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Metallic glass ribbon-reinforced glass-ceramic matrix composites

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The role of metallic glass ribbons in modifying the properties of glass-ceramics was investigated using specimens prepared by conventional pressing and sintering techniques. Even very low volume fractions of such reinforcements were found to provide significant improvements in the strength, elastic properties and fracture toughness of the glass-ceramic matrices. The observed improvement in the fracture toughness is explained on the basis of various metallic glass ribbon-related energy absorbing mechanisms.

1. Introduction

Enhancement in the tensile strength and fracture toughness of ceramics has been attempted by several techniques such as microcrack toughening and transformation toughening [1–4]. Recent studies have shown that reinforcing ceramics with high strength reinforcements is a viable alternative. In these studies glass, conventional crystalline ceramics or glass-ceramics are used as the matrices [5–7]. Potentials of various reinforcements including continuous and discontinuous fibres (or whiskers) of carbon, graphite, silicon carbide, alumina and various metals such as stainless steel and tungsten, have been investigated [5–11].

Among the various ceramic matrices, glass-ceramics possess unique advantages. They are formed in the glassy state and are converted to an almost 100% crystalline state by subsequent heat treatment. Such a feature facilitates low-temperature composite fabrication and at the same time provides for a composite with high-temperature capabilities (without softening). Conventional crystalline ceramics (which are formed by sintering powders) possess significant porosity, which limits their strength. Glass-ceramics on the other hand have little or no porosity, and hence are tougher and stronger.

The potential of metallic glass ribbons as reinforcements for ceramic matrix composites has not been explored so far. Metallic glasses possess superior fracture strengths and toughness compared to their crystalline counterparts. Metallic glasses also possess good oxidation and corrosion resistance. Their unique geometry provides a large surface area to bond with the matrix. Metallic glasses have been studied as reinforcements for brittle polymer matrices by Hornbogen *et al.* [12–14]. Significant improvement in the mechanical properties of the polymer matrices were reported by them. The main objective of the present study was to develop metallic ribbon-reinforced glass-ceramic matrix composites and to evaluate their mechanical properties. The nature of the metallic glass/glass-ceramic interface and its role on the mechanical properties of the composite system was also of interest.

2. Experimental procedure

2.1. Specimen preparation

Two metallic glasses were used as reinforcements in the present study; one was an iron-based metallic glass, Metglas® 2605S-2 alloy, and the other a nickel-based metallic glass Metglas® MBF-75 alloy*. Both of these metallic glasses were obtained from Metglas Products, a business unit of Allied-Signal Inc. The composition and properties of these metallic glasses as provided by the manufacturer are listed in Table I.

Based on initial experimentation and on the basis of the low recrystallization temperatures of the two chosen metallic glasses, Corning glasses Code 7572 and 8463 were chosen as matrices. The compositions and properties of both these glasses as provided by the manufacturer are listed in Table II.

Rectangular bar-shaped specimens (6.25 cm × 1.25 cm × 0.5 cm) were made using the conventional wet pressing and sintering techniques. Amyl acetate (3% of the weight of the glass powders) was used as the binder. After laying out the metallic glass ribbons unidirectionally within the glass powders in a steel die, the composite specimens were pressed at 3000 p.s.i. ($\sim 20.67\ \mathrm{N\,mm^{-2}}$). After pressing, the specimens were first kept at 200° C for 15 min to drive out the organic binder. The specimens were then sintered at 400° C for 90 min. Devitrification of the glassy matrix was carried out by maintaining the composites at 450° C for 20 min. After this treatment the specimens were furnace cooled to room temperature in order to minimize the thermal shock.

2.2. Testing procedures

The elastic properties of the unreinforced matrix specimens and composite specimens were obtained by

*Metglas® is a registered trademark of Allied Signal Inc for amorphous metallic alloys and brazing alloys.

0022-2461/90 $03.00 + .12

TABLE I Properties of the metallic glass ribbons

Property	Metglas 2605S-2*	Metglas MBF-75*
Chemical composition (%)	Fe 78 B 13 Si 9	Ni 50 Co 23 Cr 10 Mo 7 Fe 5 B 5
Crystallization temperature (°C)	550	605
Elastic modulus (GPa)	85	70
Yield strength (MPa)	> 700	1300
Coefficient of thermal expansion ($°C^{-1}$)	76×10^{-7}	78×10^{-7}†
Density ($g cm^{-3}$)	7.18	7.46†

*Code numbers of products of Metglas Products.
† From [22]. Rest of the entries provided by the manufacturer.

