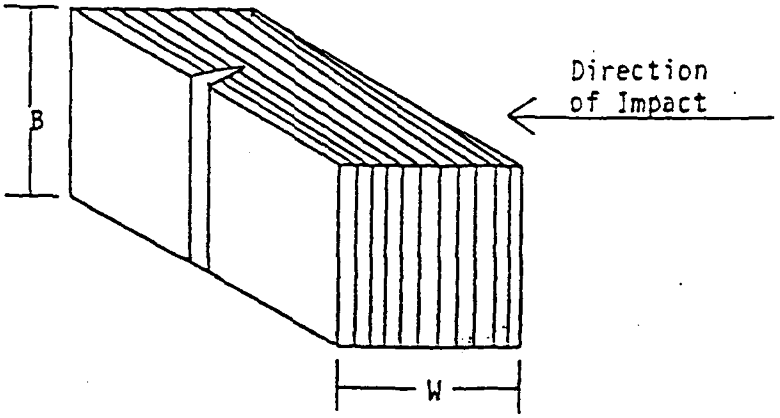
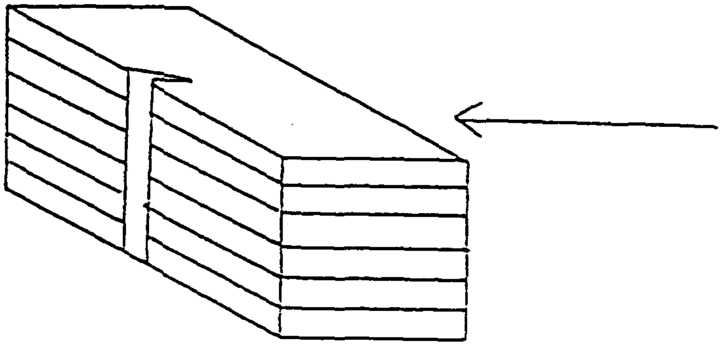


Figure 1-Schematic Load vs. Deflection Plot for a 3-pt. Flexure Test



(a) Face Notched (L-S)



(b) Edge Notched (L-T)

