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Simultaneous improvement of the strength and fracture toughness of MgO-Al_2O_3-SiO_2 glass/Mo composites by the microdispersion of flaky Mo particles

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The effect of shape and volume percent of Mo particles on the flexural strength and fracture toughness of MgO-Al_2O_3-SiO_2 (MAS) glass/Mo composites was investigated. The flexural strength and fracture toughness of composites depends heavily on Mo particle shapes, and there is greater improvement in composites reinforced with flaky rather than massive Mo particles. In the composites reinforced with flaky Mo particles, fracture toughness increases with volume percent of Mo and, at 50 vol% Mo, is 11.6 MPa$\sqrt{m}$, which is approximately 6.7 times higher than that of the matrix. Increases in fracture toughness of composites reinforced with flaky Mo particles is greater than with SiC whiskers, SiC platelets, SiC particles or ZrO_2 particles. Fabricating composites reinforced with flaky Mo particles is an effective toughening technique capable of simultaneously improving the strength and toughness of brittle materials, such as monolithic Al_2O_3 and MAS glass, by utilizing plastic deformation of ductile phase.

1. Introduction

While glass has the image of being "transparent and chemically stable", it also has the negative image of being "brittle and easily broken" in the same way as ceramics. If it becomes possible to strengthen and toughen glass, it is expected that glass will be capable of being used as a highly corrosion resistant structural material.

The strength of glass is between 1/10 and 1/100 of the theoretical value predicted from interatomic bonding strength, and this phenomenon has been explained in A. A. Griffith's theoretical strength equation considering the existence of flaws [1]. In short, the existence of flaws in brittle materials such as glass markedly decreases the strength of materials.

To improve the fracture toughness of such brittle materials, dispersing ceramic particles or whiskers, etc. with the intention of using mechanisms such as phase transformation, microcracking, crack deflection, pull-out, bridging, and the shielding effect of residual compressive stress has, to date, been applied to many ceramic materials. For glass materials too, similar techniques have been applied, and improvements of fracture toughness have been reported in composites reinforced with SiC whiskers [2, 3], SiC platelets [4], SiC particles [4], or ZrO_2 particles [5], etc. However, those improvements have not been prominent, that is, currently no effective technique has been found for drastic toughness improvement.

On the other hand, Waku *et al.* have reported that toughening is possible using a new technique by the uniform microdispersion of flaky ductile metallic particles in Al_2O_3 ceramics [6–8], and MAS glass [9]. The fundamental concept of the approach is based on increasing the plastic energy and surface energy in the Griffith-Irwin theoretical equation at the time of fracture. The technique has an effect of improving fracture toughness by increasing plastic energy, γ_p, through plastic deformation of metallic particles at a crack tip. In addition, a further increase in toughness can be expected by increasing the surface energy, γ_s, through crack deflection, when the interfacial bonding between the matrix the flaky metallic particles is weak, or by an effect of pull-out and shielding effect of flaky metallic particle.

In this study, using Mo particles, which were controlled to be flaky or massive shape, as the reinforcing phase and MAS (MgO-Al_2O_3-SiO_2) glass as the matrix, the effect of particle shape and volume percent of Mo particles on microstructures, flexural strength and fracture toughness of MAS glass composites was investigated.

2. Experimental method

Commercially available MAS (MgO 11.3 wt%, Al_2O_3 34.0 wt%, SiO_2 53.5 wt%) glass powder (GB-22, Iwaki Glass Co., Ltd., Chiba, Japan) with an average particle

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diameter of 9 μm was used as the matrix, and 32 μm Mo powder (Shouwa Denko Co., Tokyo, Japan) as the reinforcing phase.

The effect of particle shape and volume percent of Mo particles on mechanical properties of MAS/Mo composites was studied by controlling the shape of Mo powders to be flaky or massive (essentially the same as "as received") at contents of 20, 30, 40 and 50 vol%.

For producing microdispersion of flaky Mo particles in the composites, wet ball milling was carried out for 100 hours by using Si_3N_4 balls in ethyl alcohol to obtain homogeneously mixed powders of MAS glass and Mo and to plastically deform the Mo powders to flaky shapes. The obtained slurries were dried, using a rotary evaporator to remove the ethyl alcohol. For massive Mo particles, Mo powder was added to the slurries of MAS glass powder which was ball milled for 100 hours beforehand, then the slurries of mixed powders were dried, using a rotary evaporator to remove the ethyl alcohol.

