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Improving the fracture toughness of $MgO–Al_2O_3–SiO_2$ glass/molybdenum composites by the microdispersion of flaky molybdenum particles

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The flake-forming behaviour of powders of molybdenum, niobium, nickel, BS 316 S 12, Ni–17Cr–6Al–0.6Y, iron, titanium and Ti–6Al–4V, using a wet ball mill, was investigated. $MgO–Al_2O_3–SiO_2$ (MAS) glass composites reinforced with these flaked particles were fabricated, and improvements in flexural strength evaluated. The MAS glass composites reinforced with flaky metallic particles such as molybdenum, niobium, iron, nickel and Ni–17Cr–6Al–0.6Y, showed an improvement. The effect of molybdenum particle size on the flake-forming behaviour of molybdenum, flexural strength and fracture toughness of MAS glass/molybdenum composites, were investigated. The flake-forming behaviour shows a high degree of dependence on molybdenum particle size and, upto a size of 32 μm, becomes conspicuous with increasing particle size. At 32 μm, the aspect ratio reaches a value of 17 and, above 32 μm, flake forming saturates. Fracture toughness is closely related to flake-forming behaviour and the more marked the flake forming, the greater is the increase in fracture toughness. A composite of MAS glass with flaky molybdenum particles has a greater improvement effect on fracture toughness than composites with SiC whiskers, SiC platelets or ZrO_2 particles. This is closely linked to plastic deformation of the flaky metallic particles at the crack tip at the time of fracture.

1. Introduction

While glass has a positive image as a transparent, chemically stable material, it is also regarded as being fragile and breaking easily in the same way as ceramics. If it becomes possible to strengthen and toughen glass, it is expected that it will be capable of being used as a highly corrosion-resistant structural material, the secondary working of which will be possible.

The strength of glass is 0.1–0.01 of the theoretical strength estimated from its interatomic bonding. This phenomenon was explained by Griffith's theoretical equation which takes account of the existence of flaws [1]. This demonstrates that the strength of this brittle material is affected markedly by the presence of cracks and its reliability is poor. In order to overcome this shortcoming, it is necessary to improve the toughness. As means of achieving this, until now investigation of the strengthening and toughening of glass has been carried out using the screening effect of the uniform dispersion of ceramics particles and whiskers through transformation, microcracking, crack deflection, pull-out, bridging and shielding effect, due to residual compressive stress in composites with SiC whiskers [2, 3], SiC platelets [4], ZrO_2 particles [5], etc.

According to our study, by contrast, toughening by a new technique of uniformly dispersing flaky, ductile metallic particles in alumina ceramics, is possible [6–8]. At the time of fracture, flaky metallic particles at the crack tip deform plastically, and the plastic energy, γ_p, increases, thus increasing the toughness. It is expected that, when the interfacial bonding between the matrix and the particles is weak, the cracks will deflect and the surface energy, γ_s, will increase, giving a further increase in toughness. Fig. 1 is a schematic diagram showing the application of this fundamental line of thought to glass. The matrix for the figure is crystallized glass. In this study, MAS ($MgO–Al_2O_3–SiO_2$) glass, which can be sintered around 1273 K, was selected as the glass material. The strengthening effect of flaky metallic particles of refractory metals molybdenum, and niobium, as well as low-melting-point metals such as nickel, stainless steel (BS 316 S 12), iron, Ni–17Cr–6Al–0.6Y, titanium and Ti–6Al–4V, was investigated. Of these, for molybdenum, which has a great strengthening effect, the effect of particle size on flake-forming behaviour, flexural strength and fracture toughness of MAS glass/molybdenum composites was studied.

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Method

Modified Griffith theory

$\sigma_f = (1/Y)\ [2(\gamma_s + \gamma_p)E'/C]^{1/2}$
$= (1/Y)(K_{IC}C^{1/2})$
Y = geometrical factor
σ_f = fracture stress
γ_s = surface energy
γ_p = plastic energy
$E = E' = E$ for plane stress
$= E' = E/(1 - \nu_2)$ for plane strain
E = elastic modulus
C = crack length

Fracture toughness

Homogeneous dispersion of flaky metals

Strength

Homogeneous dispersion of nanosized metals and ceramics

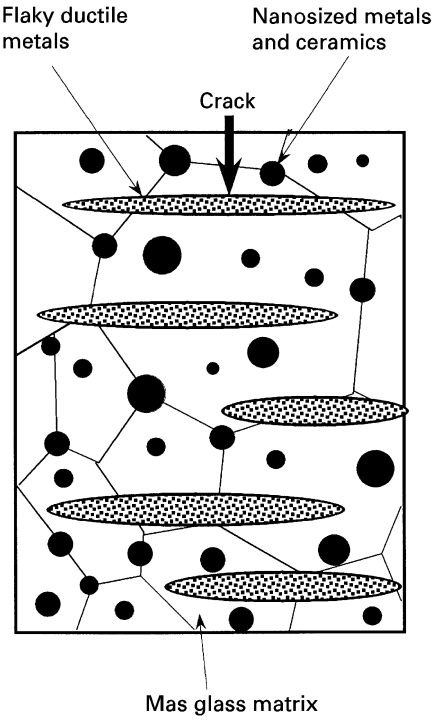


Figure 1 Schematic illustration of the fundamental concept of a new strengthening and toughening method.