Figure 2-Schematic of Notch Orientations

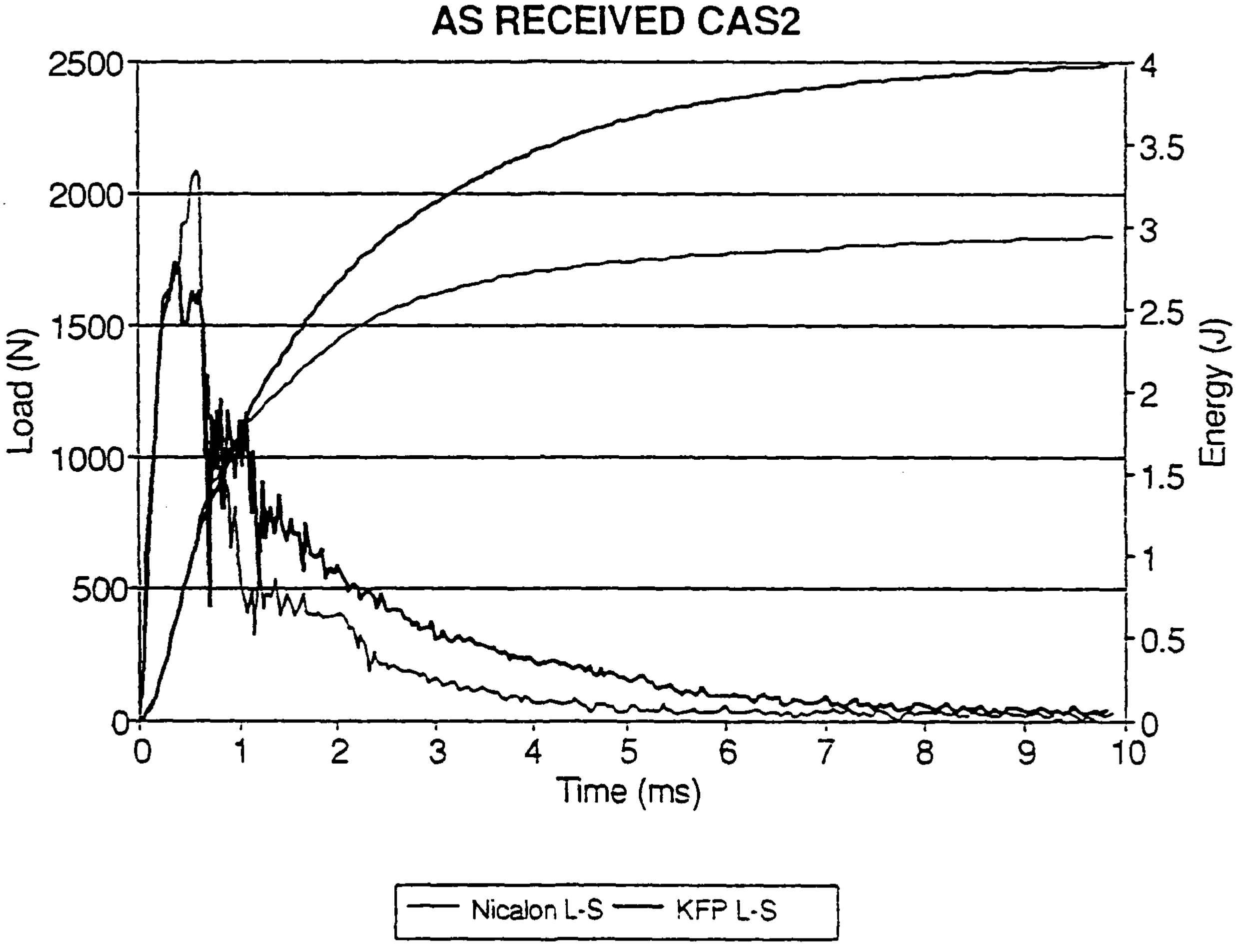