TABLE II Properties of the ceramic glass matrices (as specified by the manufacturer)

Property	Corning Glass 7572*	Corning Glass 8463*
Softening point (°C)	375	370
Coefficient of thermal expansion ($°C^{-1}$)	95×10^{-7}	105×10^{-7}
Density ($g cm^{-3}$) (powder)	3.8	3.8
(fired)	6.0	6.2
Continuous service temperature (°C)	450	450
Chemical composition (%)	PbO 70 B_2O_3 5–10 SiO_2 2–5 Al_2O_3 1–5 ZnO 10–20	PbO 84 B_2O_3 5–10 SiO_2 2–5 Al_2O_3 1–5 ZnO 10–20

*Code numbers of products of Corning Glass Co.

the non-destructive sonic resonance technique [15]. Because it was difficult to detect the torsional resonance frequency, the shear modulus was determined by using the values of the Young's modulus (which was obtained from the flexural resonant frequency), and by assuming a Poisson's ratio of 0.25 for the composite system.

Modulus of rupture (MOR) measurements were made by using the three-point bend test in an Instron testing machine with a cross-head speed of 0.05 cm min^{-1}. The span-to-depth ratio for the specimens was maintained in accordance with ASTM specification C-203/85.

Static fracture toughness tests were performed by fracturing single-edge notched beam (SENB) specimens, in three-point bending. The notches were cut using a diamond blade. The specimens were annealed after cutting the notch, at 200°C, to heal up microcracks which might have formed at the root of the notch. The fracture toughness was determined using the equations given by Gross and Srawley [16]. The fracture toughness values for the unreinforced matrix specimens were also determined by the non-destructive indentation technique [17, 18]. The specimens were indented using a Vicker's indentor with a load of 0.3 kg. The fracture toughness was determined by using the equations given by Lawn [17].

The pull-out test was carried out in order to evaluate the interfacial bond strength. An embedded length of 1.0 cm of ribbon (and width 0.5 cm) was used for this purpose. In such a technique the interfacial bond strength can be determined by balancing the tensile forces to the shear forces acting on the embedded portion of the ribbon.

Fractographic studies were carried out using a scanning electron microscope.

3. Results and discussion

3.1. Elastic properties

The values of the elastic properties of the unreinforced matrix and composite specimens as measured by the sonic resonance technique, are presented in Table III. A significant improvement in the elastic properties is observed, even with the low volume fraction of reinforcements used. The rule of mixtures (ROM) as used to characterize the elastic properties of several composite systems is given by the equation

$$E_c = E_m V_m + E_f V_f \quad (1)$$

where E is the Young's modulus, V the volume fraction and subscripts c, m and f refer to the composite, matrix and ribbon, respectively. The values of E calculated using the ROM are compared with the experimentally measured values in Table IV. As is evident from the results, the ROM does not characterize the elastic modulus of the composite system under consideration. A better estimate of E can be made by considering the equation given by Halpin and Tsai

TABLE III Elastic properties of the glass–ceramic matrices and composite systems obtained by the sonic resonance technique

Glass–ceramic matrix (Corning code)	Metallic–glass reinforcement (Metglas alloy)	Volume fraction of reinforcement (%)	E (GPa)	Increase in E (%)
7572	–	0	33.4	–
7572	2605S-2	0.73	44.0	31.7
7572	2605S-2	1.24	47.7	42.8
7572	2605S-2	1.64	69.4	108.0
7572	MBF-75	0.74	42.1	25.9
8463	–	0	28.1	–
8463	MBF-75	0.69	36.0	28.0
8463	MBF-75	0.73	40.8	45.4

