Interfacial effects in a metallic–glass ribbon reinforced glass–ceramic matrix composite

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The effect of temperature on the interfacial effects in a metallic–glass ribbon reinforced glass–ceramic matrix composite was investigated. The metallic–glass ribbon present in this composite was found to be significantly affected at elevated temperatures, owing to the diffusion of lead and zinc from the matrix. The presence of the matrix in the vicinity of the ribbon enhanced the formation of an oxide layer on the ribbon surface. The oxide layer decreased the interfacial bond strength between the ribbon and the matrix, affecting the failure mode of such composites at elevated temperatures.

1. Introduction

The potential of using metallic-glass ribbons as reinforcements for a brittle glass-ceramic matrix has been demonstrated [1-8]. The studies carried out so far have indicated the tremendous potential of developing such composites for structural applications. The elevated temperature strength of the metallic-glass/ glass-ceramic matrix composites has also been studied [5]. The results indicated that the interface behaviour had a significant effect on the overall strength and also the failure mode in such composites. Alteration of the interface changes the interfacial bond strength, and thereby affects the failure mode as a function of temperature. A proper understanding of this phenomenon would make it possible to tailor the interface in such composites for optimum strength and toughness for high temperature applications.

The thermal shock resistance of such composites is also of concern since they have significant implications on the feasibility of using such metallic–glass ribbon reinforced glass–ceramic matrix composites for elevated temperature structural applications.

2. Experimental procedure

2.1. Specimen preparation

The composite specimens used were fabricated using METGLAS 2605S-2 as the reinforcement and Corning Glass 7572 as the matrix. The rectangular barshaped specimens were prepared using conventional wet pressing techniques. The process of making the composite resulted in crystallization of the parent glass matrix. Details of the specimen fabrication process are provided elsewhere [8].

2.2. Interfacial studies

The purpose of these tests was to observe the interface, and if possible provide an explanation for the observed decrease in the interfacial bond strength as a function of temperature. The fractured surfaces of the samples that were heated to various temperatures for 90 min, were studied using scanning electron microscopy (SEM). Temperatures of 450, 400, 300 and 200 °C were used for this purpose. These temperatures were selected based on observations from earlier studies, and were also similar to the ones used for the thermal shock testing. Energy dispersive analysis (EDAX) studies were also carried out on these sample surfaces to determine compositional differences across the ribbon-matrix interface. The crystalline phases in various sections were determined by X-ray analysis.

2.3. Thermal shock testing

Tests to evaluate the thermal shock resistance of both the matrix and composite specimens were carried out using procedures described in the literature [9–11]. The surfaces of the specimens were ground to a 600 grit paper finish. The specimens were then heated in a resistance furnace for a total period of 90 min at temperatures of 200, 250, 300, 400 and 450 °C. After heating, the specimens were quenched in water (at a temperature of 42 °C). The specimens were allowed to cool for a period of 5 to 10 min prior to mechanical testing. Three point bend tests were performed on the thermally shocked specimens using an Instron machine with a cross head speed of 0.05 cm per minute.

3. Results and discussion

The micrographs of the fractured surfaces of the three point bend tested samples maintained for 90 min at temperatures and quenched in water are provided in Figs 1, 2 and 3. Fig. 1a is the fracture surface of a sample in the fabricated condition without any additional thermal exposure. The interface between the



Figure 1 Fractured surface of the composite sample in the as fabricated state. (a) The ribbon matrix interface; (b) enlarged view of a region in (a).



Figure 2 Scanning electron micrograph of a composite sample exposed to $300 \,^{\circ}$ C for 90 min. (a) Indicating the ribbon matrix interface; (b) enlarged view of the same.



Figure 3 Fractograph of a composite sample heated to $400 \,^{\circ}$ C for 90 min.

matrix and the ribbon appears to be continuous without any evidence of debonding, and can be clearly seen in the enlarged view provided in Fig. 1b. Similar features were observed on the sample heated to 200 °C. Figure 2a corresponds to a sample heated to $300 \,^{\circ}$ C for 90 min, and the ribbon-matrix interface in this case appears to have changed significantly. A layer has formed on the ribbon surface. The region in the ribbon adjacent to the ribbon-matrix interface also has changed significantly as shown in Fig. 2b. However, the centre of the ribbon does not appear to have undergone any change. For the samples heated to $400 \,^{\circ}$ C (Fig. 3), in addition to a similar layer being present at the interface, the entire structure of the ribbon is altered. The structure of the ribbon heated to $450 \,^{\circ}$ C (Fig. 4) has features which seem to be similar to those of the sample heated to $400 \,^{\circ}$ C.

X-ray studies carried out indicated that the regions of the ribbons (in the composites treated at 400 and 450 °C), which exhibited features differing from the others, had actually crystallized. This was unusual considering the fact that the composite samples were not heated above the crystallization temperature of the metallic-glass ribbon itself. The ribbons had also been subjected to a much higher temperature (450 °C) during the fabrication process itself. The fabrication steps did not seem to have any effect on the ribbon structure. The crystallization behaviour of this metallic-glass ribbon studied earlier indicates that the



Figure 4 Scanning electron micrograph of the fractured surface of a sample heated to $450 \,^{\circ}$ C for 90 min.