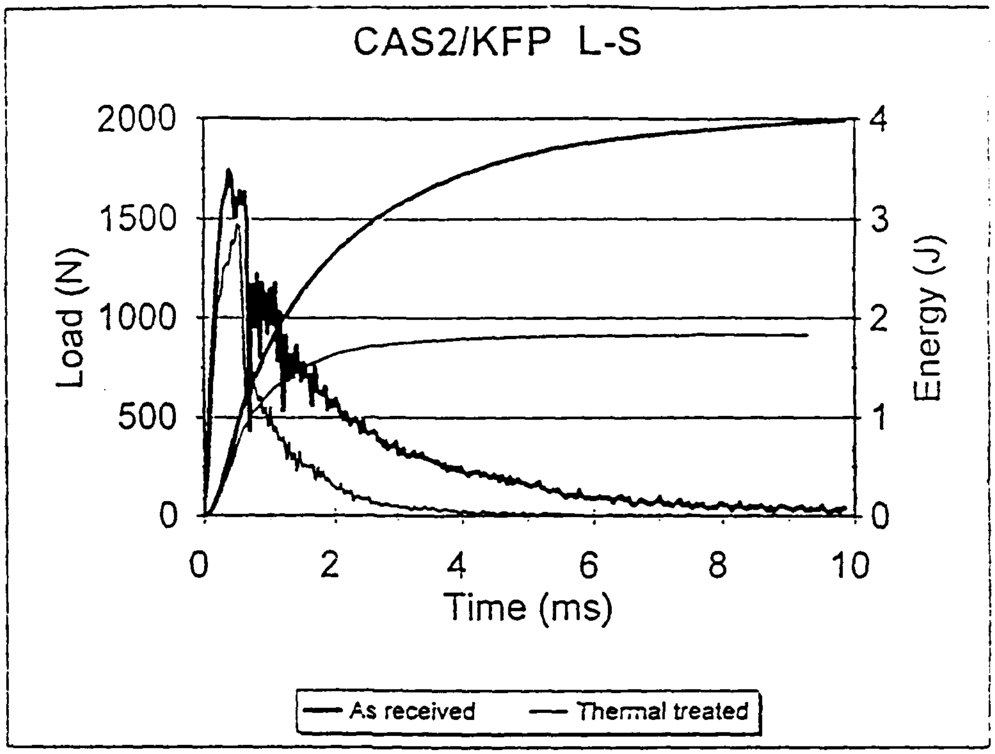
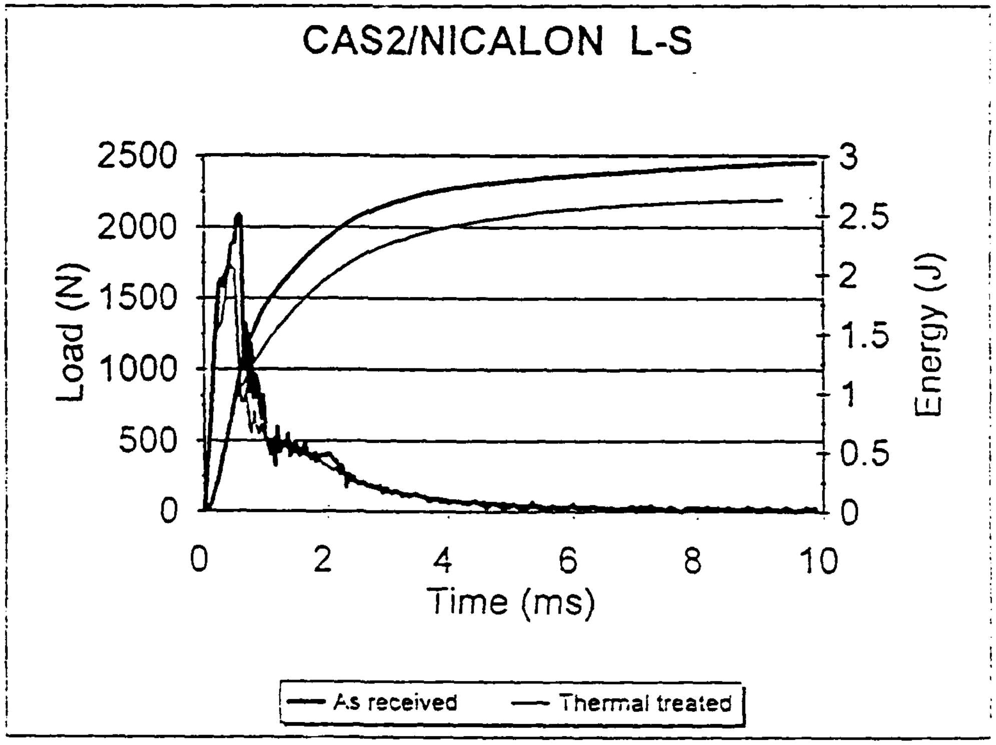