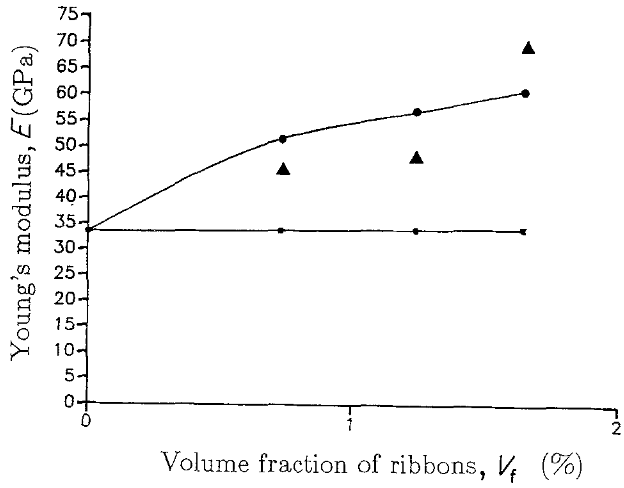

Figure 1 Plot of the Young's modulus of the Metglas 2605S-2 alloy-reinforced 7572 matrix composites as a function of volume fraction of metallic glass reinforcement. (▲) Experimentally measured, (■) obtained from the rule of mixtures, (●) fitted to the Halpin–Tsai equation for $\xi = 0.24$.

[19, 20], according to which

$$\frac{E_c}{E_m} = \frac{1 + \eta\xi V_f}{1 - \eta V_f} \quad (2)$$

where η is the reinforcing efficiency, which will be equal to one for a strongly bonded system, and ξ is an empirical constant which depends on parameters like reinforcement aspect ratio, and bond strength.

The value of ξ can be obtained by fitting the experimentally obtained values of E to the equation given by Halpin and Tsai. For the system under consideration the value of ξ is found to be 0.24 (Fig. 1). The value of the reinforcing efficiency, η, was assumed to be unity, because strong bonding was observed between the ribbon and the matrix (Fig. 2).

3.2. Strength

The MOR values of the unreinforced matrix and the composite specimens are presented in Table V. In the system under consideration, the reinforcing ribbons not only have a higher fracture stress but also a higher fracture strain as compared to the matrix. In the initial stages of loading (in three-point bending), the matrix carries a major portion of the load. When the fracture strength of the matrix is reached, the matrix cracks and the load is transferred to the reinforcing ribbons. Two different failure sequences can be envisaged depending upon the volume fraction of reinforcements used. For low volume fractions, when the matrix cracks, the transfer of the load to the ribbons overloads them and they fail. Hence

$$\sigma_c^* = \sigma_m^* V_m + \sigma_f' V_f \quad (3)$$

where σ_c^* is the fracture stress of the composite, σ_m^* is the fracture stress of the matrix, and σ_f' is the stress transferred to the ribbons when the matrix cracks.

When the volume fraction of the reinforcements is high, the transfer of load to the ribbons is not sufficient to fracture them and they continue to carry the load until their fracture strength is reached. Under these conditions

$$\sigma_c^* = \sigma_f^* V_f \quad (4)$$

where σ_f^* is the fracture stress of the ribbons.

The cross-over point between these two types of behaviour occurs at a critical volume fraction, V_c', where

$$V_c' = \frac{\sigma_m^*}{\sigma_f^* - \sigma_f' + \sigma_m^*} \quad (5)$$

For the composite system under consideration the calculated value of V_c' is 0.5%. All the composite specimens used in the current study had a volume fraction of reinforcements greater than this critical volume fraction. Hence the strength of the composite specimens is essentially a function of the volume fraction of the metallic glass reinforcements. Higher volume fractions of reinforcements should show significant improvements in the fracture strength. The variation in the MOR of the composite specimens with increasing volume fraction of metallic glass reinforcements is illustrated in Fig. 3.

TABLE IV Comparison of the experimentally measured and calculated (by ROM) values of Young's modulus for the Metglas 2605S-2-reinforced 7572 glass–ceramic system

Volume fraction of reinforcement (%)	Young's modulus calculated by ROM (GPa)	Young's modulus measured experimentally (GPa)
0.73	33.78	44.03
1.24	34.04	47.70
1.64	34.24	69.43