The mixed powders were then hot-pressed in a graphite die to fabricate composites of $50 \times 50 \times 5$ mm at 1273 K under a 10 MPa pressure in a vacuum ($\sim 6.7 \times 10^{-2}$ Pa). Monolithic MAS glass was also fabricated by the same procedure described previously.

Measurement of the densities of the composites was performed by the Archimedes method in a water solution. The degree of Mo 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† JSM-T220 or Hitachi, Ltd., Tokyo, S-4200). 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.: Tokyo 196, Japan, RAD-RB type).

The three-point flexural strength was measured at room temperature with a 30 mm span by using specimens of $3 \times 4 \times 40$ mm at a crosshead speed of 0.5 mm/min. The fracture toughness was evaluated at room temperature according to the SEVNB (Single Edge V-notched Beam) method [10], by using the V-notched specimen.

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. Mo particle shape

Fig. 1 shows SEM images of as received Mo powder, 20 vol% massive Mo powder mixed with 80 vol% MAS glass powder, 20 vol% flaky Mo powder mixed with 80 vol% MAS glass powder, and optical micrograph of cross section of 20 vol% flaky Mo powder mixed with 80 vol% MAS glass powder. From Fig. 1a and b, particle shape of 20 vol% massive Mo powder is virtually the same as "as received" condition. However, from Fig. 1c and d, Mo powder is plastically deformed to flaky shape with 100 hours of wet ball milling and MAS glass powder is adhered uniformly to the the flaky Mo powder. The aspect ratio of flaky Mo particles which is evaluated by measuring length and thickness of cross-section of flaky Mo powders is around 17, which is small compared with the aspect ratio of 21 for case of Al_2O_3 matrix, but is virtually unaffected by volume percent of Mo powder, similarly to the case of Al_2O_3 matrix [7].

3.2. Microstructures of MAS glass/Mo composites

Fig. 2 shows optical micrographs of microstructures perpendicular (L cross section) to the hot pressed planes of the MAS glass/massive Mo particle and MAS glass/flaky Mo particle composites with 20, 30, 40 and 50 vol% Mo particles and parallel (T cross section) to the hot pressed planes of the composites with 50 vol% Mo particles. From Fig. 2a–d and f–i, the massive or flaky Mo particles are comparative uniformly dispersed within the MAS glass matrix, but the difference in configuration between massive and flaky is large. In case of the flaky Mo particles, longitudinal sections of flaky Mo particles have a tendency to align perpendicular to the hot pressing direction. The degree to which Mo particles form flakes in the composites is almost the same as in the mixed powders after ball milling, as shown Fig. 1d. The spacing between Mo particles decreases with increasing volume percent of Mo, and the spacing between flaky Mo particles tends to be smaller than that of massive Mo particles. According to Fullman [11], the mean free path λ between spherical particles of uniform radius R distributed randomly is given by:

$$\lambda = \frac{4R(1 - \mathrm{vf})}{3\mathrm{vf}} \tag{1}$$

Where vf is the volume fraction of spherical particles. Fig. 3 shows the relationships between vf and mean free path λ calculated using Equation 1 and the relationships for massive and flaky Mo particles measured in the L cross section. The mean free paths for massive Mo particles are about half of the calculated values for a given vf, however, the mean free paths for flaky Mo particles are considerably smaller than the Equation 1 values, which are about one tenth for a given vf.

Compared with Fig. 2d and e, and i and j, there is virtually no anisotropy in the composites of the L and T cross sections for the case of massive Mo particles but, for the composites with flaky Mo particles, various sections of flaky Mo particles are observed in the T cross section, which is considerably different from the L cross section. Hence, the flaky Mo particle-reinforced MAS glass composites exhibit anisotropic microstructures.

