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STRESS-RUPTURE OF NEW TYRANNO Si-C-O-Zr FIBER REINFORCED MINICOMPOSITES

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ABSTRACT

Minicomposites consisting of two varieties of Zr containing SiC-based fibers from Ube (Tyranno) with BN interphases and CVI SiC matrices were studied. The two fiber-types were the ZMI and ZE fiber-types that contain approximately 8 and 2% oxygen, respectively. The minicomposites were precracked and tested under constant load testing at temperatures ranging from 700 to 1200°C. The data were then compared to the rupture behavior of Hi-Nicalon™ fiber reinforced minicomposites tested under identical conditions. It was found that the Ube fiber-types had stress rupture life equivalent to Hi-Nicalon™ over the entire temperature range. A potential benefit of the ZMI fiber-type is that it offers rupture properties almost as good as Hi-Nicalon™ at the cost of ceramic grade Nicalon™.

INTRODUCTION

The polymer-derived Ceramic Grade Nicalon™ (NIC) [1] and Hi-Nicalon™ (HN) [2] SiC-based fiber-types produced by Nippon Carbon are the most used and most mature commercially available SiC-based fiber-types. Processing of HN includes an irradiation curing step which reduces the oxygen content of this fiber (~ 1 w/o O) compared to NIC (~ 10% O). This results in a fiber that has greater thermal stability and improved creep resistance over NIC. Unfortunately, it also results in a significantly more expensive fiber.

The high temperature properties for constant-load tests of these fibers are now well known as well as the high temperature properties of many composite systems processed with these fibers. High temperature stress-rupture and creep testing have been reported for these fibers by Bodet et al. [3] and Yun and

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DiCarlo[4]. The rupture of single-tow minicomposites with these fibers has also been reported for various temperatures in air [5,6].

More recently, SiC-based fibers [7] have been developed by Ube Industries which contain small amounts of Zr (1 w/o) in the composition. These fibers have similar oxygen contents and SiC crystallite sizes for air-cured (ZMI: 8 w/o O) and irradiation cured (ZE: 2 w/o O) fibers compared to NiC and HN, respectively. The high temperature strength and retained strength for fibers subjected to elevated temperature heat treatments were very good for both Ube fibers. This is especially surprising for the ZMI fiber since it contains a high oxygen-content which usually correlates with poor thermal stability properties.

However, little if any high temperature data has been reported for the fibers themselves or for composites processed with these fibers. In this study, single tows of ZE and ZMI fibers were coated with a boron nitride interphase and composited with a CVI SiC matrix to form minicomposites. The stress-rupture properties of the minicomposites were then determined at elevated temperatures in order to compare the rupture properties of these Ube fiber minicomposites with the Nippon fiber minicomposites tested in earlier studies [5,6].

EXPERIMENTAL

Some properties of the Ube fibers used in this study as well as the Nippon Carbon fibers used in the other studies [5,6] are listed in Table I.

Table I: Properties of Ube and Nippon Fibers from Product Literature

Fiber	Filaments in tow	Fiber diameter, μm	Elastic Modulus, Gpa	Tensile Strength, MPa	Oxygen Content, w/o
NIC	250	14	210	3000	11.7
HN	500	14	270	2800	0.5
ZMI	800	13	210	3070	7.9
ZE	400	13	234	3260	2.0

Minicomposites were fabricated as described in an earlier study [5,6]. Boron nitride coating was performed on a continuous tow-coater at 1400°C*. The boron nitride coated at this temperature is more stable than BN coatings deposited at lower temperatures and will be referred to as PBN (pyrolytic BN). The coated tow was then wound on graphite racks and was infiltrated with CVI SiC** to form single-tow unidirectional minicomposites with a fiber volume fraction of ~ 0.15.

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Several minicomposites were tensile tested to failure at room temperature in order to determine a sufficient load for precracking based on the non-linearity in the load-time curve and acoustic emission activity [8]. This load ranged from 70 to 85 % of the ultimate load to failure for the minicomposites and corresponded to a matrix crack spacing on the order of 1mm.