Figure 3-Comparison of load and energy vs. time curves for CAS2



(a)



(b)

Figure 4-Effect of thermal treatment on impact energy for (a) CAS2/KFP and (b) CAS2/Nicalon

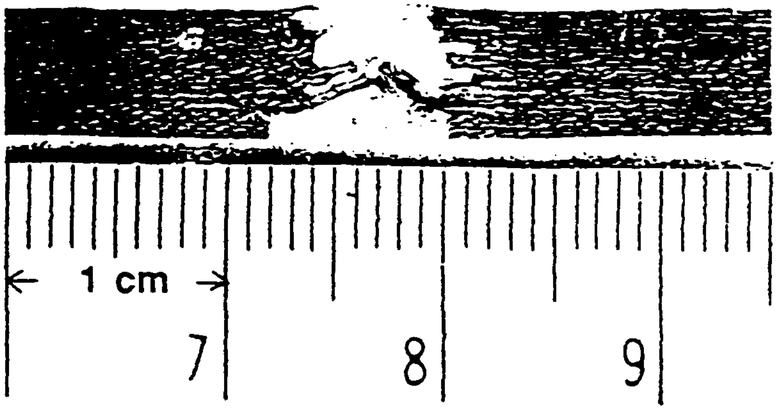
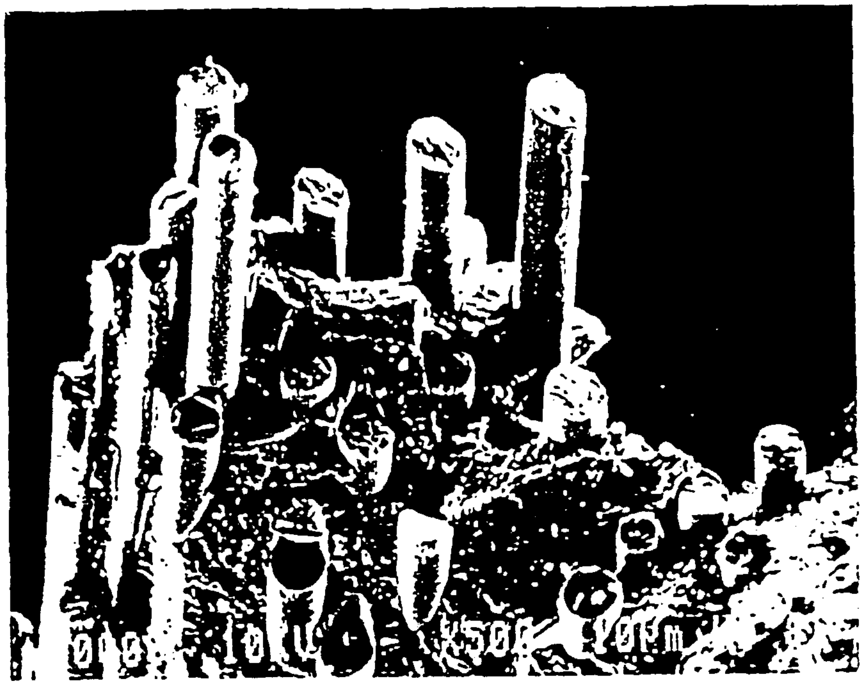
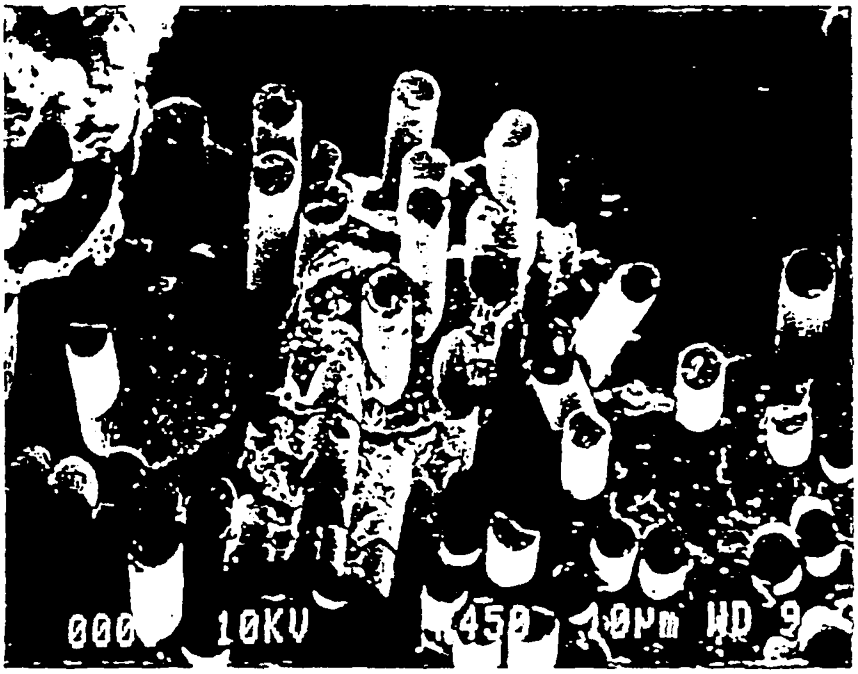


Figure 5-Representative macrograph of impact tested CAS II CMC



(a) As received



(b) Thermal treated

Figure 6-Comparison of as received and
thermal treated CAS2 Nicalon
fracture features, L-T orientation