2. Experimental procedure

Commercially available MAS (MgO 11.3 wt %, Al_2O_3 34.0 wt %, SiO_2 53.5 wt %) glass powders (GB-22, Iwaki Glass Co., Ltd., Chiba, Japan) with an average particle size of 9 μm were used for the matrix. Investigations were carried out on the effects of the type of metallic particles as the reinforcement phase, at a fixed 20 vol %. The particles used were, average 32 μm molybdenum powder (Shouwa Denko Co., Tokyo, Japan), − 45 μm niobium powder (Ishizu Seiyaku Ltd., Osaka, Japan), average 28 μm Ni–17Cr–6Al–0.6Y powder (Shouwa Denko Co., Tokyo, Japan), − 44 μm austenite stainless steel (BS 316 S 12) powder (Sanyo Special Steel Co., Ltd., Hyogo, Japan), − 45 μm nickel powder (High Purity Chemicals Laboratory Co., Ltd., Saitama, Japan), − 50 μm iron powder (High Purity Chemicals Laboratory Co., Ltd., Saitama, Japan), − 45 μm titanium powder (Osaka Titanium Co., Ltd., Osaka, Japan) and − 74 μm Ti–6Al–4V powder (Osaka Titanium Co., Ltd., Osaka, Japan). The effect of the size of particles of 20 vol % Mo on flake-forming behaviour, flexural strength and fracture toughness of MAS glass/molybdenum composites was investigated using average particle sizes of 0.7, 3, 9.3, 32 and 64 μm.

Wet ball milling was carried out for 100 h using Si_3N_4 balls in ethyl alcohol to obtain homogeneously mixed powders of MAS glass and metals and to deform plastically the metal powders to flaky shapes. The obtained slurries were dried, using a rotary evaporator to remove the ethyl alcohol. The mixed powders were then hot-pressed in a carbon die to fabricate composites of 50 mm × 50 mm × 5 mm at 1273 K under a 10 MPa pressure in a vacuum ($\sim 6.7 \times 10^{-2}$ Pa).

The degree of molybdenum flake formation in the mixed powders after ball milling, and the microstructures and fracture surfaces of the composites, were observed by optical microscopy and scanning electron microscopy (SEM; JEOL JM-T220 or JEM-840). Furthermore, the detailed microstructures also were examined by transmission electron microscopy (TEM) (JEOL JEM-2010). The constitutional phases of the mixed powders and the composites were examined by X-ray diffraction (Rigaku-Denki Co., RAD-RD type, Tokyo, Japan).

The three-point flexural strength was measured at room temperature with a 30 mm span by using specimens of 3 mm × 4 mm × 40 mm at a crosshead speed of 0.5 mm min^{-1}. The fracture toughness is evaluated at room temperature according to the SEVNB (single-edge V-notched beam) method [9], by using V-notched specimens. These mechanical tests were conducted in loading directions parallel to (L direction) and perpendicular to (T direction) the hot-pressing direction.

3. Results and discussion

3.1. Flaky metallic particle type and flexural strength

Fig. 2a and b show the relationship between flexural strength and metallic type for composites with 20 vol % flaky metallic particles in the L and T directions, respectively. The effect varies greatly depending on the type of metal, with flexural strength in both directions being increased by some metals, being practically unaffected by others and, conversely, being decreased by yet others. Positive effects are observed for composites with molybdenum, Ni–17Cr–6Al–0.6Y, iron and niobium, whereas austenite stainless steel (BS 316 S 12) and nickel have a negligible effect, and titanium and Ti–6Al–4V decrease flexural strength.

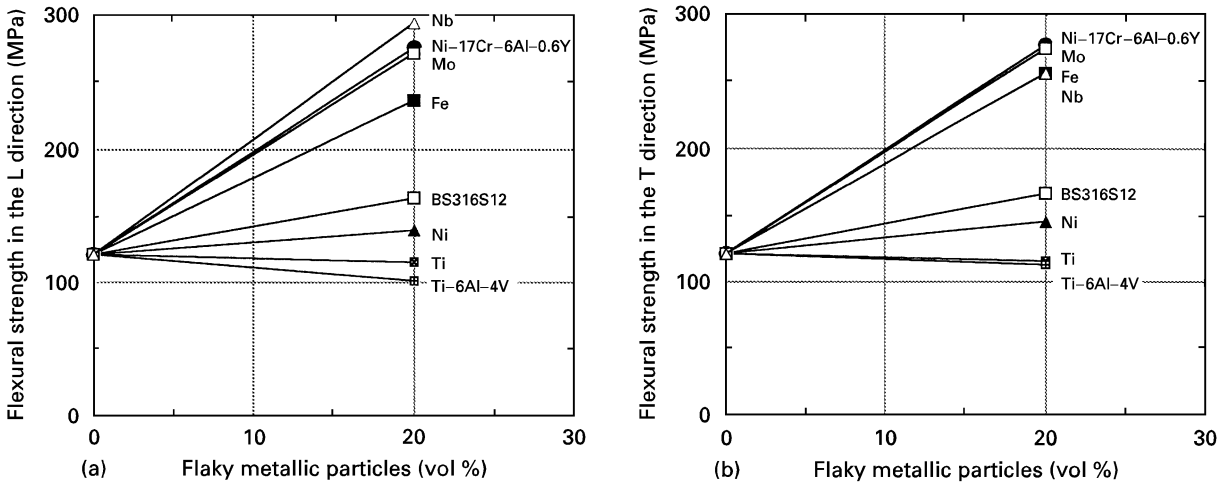


Figure 2 The effect of the type of flaky metallic particle on flexural strength in (a) the L direction, and (b) the T direction.