Precracked minicomposites (gage length ~ 150 mm) were cold-gripped and dead-weight loaded. A 35 mm C-clamp SiC element resistance-heated furnace was inserted around the gage section. The hot zone of the furnace was ~ 12 mm and the temperature profile of the furnace was well characterized. As in the earlier studies, tests were performed at 700, 950, and 1200°C (at the center of the hot zone).

RESULTS

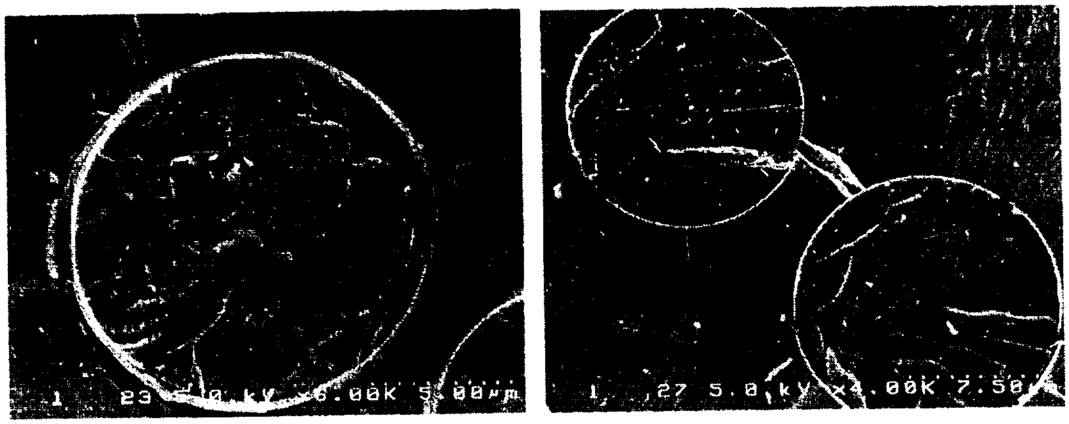
The room temperature properties of the minicomposites are shown in Table II for the minicomposites tested in this study and in earlier studies. The failure stress determined in the table was determined by dividing the failure load by the cross-sectional area of the fibers in the tow. Note that all of the fiber strengths are greater than 2000 MPa except for the ZMI-PBN minicomposites. For the NIC and HN minicomposite systems, the BN interphase was usually at least 0.4 μm thick [5,6]. For the ZMI minicomposites, the exterior fibers had a 1 μm thick BN layer (Figure 1a), whereas the interior fibers had a ~ 0.1 μm thick BN layer (Figure 1b). ZE minicomposites had some similar thin interphase regions but not to the same extent as for ZMI minicomposites, probably because there were fewer fibers per tow for ZE (Table I). Pullout of ZMI and ZE fibers with thin interphases was usually less than a fiber diameter whereas pullout of ZMI and ZE fibers with thicker interphases was on the order of several hundred microns. The predominantly thin interphase for ZMI and ZE probably accounts for the poor ultimate strength properties of these minicomposite systems.

Table II: Room Temperature Minicomposite Strength Properties

Minicomposite	Number Tested	Avg. Failure Load, N	Avg. Failure Stress on Fibers if Fully Loaded, MPa
ZE – PBN	3	114 ± 17	2100 ± 300
ZMI – PBN	4	171 ± 8	1800 ± 100
NIC – 3MBN[b]	4	980 ± 10	2400 ± 100
HN – 3MBN[b]	4	140 ± 10	2100 ± 100
HN – PBN	Several batches[a]	140[5] to 186[6]	2100 [5] to 2750 [6]

[a] The loads to failure and room temperature stress are for the widest range of values obtained from different batches of minicomposite. To date, four batches have been fabricated for this system and all fall in the range specified in Table II.

[b] BN deposited at ~ 1050°C by 3M Corporation, St. Paul Minnesota



(a) (b)

Figure 1: SEM micrographs of fibers from ZMI-PBN minicomposite after room temperature fracture. (a) is an exterior fiber and (b) are interior fibers. Note the thin interphase for the interior fibers.