3.3. Flexural strength for MAS glass/Mo composites

Fig. 4 shows the relationship between flexural strength in the L and T directions and volume percent of Mo particles for MAS glass/massive Mo particle and MAS glass/flaky Mo particle composites. In both cases, virtually no difference is observed between the L and T directions, but improvement of flexural strength differs

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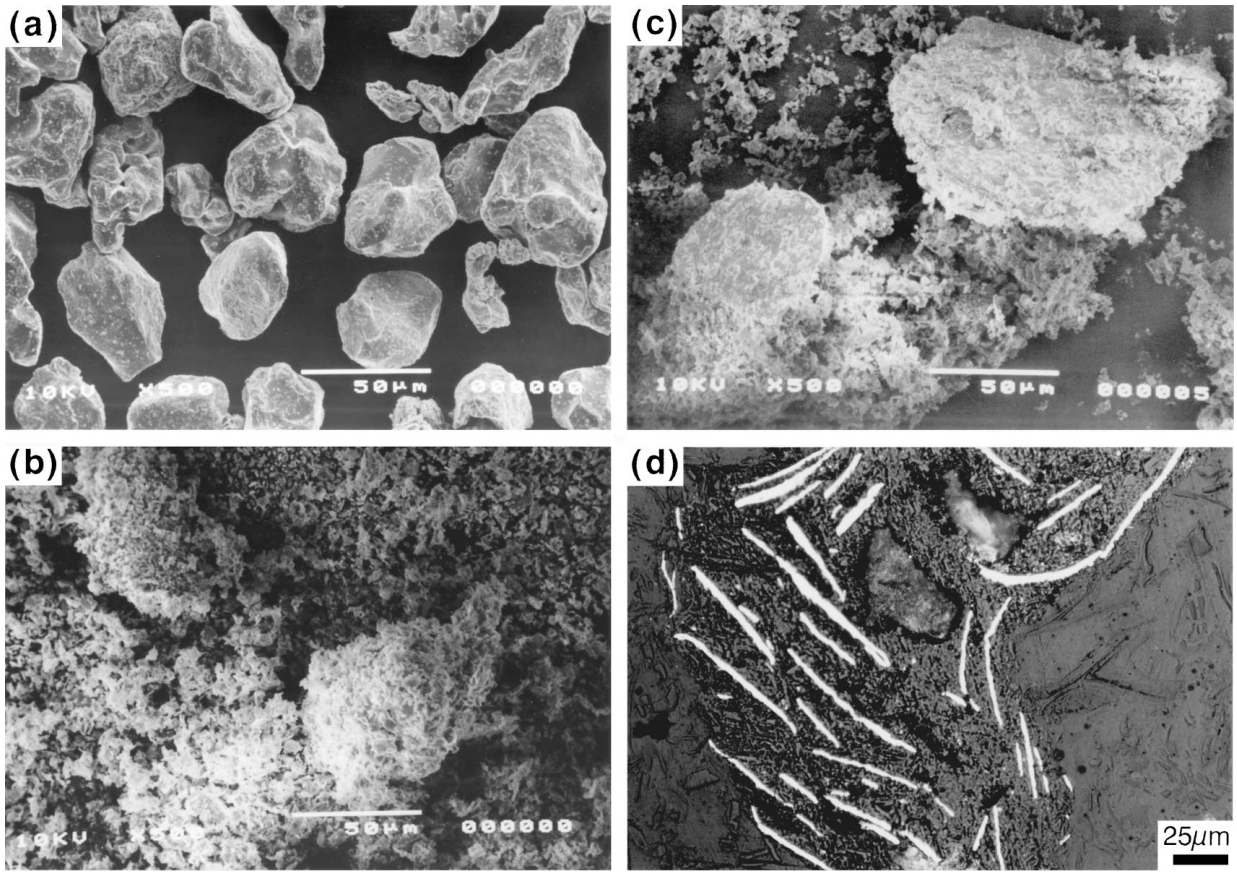

Figure 1 SEM images of (a) as received Mo powder, (b) 20 vol% massive Mo powder mixed with 80 vol% MAS glass powder, (c) 20 vol% flaky Mo powder mixed with 80 vol% MAS glass powder, and (d) optical micrograph of cross section of 20 vol% flaky Mo powder mixed with 80 vol% MAS glass powder.

according to the shape of Mo particles in the composite. That is to say, in the case of flaky Mo particles, flexural strength increases markedly with increasing volume fraction of Mo particles and, at 50 vol% Mo, flexural strength increase to 450 MPa, around 3.4 times the value of 131 MPa for monolithic MAS glass. By contrast, although flexural strength in the case of massive Mo particles increases with volume fraction of Mo particles, the ratio of increase is small and, at 50 vol% Mo, flexural strength is 250 MPa, around 1.9 times the value for monolithic MAS glass. In this way, effect of Mo particles on flexural strength differs greatly depending on shape of Mo particles at a given volume fraction of Mo.