3.2. Flake-forming behaviour of molybdenum

Fig. 3 shows scanning electron micrographs of 32 μm Mo powder, MAS glass powder and the mixed powder after 100 h ball milling. From Fig. 3a and b, before ball milling, the MAS glass and molybdenum powders were massive but afterwards, as shown in Fig. 3c, the molybdenum powder is plastically deformed to flaky shape and the pulverized MAS glass powder is adhering to its surface. To clarify the flake-forming behaviour of the molybdenum powder, cross-sections of 20 vol % Mo powders for average particle sizes of 0.7 and 32 μm after 100 h wet ball milling are shown in Fig. 4. It can be seen that the 32 μm powder is markedly flaked but the 0.7 μm powder is virtually unflaked. The relationship between the aspect ratio of flaky molybdenum particles which is evaluated by measuring length and thickness of cross-section of 20 vol % molybdenum powder specimens after ball milling, and molybdenum particle size prior to ball milling is shown in Fig. 5. Flake-forming behaviour becomes conspicuous with increasing particle size, giving an aspect ratio of 17 at 32 μm. For particle sizes of greater than 32 μm, the aspect ratio remains at approximately 17. This is small compared with the aspect ratio of 21 [7] for Al_2O_3/Mo composites, but the cross-section of the flaky molybdenum particles is acutely uneven. This is inferred to be closely linked with the MAS glass powder being large compared with the Al_2O_3 powder before ball milling, the pulverization of the MAS glass powder during milling, and the MAS glass cleavage fracture characteristics and hardness during ball milling.

3.3. Microstructures of the MAS glass/molybdenum composites

Fig. 6 shows optical micrographs of microstructures perpendicular (L cross-section) and parallel (T cross-section) to the hot-pressed planes of the composites with five different molybdenum particle sizes. It can be seen from photographs that, for composites with all sizes of molybdenum particles, in the L cross-section molybdenum particles are uniformly dispersed in the MAS glass matrix, but the shape of the molybdenum particles varies greatly with particle size. The 0.7 μm molybdenum particles are uniformly dispersed in the matrix, but with increasing particle size, flake formation becomes more conspicuous and for 32 μm molybdenum particles in the L cross-section, longitudinal sections of flaky molybdenum particles are dispersed uniformly in the matrix. Whatever the particle size of molybdenum, the non-flaked fine particles are uniformly dispersed within the matrix. In the T cross-section, the 0.7 μm molybdenum particles are uniformly dispersed but, as flake forming becomes conspicuous, various sections of flaky molybdenum particles are observed in the microstructures. The microstructures of composites reinforced with flaky molybdenum particles is anisotropic in the cross-sections perpendicular and parallel to the hot-pressed planes. The degree to which molybdenum particles form flakes in the composites is virtually the same as in the mixed powders after ball milling, shown in Fig. 5. It can thus be said that flake-forming behaviour of molybdenum powders is largely determined by the conditions of ball milling.

3.4. Dependence of flexural strength on molybdenum particle size

The relationship between flexural strength and molybdenum particle size in the L and T directions is shown in Fig. 7. Flexural strength increases with increasing molybdenum particle size up to 3 μm. The flexural strength of the composite reinforced with 0.7 μm molybdenum is 337 MPa in the L direction and 375 MPa in the T direction, which are around 2.8 times and 3.1 times larger than the value of 121 MPa for the MAS glass matrix, respectively. The strength of the composite reinforced with 3 μm molybdenum increases to approximately 3.1 times larger in the L direction and 3.3 times larger in the T direction, than that of MAS glass matrix. The effect of 9.3 μm molybdenum on flexural strength is virtually the same as 3 μm molybdenum, the strength of the 9.3 μm

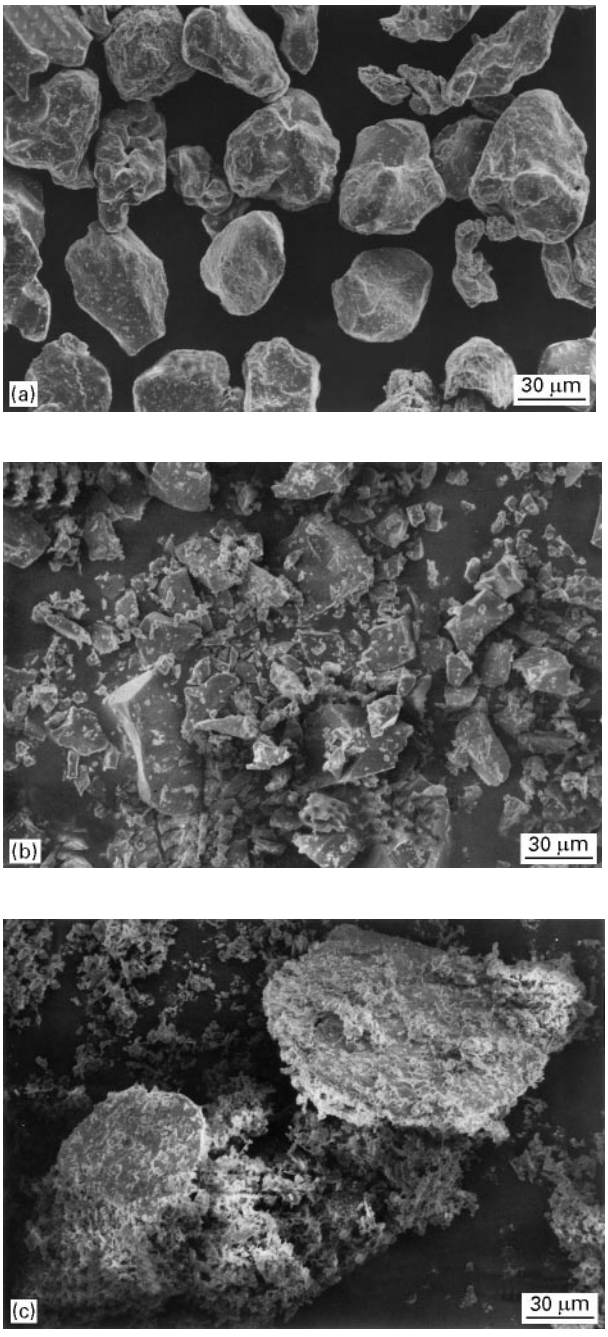


Figure 3 Scanning electron micrographs of molybdenum powder, MAS glass powder and mixed powder after wet ball milling for 100 h. (a) 32 μm molybdenum powder, (b) 9 μm MAS glass powder, (c) mixed powder.