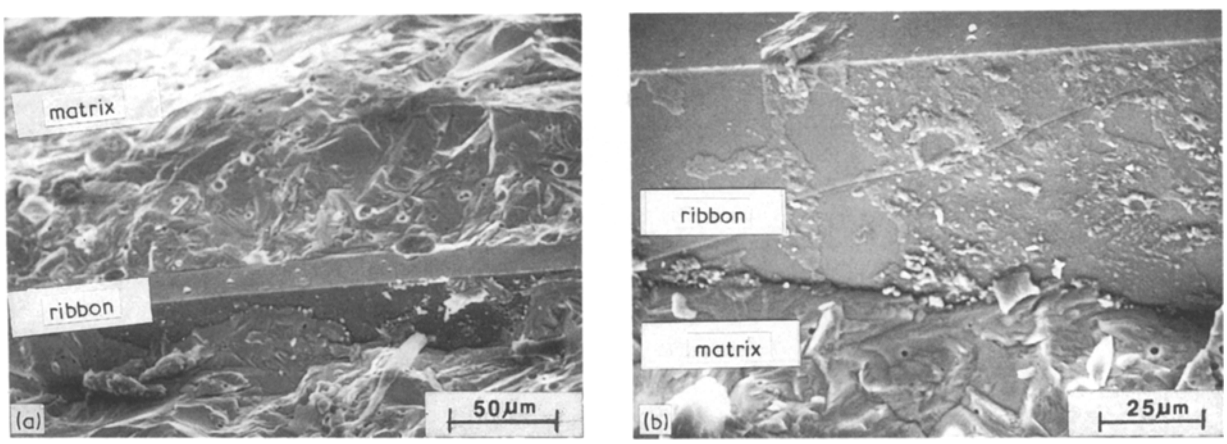

Figure 2 Strong (void-free) bonding between the Metglas 2605S-2 alloy ribbon and 7572 matrix. (a) The matrix is observed to be almost 100% crystalline. (b) Matrix material adhering to the ribbon surface.

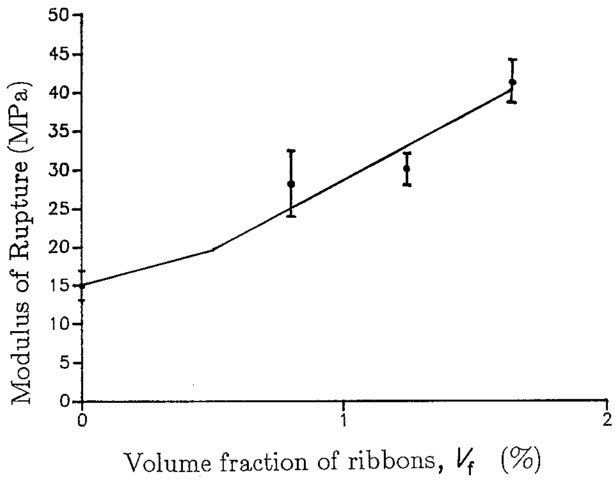

Figure 3 Plot of the fracture strength of the Metglas 2605S-2 alloy reinforced 7572 matrix composites as a function of volume fraction of metallic glass reinforcement.

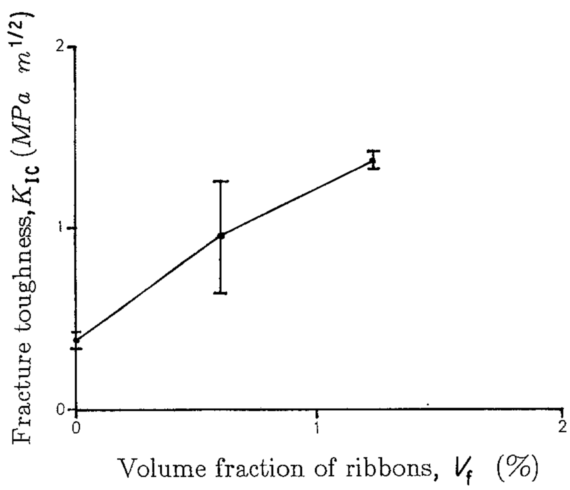

Figure 4 Plot of the fracture toughness of the Metglas 2605S-2 alloy-reinforced 7572 matrix composites as a function of volume fraction of metallic glass reinforcement.

The Young's modulus (E) of the specimens was also calculated from the results of the three-point bend test. The values of E obtained from the three-point bend test with those obtained from the sonic resonance test are compared in Table VI. The values of E obtained for the unreinforced matrix specimen by both techniques agree well; on the other hand, the values obtained for the composite specimen do not. This discrepancy may be attributed to the non-uniform load carrying characteristics of the composite system.

3.3. Fracture toughness

The fracture toughness values for the unreinforced matrix and composite specimens as measured by the single-edge notched beam technique, are listed in Table VII. The fracture toughness values for the unreinforced matrix specimens as measured by the indentation technique, are listed in Table VIII. The indentation technique cannot be used to measure the fracture toughness of the composite specimens because the reinforcing ribbons are positioned far away from the surface (where the indentation is carried out), and as a result do not affect the crack growth behaviour at the indentation. A plot of the fracture toughness against the volume fraction of metallic glass reinforcements is provided in Fig. 4. A clear enhancement in the fracture toughness with respect to the unreinforced matrix is evident from this plot. This behaviour can be attributed to improvements in the various mechanical properties such as Young's modulus, fracture stress and fracture strain, which can be correlated to the fracture toughness using the empirical equation given by Hahn and Rosenfield [21], according to which

$$K_{Ic} = (E\sigma_f\varepsilon_f L)^{0.5} \quad (6)$$

where K_{Ic} is the fracture toughness, σ_f is the fracture stress, ε_f is the fracture strain, and L is a geometrical correction factor.