As can be seen from Figs 3 and 4, mean Mo particle free path λ in the L cross section and flexural strength σ_b differ greatly for the cases of flaky and massive Mo particles. Fig. 5 shows the relationship between σ_b and $\lambda^{-1/2}$, which exhibits fairly a linear relationship between them. From Fig. 5, flexural strength can be expressed as a function of $\lambda^{-1/2}$, independent of Mo particle shape, which is similar with Hall-Petch equation and written as,

$$\sigma_b \propto \lambda^{-1/2} \tag{2}$$

From Equation 2, further increases in flexural strength can be expected by decreasing mean free path through facilitating a degree of flake-forming of Mo particles by changing ball milling conditions (treatment time, container shape or ball material, etc.).

In the case of Al_2O_3 matrix [7], the ratio of flexural strength increase is smaller than that of the MAS glass matrix in this study. At 50 vol% Mo, flexural strength was 450 MPa, around 1.4 times the value of 330 MPa for monolithic Al_2O_3, which is considerably smaller than the 3.4 times for MAS glass matrix. The effect of flaky Mo particles on ratio of increase in flexural strength is different from Al_2O_3 and MAS glass matrices.

3.4. Fracture toughness for MAS glass/Mo composites

Fig. 6 shows the dependence of fracture toughness in the L and T directions on volume percent of Mo particles. It can be seen that the fracture toughness of both MAS glass/massive Mo particle and MAS glass/flaky Mo particle composites increases with increasing volume percent of Mo particles, however the ratio of increase in fracture toughness on volume percent of Mo differs greatly with shape of Mo particles. For the case of massive Mo particles, fracture toughness in the L direction at 50 vol% Mo is increased to 4.3 MPa$\sqrt{m}$, which is 2.5 times the value of 1.7 MPa$\sqrt{m}$ for monolithic MAS glass, whereas in the case of flaky Mo particles fracture toughness in the L direction at 30 vol% Mo is 7.6 MPa$\sqrt{m}$, which is 4.5 times higher than that of monolithic MAS glass, and greater than that of massive Mo particles at 50 vol%. At 50 vol% of flaky Mo particles, fracture toughness in the L direction is greatly increased to 11.6 MPa$\sqrt{m}$, which is 6.8 times higher than that of monolithic MAS glass. In this way, ratio of improvement of fracture toughness differ greatly depending on particle shape of Mo, even the same Mo