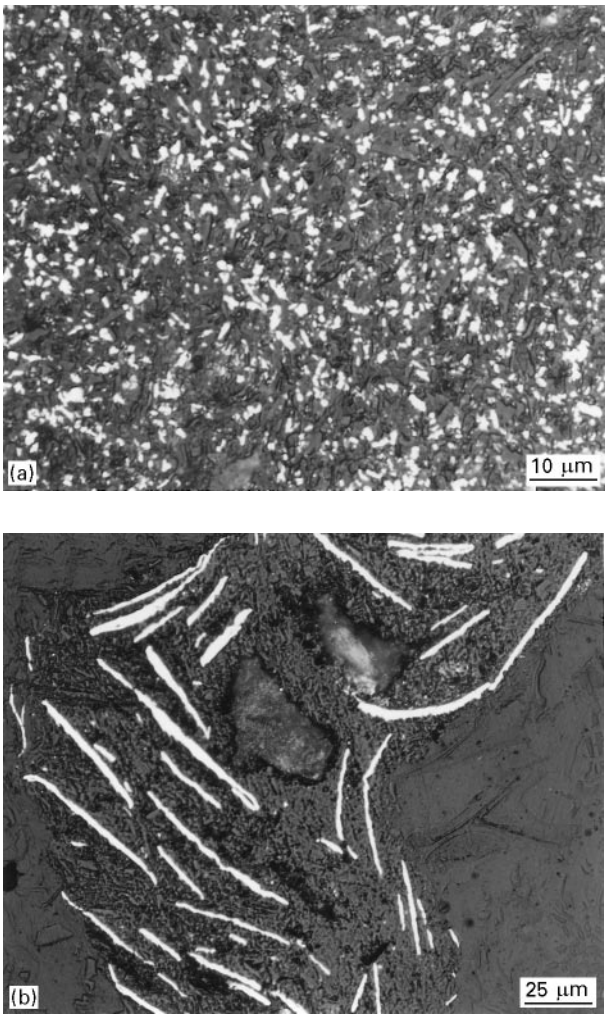


Figure 4 Optical micrographs of cross-sections of 20 vol % Mo powder: (a) 0.7 μm molybdenum and (b) 32 μm molybdenum mixed with 80 vol % MAS glass powder after ball mill treatment for 100 h, respectively.

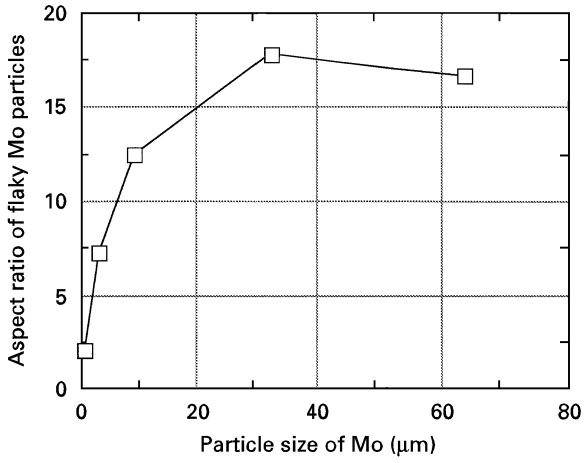


Figure 5 Effect of particle size of molybdenum on aspect ratio of flaky molybdenum particles after ball milling.

molybdenum-reinforced composite is 2.9 times larger in the L direction and 3.3 times larger in the T direction, than that of MAS glass matrix, respectively. The flexural strength decreases above 32 μm where the flake forming of the molybdenum particles becomes conspicuous, and the strength of the composites reinforced with 32 and 64 μm molybdenum is still 2.2–2.3 times larger than that of MAS glass matrix, with very little difference in the strength between the L and T directions.

In a composite of Al_2O_3 reinforced with 0.7 μm molybdenum particles, flexural strength of 800 MPa, approximately 2.4 times larger than that of the Al_2O_3 matrix, is achieved, but as the molybdenum particle size increases, the strength improvement effect decreases abruptly [7]. By contrast, in the MAS glass/molybdenum particle composites of this study, the strength increases of 2.8–3.3 times that of the matrix are seen up to molybdenum particle sizes of 9.3 μm, which exhibits a different tendency from the case of Al_2O_3 matrix.