Figure 5 Schematic of the phases detected in the ribbon, matrix and interface regions of the sample heated at 300 °C for .90 min.

temperature and time used in the present study were inadequate to initiate crystallization in the ribbon [12]. Hence the only viable explanation that could be given is that the crystallization process in the ribbon was being initiated externally. The layer present on the surface of the ribbon was also identified as primarily consisting of iron oxide. The phases detected in various regions of the ribbon, matrix and interface are schematically shown in Fig. 5.

EDAX was carried out on various locations of the ribbon and interface to investigate the cause of the crystallization process of the ribbon. The layer formed on the surface of the ribbon indicated the presence of lead and zinc. Some lead and zinc were also present within the ribbon in regions near the interface. These elements were found to be diffusing out of a region of the matrix very close to the ribbon surface. A schematic of the lead and zinc profiles in the ribbon, matrix and the interface is provided in Fig. 6. From these results it can be deduced that the diffusion of lead and zinc was probably the cause of crystallization of the metallic–glass ribbon. Once the crystallization was initiated at the ribbon surface, the entire ribbon crystallized in a short period of time.

The results of the experimentally measured strength of the thermally shocked matrix and composite specimens are given in Fig. 7. The effect of thermal shocking on the modulus of rupture is similar to that predicted by Hasselman [9] with some variations. The strength of both the matrix and composite did not change up to a temperature difference of about 200 °C. While the strength of the unreinforced specimens levelled off at about 260 °C, the strength of the composites specimens levelled off at about 300 °C. However, the drop in the strength of the composite specimens was very steep in the 200-300 °C temperature range. The "critical temperature difference" for the reinforced specimens, though slightly higher compared with the unreinforced matrix specimens, was not significantly different. The "critical temperature difference" is the temperature difference necessary to cause critical crack propagation in the sample.



Figure 6 Schematic of the diffusion profiles of lead and zinc across the ribbon-matrix interface.

The lack in the increase in the "critical temperature difference" due to the reinforcement, can be partially attributed to the diffusion of zinc and lead, and associated crystallization of the metallic glass ribbon (and hence a decrease in the strength of the ribbon itself). This would also explain the precipitous decrease in the strength of the composite after the thermal shock. Once the ribbons have crystallized, they do not play a significant role in preventing crack growth in the matrix. Hence the thermal shock response of the composite samples for a temperature difference exceeding $250 \,^{\circ}$ C is very similar to that of the matrix itself.

The changes observed in the failure mode of these composites (single matrix crack versus multiple matrix cracks) as a function of temperature is due to the oxide layer formed on the ribbon surface. The oxide layer probably aided in the debonding process. The equation derived in an earlier study has the form [5]

$$x = \frac{V_{\rm m}}{V_{\rm f}} \frac{\sigma_{\rm m}^* \, \omega t}{2\tau(\omega + t)}$$



Figure 7 Experimentally measured strength of the thermally shocked matrix and composite specimens as a function of increasing temperature difference. (\bullet matrix, \blacktriangle composite containing 0.8 volume percent of ribbons.)

where x is the length of the blocks into which the matrix cracks, $V_{\rm m}$ is the volume fraction of the matrix, $V_{\rm r}$ is the volume fraction of the ribbons, ω is the width of the ribbon, t is the ribbon thickness, $\sigma_{\rm m}^*$ is the matrix cracking stress and τ is the interfacial shear strength.

This equation can be used to predict the mode of matrix failure. A lower τ leads to an increased x, and makes multiple matrix cracking more viable. The oxide layer on the ribbon surface probably reduces the interfacial strength between the ribbon and the matrix. It is interesting to note that the interfacial bond strength measured in an earlier study [5] exhibited a steep drop in the temperature range corresponding to the onset of oxide formation in the present study. The same metallic–glass when heated to elevated temperatures (as high as 500 °C) for prolonged periods of time, did not form any oxide layer [12]. It can be concluded that the presence of the oxide glass matrix in the vicinity of the metallic–glass ribbon enhanced the oxidation of the ribbon itself.

4. Conclusions

1. Decrease in the interfacial strength of Metglas 2605S-2 reinforced Corning 7572 composite at elevated temperatures can be attributed to the formation of

an oxide layer on the ribbon surface. Such a layer aids in the sliding process of the ribbon relative to the matrix.

2. In such composites, lead and zinc appear to diffuse from the matrix into the ribbon at elevated temperatures. This diffusion initiates crystallization of the amorphous metallic-glass ribbon, which subsequently leads to degradation of the ribbon strength, and eventually the composite strength. Such a diffusion process was observed to be more pronounced at temperatures above 300 °C.

3. The thermal shock resistance of the matrix was not enhanced by the presence of the metallic-glass ribbons. This can be attributed to the interfacial effects that occur at elevated temperatures.

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