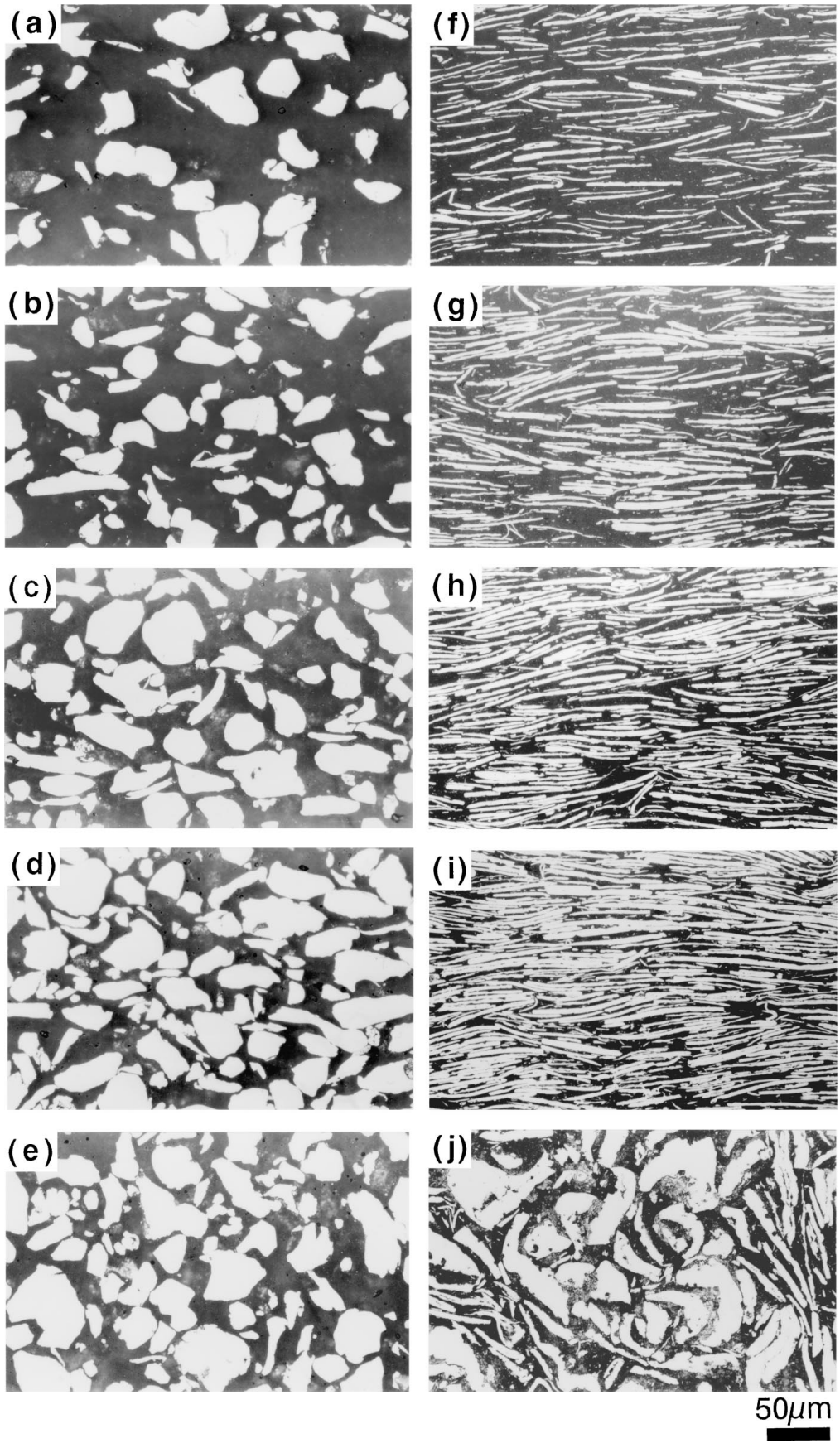

Figure 2 Optical micrographs of microstructures of (a–e) MAS glass/massive Mo particle and (f–j) MAS glass/flaky Mo particle composites: (a, f) 20 vol% Mo, (b, g) 30 vol% Mo, (c, h) 40 vol% Mo, (d, e, i, j) 50 vol% Mo. (a–d, f–i) perpendicular to the hot pressed planes (L cross section), (e, f) parallel to the hot pressed planes (T cross section).

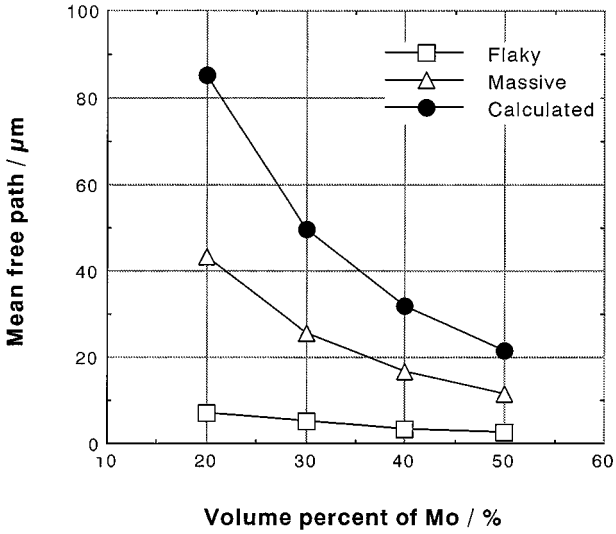

Figure 3 Relationship between volume percent of Mo particles and mean free path for calculated using Equation 1, MAS glass/massive Mo particle and MAS glass/flaky Mo particle composites in the L cross section.