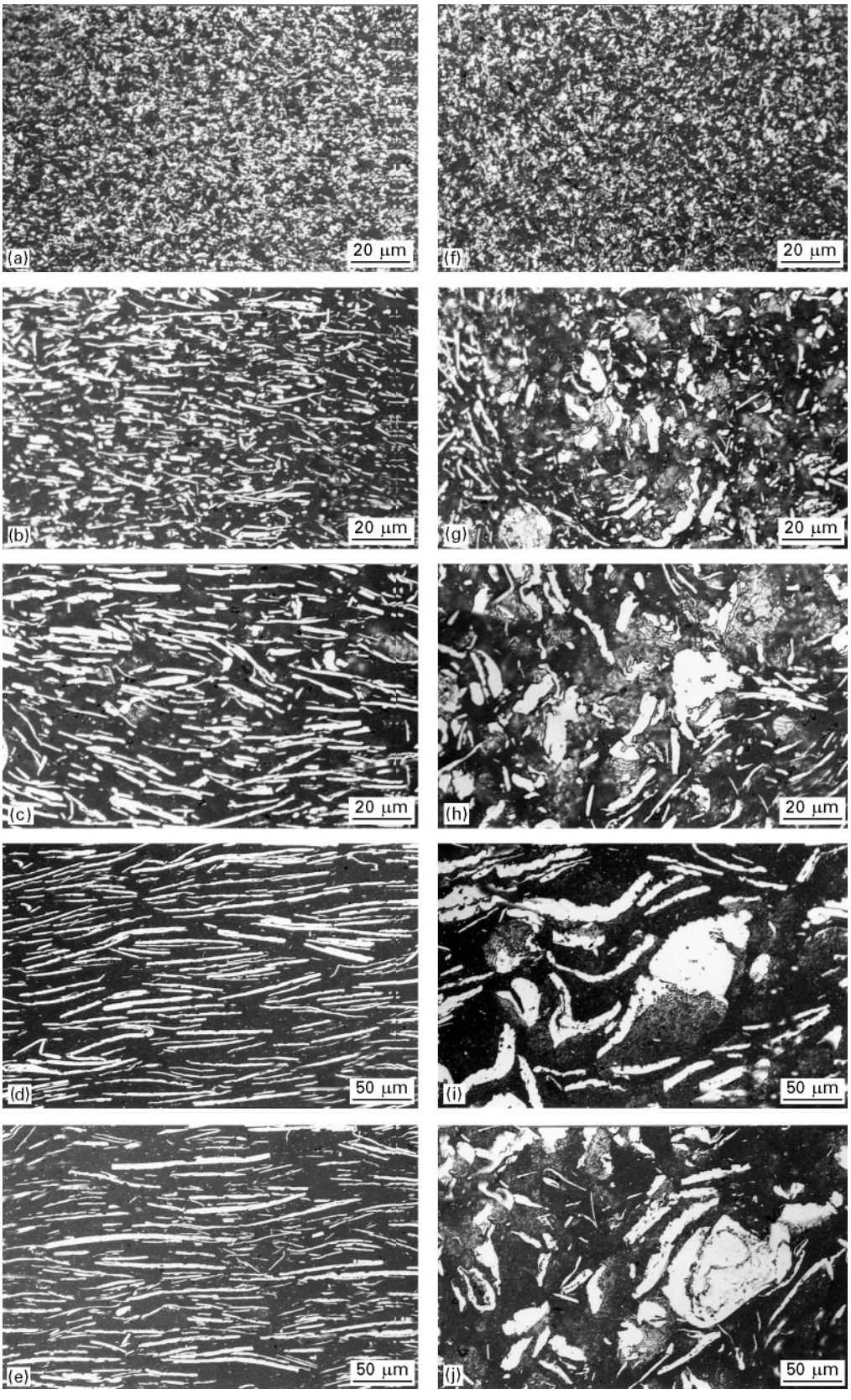


Figure 6 Optical micrographs of MAS glass/molybdenum composites containing five different molybdenum particle sizes: (a, f) 0.7 μm, (b, g) 3 μm, (c, h) 9.3 μm, (d, i) 32 μm, (e, j) 64 μm. (a–e) Perpendicular to the hot-pressed planes (L cross-section); (f–j) parallel to the hot-pressed planes (T cross-section).

3.5. Dependence of fracture toughness on molybdenum particle size

Fig. 8 shows the effect of molybdenum particle size on fracture toughness in the L and T directions. In both directions, fracture toughness increases greatly with molybdenum particle size up to 32 μm, above which size no increase in toughness is seen, irrespective of size increases. This tendency is similar to the dependence of the aspect ratio of flaky molybdenum particles on particle size shown in Fig. 5. That is, that toughness increases and molybdenum particle flake-forming behaviour are closely related, and the more marked

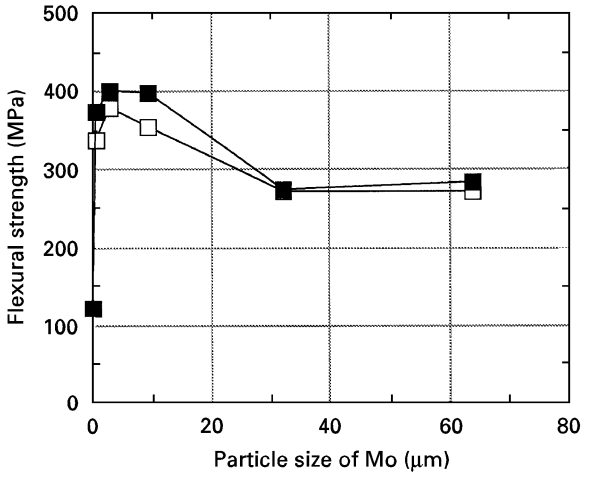


Figure 7 Effect of particle size of molybdenum on the flexural strength in the (□) L and (■) T directions.