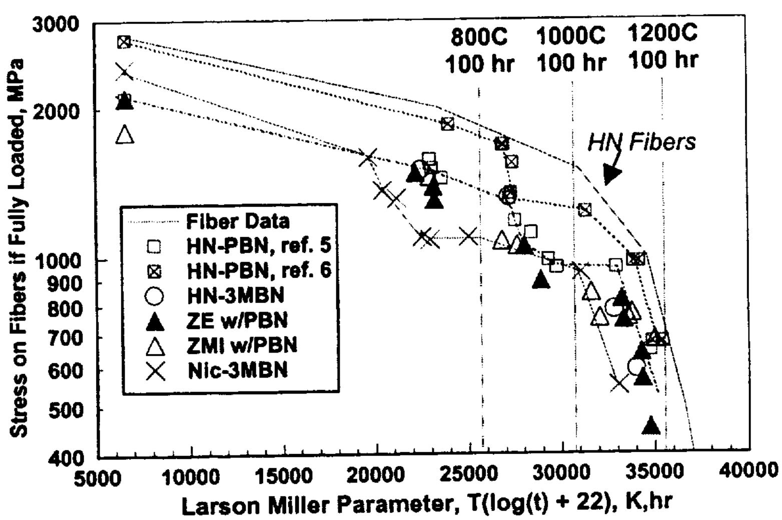


Figure 2: Absolute stress Larson-Miller plot of SiC-fiber/BN interphase CVI-SiC minicomposites.

The high temperature stress-rupture data are shown in Figures 2 and 3. The stress data is plotted versus a temperature compensated time "Larson-Miller" parameter. The Larson-Miller parameter was determined from the relationship:

$$LM = T\,[\log(t) + 22] \quad (1)$$

where T is the temperature in K and t is time in hours. This relationship was found to best fit the NIC and HN rupture data [4]. The actual "Larson-Miller" relationship has not yet been determined for the Ube fibers. However, the plots are used here for comparing all of the minicomposite rupture data and the rupture properties of as-produced HN and NIC on a single curve.

Figure 2 is a plot of the absolute stress on the fibers whereas Figure 3 is a plot of the normalized stress on the fibers. For HN-PBN, minicomposite strengths can vary for different batches (Table II). Figure 2 shows the two most extreme ultimate and rupture strengths for two different minicomposite batches over the entire temperature range (25°C to 1200°C). However, the data normalized with room temperature ultimate strength are identical for the two different batches of HN-PBN (Figure 3). In addition, other data corresponding to a batch of minicomposites tested recently, "HN-PBN 1998", is plotted in Figure 3 which correlates well with the other HN-PBN data. Also plotted is HN-3MBN [5]. This minicomposite system consists of HN fibers fabricated with a lower processing temperature BN. Even though this BN was processed at lower temperatures little difference was observed in the rupture properties of this minicomposite system when tested in air. However, in higher water containing environments, significantly greater amounts of interphase oxidation and recession have been observed [9].

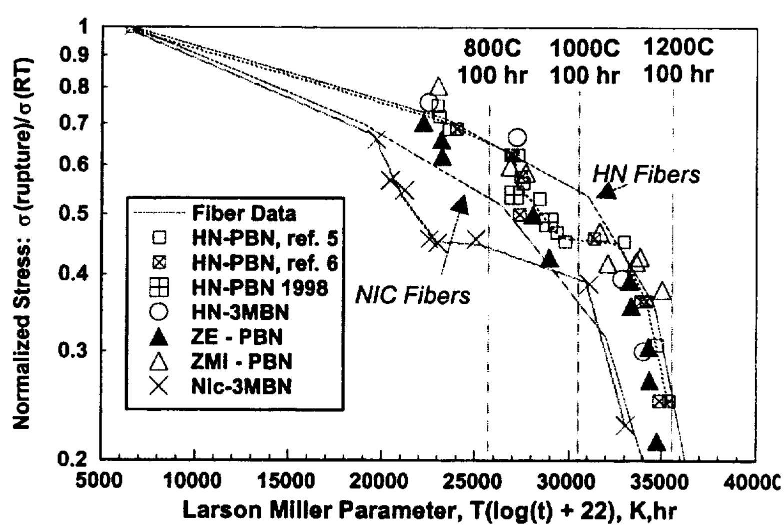


Figure 3: Normalized stress Larson-Miller plot of SiC-fiber/BN interphase CVI-SiC minicomposites.