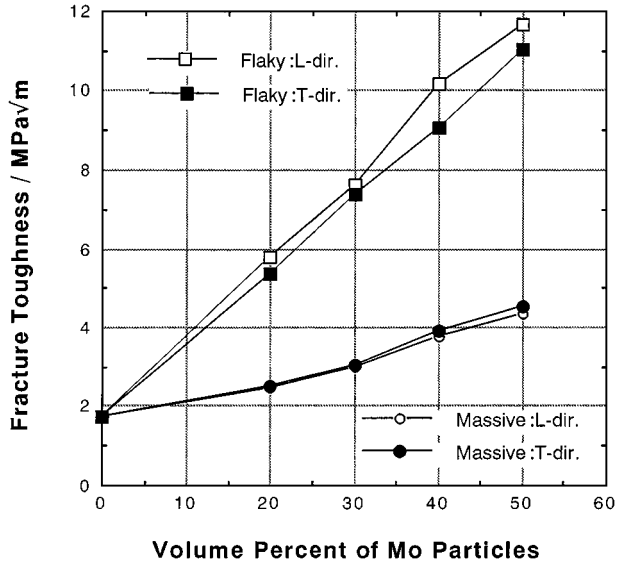

Figure 6 Dependence of fracture toughness on volume percent of Mo particles for MAS glass/massive Mo particle and MAS glass/flaky Mo particle composites.

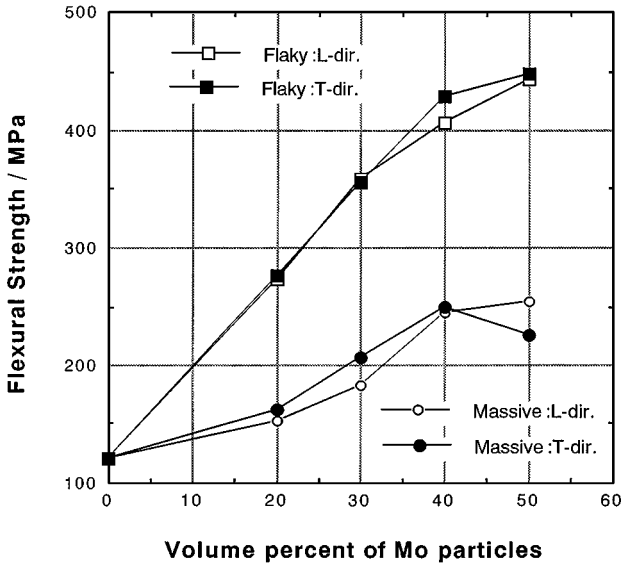

Figure 4 Relationship between volume percent of Mo particles and flexural strength for MAS glass/massive Mo particle and MAS glass/flaky Mo particle composites.

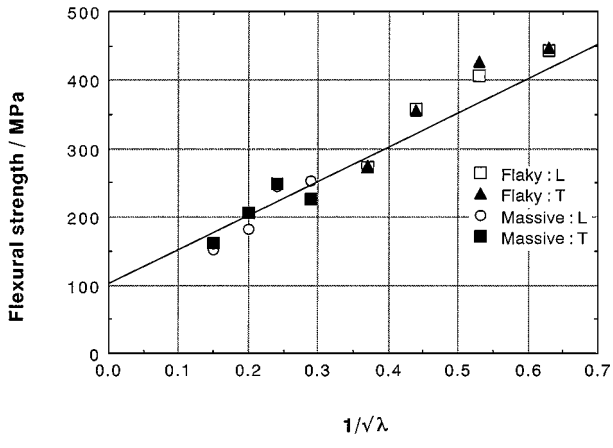

Figure 5 Relationship between flexural strength and $\lambda^{-1/2}$ for MAS glass/massive Mo particle and MAS glass/flaky Mo particle composites.

particles are used as starting materials, with flaky particles being extremely effective.

In the case of flaky Mo particles, fracture toughness in the L direction tends to be higher than that in the T direction as shown in Fig. 6. Fig. 7 shows typical load-displacement curves and photographs of the tested specimen showing crack propagation in the L and T directions. In the T direction, cracks propagate linearly from notches, while crack deflection is observed in the L direction. This is considered to be the cause of higher fracture toughness in the L direction

The reason for the dispersion of flaky Mo particles being an effective method for increasing fracture toughness is considered to be as follows. Fig. 8 shows SEM photographs of fracture surfaces of tested MAS glass/massive Mo particle and MAS glass/flaky Mo particle composites with 20 and 50 vol% Mo for fracture toughness in the L direction. Fig. 9 shows SEM micrographs of representative crack propagation around the Vickers indentation for the composites with 30 vol% massive and flaky Mo particles in the L cross section. For the case of massive Mo particles, in which improvement of fracture toughness is small, there are not many traces of plastic deformation of Mo particles in the fracture surfaces, irrespective of volume fraction of Mo as shown in Fig. 8a and b. From Fig. 9a, it is observed that cracks propagate along the interfaces between Mo particles and the matrix. Those observations indicate that the toughness increase results mainly from effect of crack deflection and pull-out of Mo particles from the matrix. By contrast, in case that flaky Mo particles are dispersed, irrespective of volume fraction of Mo, there is conspicuous plastic deformation of Mo particles in the fracture surfaces, and the increase in plastic energy is considered to increase the fracture toughness. With increasing the volume fraction of flaky Mo particle, the amount of plastic deformation of Mo particles further increases, which contributes to an increase in plastic energy. This is considered to be the main cause of the