In the system studied, the Young's modulus, fracture stress and fracture strain all increase with increasing volume fraction of reinforcements, and hence the fracture toughness is also expected to improve. The improvement in the fracture toughness can also be explained on the basis of fracture energy considerations. The fracture toughness is related to the Young's modulus and fracture energy (G_{Ic}) by the equation

$$K_{Ic} = (EG_{Ic})^{0.5} \quad (7)$$

The total energy absorbed during fracture of the composite is the sum of the energies absorbed by the

TABLE V Results of the three-point bend tests carried out on the glass–ceramic matrices and composite specimens

Glass–ceramic matrix (Corning code)	Metallic–glass reinforcement (Metglas alloy)	Volume fraction of reinforcement (%)	MOR (MPa)	Increase in MOR (%)	E (GPa)
7572	–	0	14.98	–	26.15
7572	2605S-2	0.80	28.25	88.59	5.32*
7572	2605S-2	1.24	30.22	101.70	–
7572	2605S-2	1.64	41.25	175.40	–
7572	MBF-75	0.74	32.27	115.39	–
7572	MBF-75	1.01	33.25	121.96	–
8463	–	0	11.30	–	–
8463	MBF-75	0.68	20.42	80.70	–
8463	MBF-75	0.69	21.62	91.33	–
8463	MBF-75	0.71	22.60	100.00	–
8463	MBF-75	0.73	23.16	104.95	–
8463	MBF-75	0.77	25.30	124.20	–

*Value which does not agree with that obtained by the sonic resonance technique.

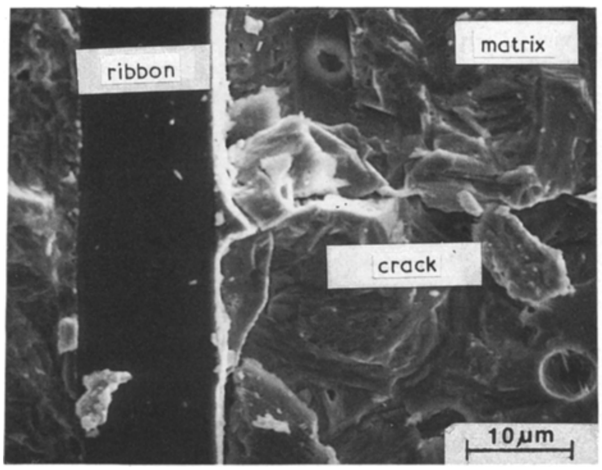

Figure 5 Crack arrest and deflection at the metallic glass ribbon (Metglas 2605S-2)–matrix (7572) interface. The crack originated at the tensile surface during the bend test.

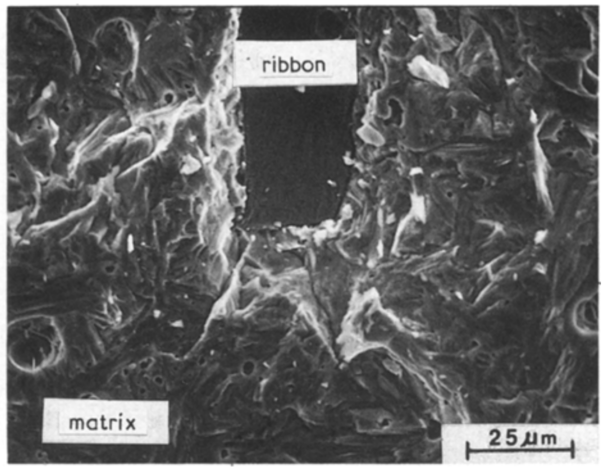

Figure 6 Microcracks originating at the edges of the reinforcing ribbons (Metglas 2605S-2) in the 7572 matrix.