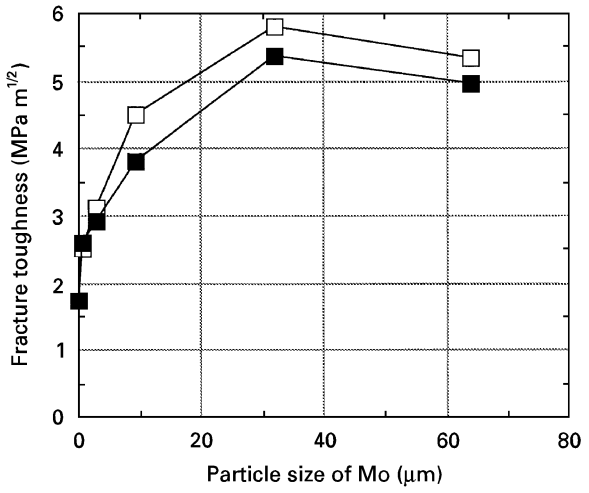


Figure 8 Effect of particle size of molybdenum on the fracture toughness in the (□) L and (■) T directions.

the flake forming, the more marked is the increase in toughness. The fracture toughness of the composites reinforced with 0.7 μm molybdenum particles is 2.5 MPa $m^{1/2}$ in the L direction and 2.6 MPa $m^{1/2}$ in the T direction, both approximately 1.5 times the value of 1.7 MPa $m^{1/2}$ for the MAS glass matrix. The increase of the fracture toughness of the composite reinforced with 3 μm molybdenum is approximately 1.8 and 1.7 times greater in the L and T directions, respectively, and for the 9.3 μm molybdenum-reinforced composite, is approximately 2.6–2.2 times greater than that of the MAS glass matrix. Above 32 μm, where molybdenum particle flake forming becomes more conspicuous, the toughness increase is saturated and the fracture toughness of the composite reinforced with 32 μm molybdenum is 3.3 and 3.1 times that of the MAS glass matrix in the L and T directions, respectively. From the above, it can be said that the uniform dispersion of flaky molybdenum particles is an effective new method of increasing fracture toughness.

The reasons for the dispersion of flaky molybdenum particles being an effective method of increasing fracture toughness are considered below. Fig. 9 shows scanning electron micrographs of fracture surfaces of tested specimens for fracture toughness in the L direction. In the case of the composite reinforced with 0.7 μm molybdenum particles, with almost no flake forming, no traces of plastic deformation of molybdenum particles are observed. When molybdenum particles become larger and flake forming becomes more conspicuous (particle size 3, 9.3 μm), the plastic deformation of molybdenum particles at the time of fracture becomes marked, the plastic deformation energy becomes large and fracture toughness is increased. Furthermore, at the large molybdenum particle of 32 μm, flake forming becomes yet more conspicuous and fracture toughness increases further. Above 32 μm, as can be seen from Fig. 5, the aspect ratio of flaky molybdenum particles saturates and the flake forming remains at around the 32 μm level, and the increase in fracture toughness is also around the same as at 32 μm. In addition, from the high-resolution TEM image of the interface between flaky molybdenum particle and the MAS glass matrix shown in Fig. 10, no reaction phases are observed at the interface, which is comparatively coherent. Secondary cracks observed at the interface between the matrix and plastically deformed molybdenum particles, as can be seen in Fig. 9b–e, indicate that the interface between the matrix and molybdenum particles is not very strongly bonded and is thought to function effectively as a route for crack deflection. Therefore, the reasons for the improvement in fracture toughness are considered to be: (1) increase in plastic deformation energy caused by plastic deformation of flaky molybdenum particles at the time of fracture; (2) the crack deflection effect of flaky molybdenum particle/matrix interface; and (3) the pull-out effect of flaky molybdenum particles from the matrix.

Reasons for the differences in fracture toughness in the L and T directions are considered from typical load–displacement curves and appearances of the tested specimen showing the crack propagation in the L and T directions as shown in Fig. 11.

The propagation of cracks in the L direction is affected by the presence of flaky molybdenum particles and crack deflection is observed, but in the T direction, the molybdenum particles have virtually no effect and cracks propagate rectilinearly. This is because, in the L direction, there are the flaky molybdenum particles/matrix interfaces perpendicular to crack propagation and, as the interface bonding is weak, the cracks are deflected, which is responsible for the corresponding higher toughness.

3.6. Comparison with other strengthening methods

Fig. 12 compares the relationship between flexural strength and fracture toughness for MAS glass composites reinforced with 20 vol % flaky molybdenum particle (32 μm) with those for other strengthening methods, namely the composites reinforced with SiC whiskers [2, 3], SiC platelets [4] and ZrO_2 particles [5]. The results are for SiC whiskers and SiC platelets