At low (< 900°C) and high (> 1050°C) temperatures, the HN-BN minicomposites show rupture behavior similar to the rupture of as-produced fibers. At intermediate temperatures (1050°C > T > 900°C), the minicomposite rupture strengths fall below the as-produced fiber rupture strengths. This "embrittlement" was shown to be due to the oxidation of the interphase resulting in some weakening of the fibers and strong bonding of the fibers to the matrix [5,6].

Also shown in Figures 2 and 3 are data from NIC-3MBN minicomposites [5,8]. The lower processing temperature interphase had to be used for NIC minicomposites because the NIC fibers were severely degraded after PBN coating. The NIC-3MBN minicomposites also show the same fiber-dominated rupture behavior at low (< 700°C) and high (> 1000°C) temperatures and an intermediate temperature decrease in the load carrying ability of the minicomposites compared to the as-produced fiber data (Figure 3). The rupture strengths of NIC fibers are lower than the HN fibers as can be seen in Figure 3.

The room temperature ZE minicomposite ultimate strengths correspond to the low range of HN minicomposite ultimate strengths. The ZMI ultimate strengths are below the HN and NIC minicomposite room temperature strengths. The high temperature data for ZE and ZMI minicomposites also fall in the low range or below the rupture strengths obtained for the HN minicomposites (Figure 2). However, the ZE and ZMI rupture data are better than the NIC minicomposite data at elevated temperatures even though the room temperature strengths are lower for ZE and ZMI minicomposites than for NIC minicomposites (Figure 2). When the ZMI and ZE minicomposite data are normalized with room temperature strength, the rupture behavior is nearly identical to the HN-PBN minicomposites and significantly better than the NIC-3MBN minicomposites (Figure 3).

It is evident that the ZE and ZMI minicomposites are performing as well as HN-PBN minicomposites for tensile rupture conditions in air. It would be expected that with thicker interphases, the ZMI minicomposite strengths would increase as well as the absolute rupture strengths. However, the normalized rupture strengths would be expected to remain the same as is the case for HN-PBN minicomposites.

This result is not too surprising for ZE minicomposites since ZE fibers are processed similarly to HN fibers. The rupture behavior of ZMI minicomposites is somewhat surprising since this fiber-type contains a significant amount of oxygen. The claim that the thermal stability of ZMI is as good as ZE, and in this study HN as well, by Kumagawa et al [7] appears to be true not only for retained strength properties after heat treatment [7], but also for elevated temperature stress-rupture conditions as well.

The significance of this result is economic. At the time this report was written, the ZMI fiber-type was about one-fifth the price of ZE or HN fiber-types, i.e. about the same price as NIC. The savings that would be gained using the ZMI fiber-type in place of ZE or HN in the fabrication of a BN interphase composite with a CVI or melt-infiltrated SiC matrix could be as much as 50%* [10].

CONCLUSION

Minicomposites fabricated with the Zr-containing SiC fibers, ZMI and ZE, have the same elevated temperature stress-rupture properties as minicomposites fabricated with Hi-Nicalon™ fibers on a relative stress basis and significantly better stress-rupture properties than minicomposites fabricated with Nicalon™ fibers. Some improvement in rupture-strength and room temperature strength is expected if thicker interphase coatings were achieved for the ZMI and ZE minicomposites. The significance of this is that the ZMI fiber can be considered an inexpensive fiber choice, compared to ZE and Hi-Nicalon™, as the reinforcement for ceramic matrix composites aimed at higher temperature applications.

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* This approximation was based on the cost to fabricate 8-ply woven (5 harness satin) 6 in. x 9 in. plates of MI and CVI SiC composites. For example, the cost of a composite plate fabricated with HN fibers is $3500 whereas the same plate fabricated with NIC or ZMI fibers would be $2300.[10]

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