matrix-related processes (G_m) and by the ribbon-related processes (G_f). Hence

$$G_{Ic} = G_f V_f + G_m V_m \quad (8)$$

The contribution to G_f arises from four different ribbon-related processes. In addition to energy absorbed by ribbon failure (specific ribbon fracture energy, w_f), energy is also dissipated as a result of ribbon-matrix debonding (w_d) and ribbon pull-out (w_p). Furthermore, there exists a bending component (w_b) as the crack in the surrounding matrix opens before the reinforcing component is broken. Hence,

$$G_f = w_p + w_b + w_d + w_f \quad (9)$$

It is believed that this crack deflection at the ribbon–matrix interface, strengthens the composite and makes it tougher by causing secondary processes such as debonding and pull-out to come into play, thereby absorbing energy. This particular phenomenon can be observed in Fig. 5. Another mechanism of energy absorption is the initiation of secondary cracks at the edges of the reinforcing ribbons (Fig. 6). These are created when under the influence of bending moments, the sharp edges of the ribbons tend to wedge open the brittle matrix. The ribbons can also be assumed to exhibit higher fracture strengths as a result of hinderance of shear failure due to the surrounding rigid matrix, increasing the contribution of w_f (Fig. 7).

A very strong bond between the ribbon and matrix was observed, as was evinced by the absence of ribbon–matrix debonding in the pull-out test. Hence the w_d and w_p contributions are low in the case of the system under consideration. The main contribution to the fracture energy of the present system are believed to arise from the w_f and w_b components.

4. Conclusions

1. Introduction of even a very low volume fraction of metallic glass reinforcements, provide significant improvements in the elastic properties, fracture strength and fracture toughness of the brittle glass-ceramic matrices. The strength of the composite system is a function of the fracture strength and the volume fraction of the ribbons, and increases proportionately with increasing volume fraction of reinforcements.

2. The elastic properties of the present composite system do not obey the rule of mixtures. They can be

TABLE VI Comparison of the values of the Young's modulus of the Metglas 2605S-2 reinforced 7572 glass–ceramic specimens obtained from the sonic resonance and three-point bend tests

Test	Average Young's modulus 7572 matrix (GPa)	Average Young's modulus 7572 + 2605S-2 composite (GPa)
Dynamic resonance	33.40	44.00
Three-point bending	26.15	5.32

TABLE VII Fracture toughness obtained by the notched beam tests

Sample	K_{Ic} (MPa m$^{1/2}$)	Average K_{Ic} (MPa m$^{1/2}$)	Standard deviation	Variance (%)
7572 matrix	0.4046 0.3580 0.3730	0.378	0.0237	6.26
7572 matrix reinforced with 0.6% Metglas 2605S-2	1.0886 0.8320 1.1800 0.7080	0.952	0.3022	31.74
7572 matrix reinforced with 1.24% Metglas 2605S-2	1.372 1.430	1.401	0.041	2.93

TABLE VIII Fracture toughness obtained by the indentation technique

Specimen	Lead Borosilicate glass, code 7572.
Indentation load (kg)	0.3
Loading time (sec)	20
Loading speed (μm sec^{-1})	50
Number of specimens	3
Indentations per specimen	25
Fracture toughness, K_{Ic} (MPa m$^{1/2}$)	0.496 0.433 } Average 0.46 0.450
Standard deviation	0.0327
Variance (%)	7.11