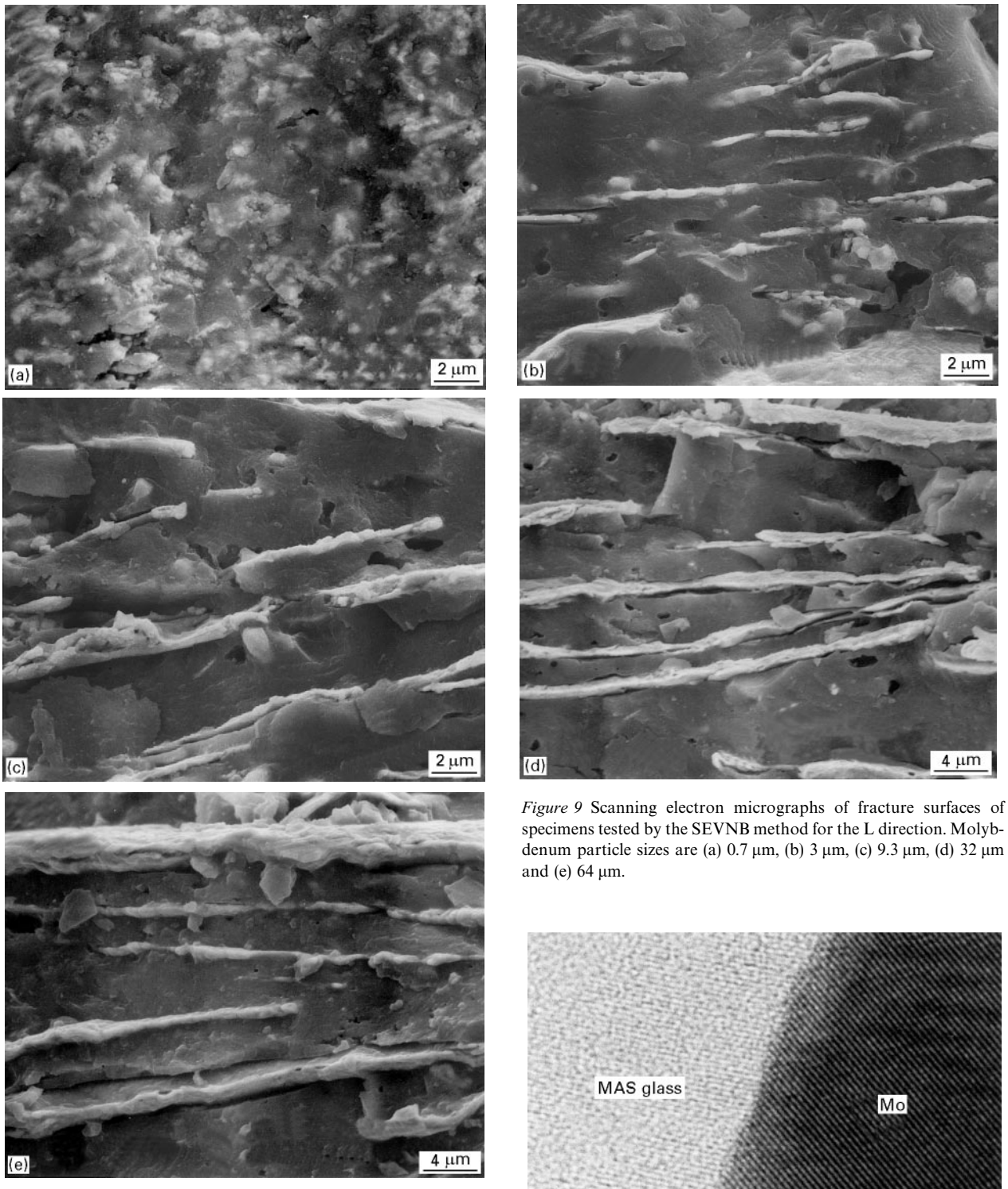
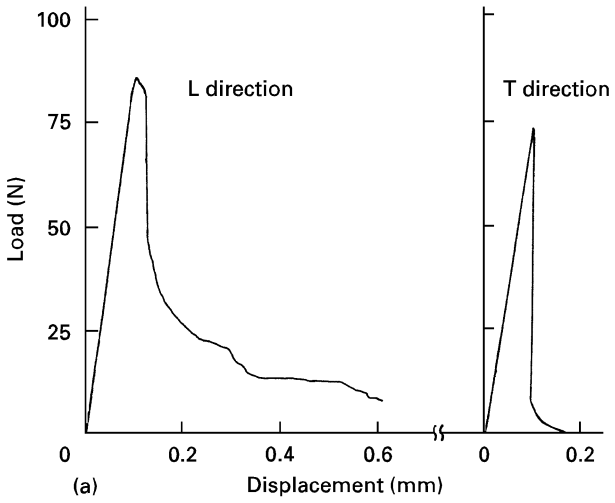


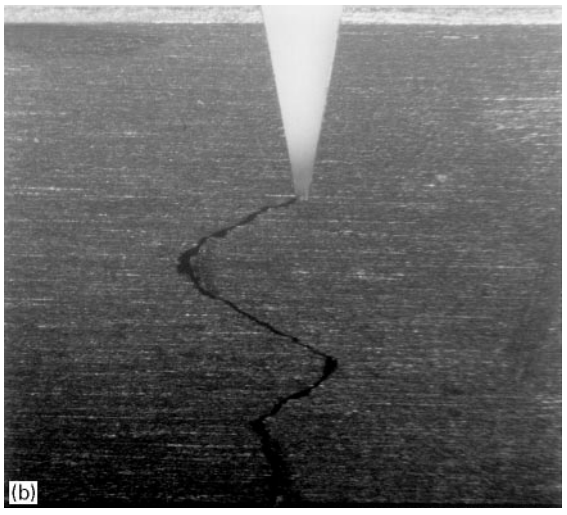
Figure 9 Scanning electron micrographs of fracture surfaces of specimens tested by the SEVNB method for the L direction. Molybdenum particle sizes are (a) 0.7 μm, (b) 3 μm, (c) 9.3 μm, (d) 32 μm and (e) 64 μm.

Figure 10 High-resolution TEM image of the interface between the MAS glass matrix and a molybdenum particle.

as 20 vol %, the same fraction as in this study, and for ZrO_2 particles as 18.7 vol %. The effect on flexural strength is lowest for SiC platelets and the increase in strength by flaky molybdenum particles is about 2.2 times that of the MAS glass matrix, which is almost the same effect of SiC whiskers or ZrO_2 particles on flexural strength.

However, the effect of flaky molybdenum particles on fracture toughness differs markedly from SiC whiskers, SiC platelets or ZrO_2 particles. The increase in fracture toughness by flaky molybdenum particles is about 3.1–3.3 times that of the matrix, showing an improvement effect superior to the 2.1–2.4 times for SiC whiskers, approximately 1.8 times for ZrO_2 particles and 1.5 times for SiC platelets. Hence, the new method for strengthening and toughening by the dispersion of flaky metallic particles shown in Fig. 1 has been proved to be effective for simultaneously increasing the strength and toughness of glass matrix composites.





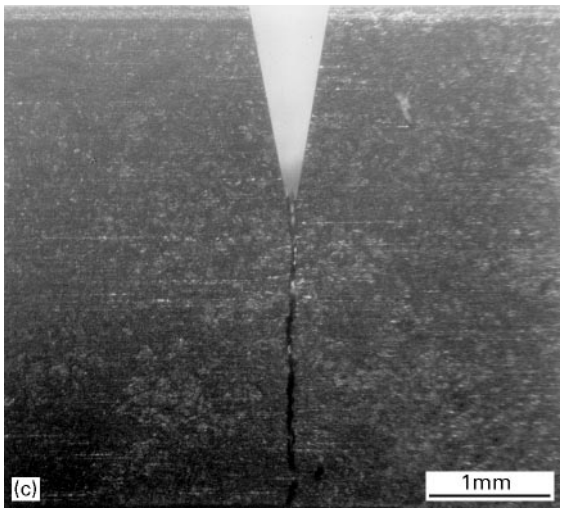


Figure 11 (a) Typical load–displacement curves of the fracture toughness test, and appearances of tested specimens for the (b) L and (c) T directions.

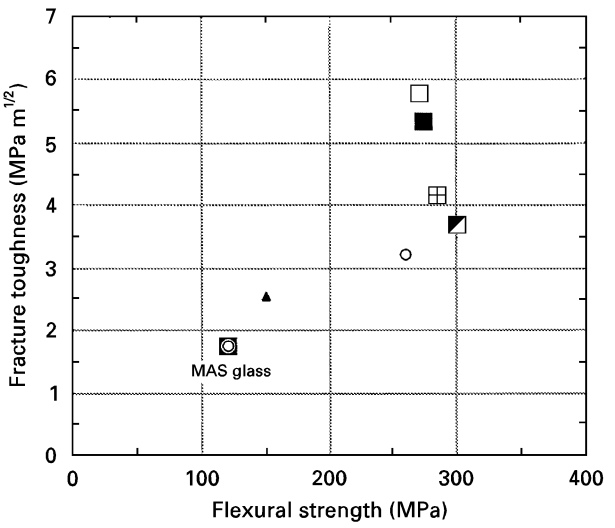


Figure 12 Relationship between fracture toughness and flexural strength for MAS glass/flaky molybdenum (32 μm) composite in the (□) L and (■) T directions, in comparison with (◩ [2], ⊞ [3]) MAS glass/SiC whisker, (▲) MAS glass/SiC platelet [4] and (○) MAS glass/18.7 % ZrO_2 particle composites [5].

4. Conclusions

The flake-forming behaviour of powders of molybdenum, niobium, nickel BS 316 S 12, Ni–17Cr–6Al–0.6Y, titanium and Ti–6Al–4V, was investigated and MAS glass composites reinforced with these flaky metallic particles were fabricated and evaluated. In addition, the effect of molybdenum particle size on flake-forming behaviour and the flexural strength and fracture toughness on the composites reinforced with flaky molybdenum particles were studied.

These investigations yielded the following results.

1. It is possible to deform molybdenum, niobium, iron, nickel, BS 316 S 12, Ni–17Cr–6Al–0.6Y, titanium and Ti–6Al–4V powders to flaky shape by 100 h wet ball milling with Si_3N_4 balls, and MAS glass composites reinforced with flaky metallic particles can be fabricated by hot-pressing, using the mixed powders (MAS glass/flaky metallic particles).

2. The strength of these composites shows a high degree of dependence on the type of metal used. Molybdenum, niobium, Ni–17Cr–6Al–0.6Y or iron-reinforced composites exhibit higher strength, whereas no effect is seen with composites reinforced with BS 316 S 12, nickel, titanium and Ti–6Al–4V.

3. The flake-forming behaviour of molybdenum particles depends markedly on particle size. Almost no flake forming is seen at 0.7 μm but as size increases, flake-forming becomes conspicuous and the aspect ratio of flaky molybdenum particles increases to a value of 17 at 32 μm. Above this size, the aspect ratio increases no further with particle size.

4. The flexural strength of the composites increases with increasing molybdenum particle size up to 3 μm and, at 9.3 μm, is the same or somewhat lower. Furthermore, above 32 μm, until which size flake-forming behaviour with increasing particle size is conspicuous, the effect of molybdenum particles on flexural strength decreases but still shows an increase in strength over MAS glass of around 150 MPa.

5. The fracture toughness of the composites depends greatly on the degree of flake forming of molybdenum particles. Flake forming of molybdenum particles becomes conspicuous with increasing molybdenum particle size up to 32 μm and, along with this, the fracture toughness of the composites increases to

approximately 5.5 MPa $m^{1/2}$ obtained by 32 μm molybdenum-reinforced composite. Above this size, fracture toughness becomes saturated along with flake forming.

6. The increase in fracture toughness of the composites reinforced with flaky molybdenum particles is greater than that of the composites reinforced with SiC whiskers, SiC platelets or ZrO_2 particles. This is because the plastic deformation of the flaky metals can be used efficiently.

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