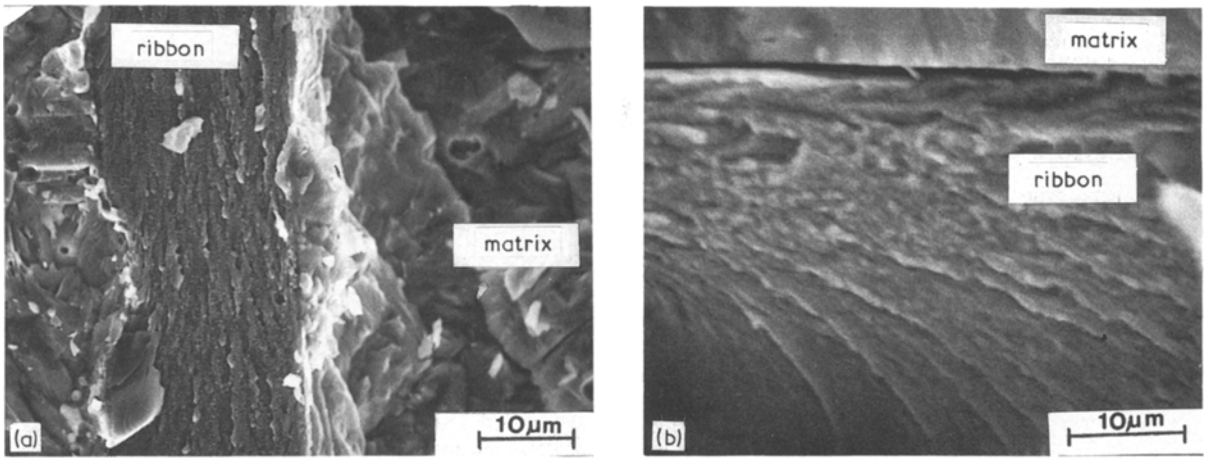

Figure 7 Micrographs illustrating the high ductility of the metallic glass ribbons. (a) A crushed ribbon (Metglas 2605S-2) in composite failure. (b) Vein type of fracture pattern on the metallic glass (Metglas 2605S-2) ribbon surface.

predicted by using the empirical equation given by Halpin and Tasi [19, 20].

3. The improvement in the fracture toughness of the present composite system is due to the introduction of various ribbon-related energy-absorbing mechanisms such as crack arrest and deflection and elastic bending and fracture of the ribbons. Microcracking of the matrix at the edges of the ribbons also contributes to the fracture toughness.

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References

1. K. FABER and A. EVANS, *J. Amer. Ceram. Soc.* **67** (1984) 255.
2. A. EVANS and A. HEUER, *ibid.* **63** (1980) 241.
3. A. EVANS, in "Advances in ceramics", Vol 12, edited by N. Claussen, M. Ruhle and A. Heuer (American Ceramic Society, Ohio, 1984) p. 193.
4. R. McMEEKING and A. EVANS, *J. Amer. Ceram. Soc.* **65** (1982) 242.
5. R. SAMBELL, D. BROWN and D. PHILLIPS, *J. Mater. Sci.* **7** (1972) 663.
6. *Idem, ibid.* **7** (1972) 676.
7. M. SAHEBKAR, J. SCHILCHTING and P. SCHUBERT, *Ber. Deut. Keram. Gesell.* **55** (1978) 265.
8. K. GADKAREE and K. CHYUNG, *Amer. Ceram. Soc. Bull.* **65** (1986) 370.
9. P. SHALEK, J. PETROVIK and F. GAC, *ibid,* **65** (1986) 351.
10. S. RISBUD and M. HERRON, *ibid.* **65** (1986) 342.
11. A. CAPUTO, D. STINTON and T. BESMANN. *ibid.* **66** (1987) 368.
12. A. FELS, K. FRIEDRICH and E. HORNBOGEN, *J. Mater. Sci. Lett.* **3** (1984) 569.
13. *Idem, ibid.* **3** (1984) 639.
14. T. TIO, K. FRIEDRICH, E. HORNBOGEN, U. KOSTER and A. FELS, *ibid.* **3** (1984) 415.
15. S. SCRIEBER, D. ANDERSON and N. SOGA, "Elastic constants and their measurements" (McGraw-Hill, New York, 1974) p.82.
16. M. SRINIVASAN and S. SESHADRI, "Fracture mechanics for ceramics, rocks and concrete", ASTM special technical publication No. 745 (Re: B. Gross and J. E. Srawley) (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1977) p. 46.
17. B. LAWN, in "Fracture mechanics of ceramics", Vol. 5, edited by R. Bradt, A. Evans and D. P. H. Hasselmann (Plenum press, New York, 1983) p. 1.
18. D. SHETTY, A. ROSENFIELD and W. DUCKWORTH, *J. Amer. Ceram. Soc.* **68** (1985) 65.
19. J. HALPIN and S. TSAI, Air Force Materials Laboratory Technical Report AFML-TR-67-423 (1967)
20. D. HULL, in "An introduction to composite materials", edited by R. Cahn, E. Davis and I. Ward (Re: J. Halpin and S. Tsai) (Cambridge University Press, Cambridge, 1985) p. 127,
21. G. HAHN and A. ROSENFIELD, Proceedings of the 3rd International Conference on Fracture, Munich (1973), West Germany (1987), Vol. 1 (VDE, Dusseldorf, 1973) p. 13.
22. J. C. M. LI, in "Treatise on Material Science and Technology", Vol 20, edited by Herbert Herman (Academic Press, New York, 1981) p. 325.

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