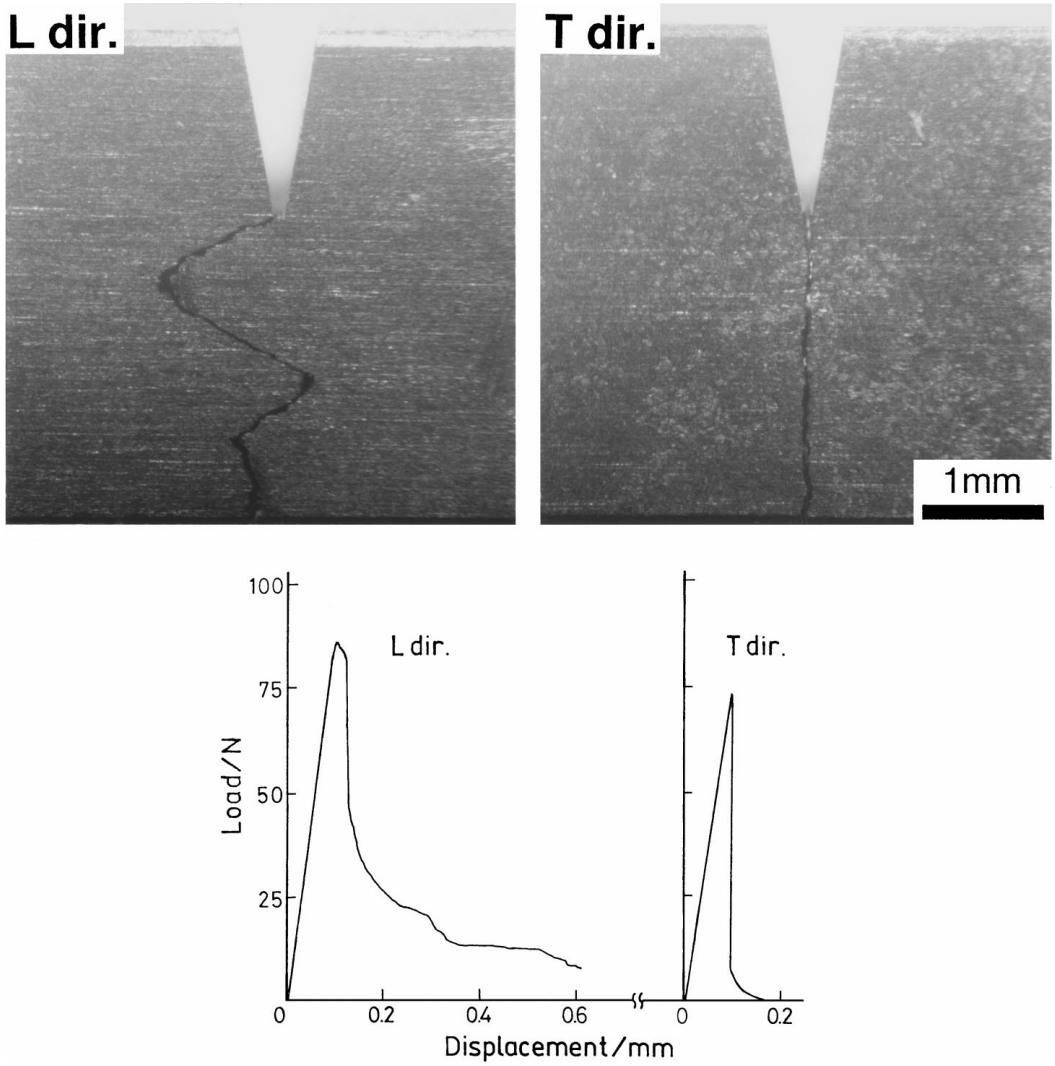

Figure 7 Typical load-displacement curves and photographs of the tested specimen of MAS glass/20 vol% flaky Mo particle composites in the L and T directions.

fracture toughness dependence on volume fraction of Mo, as seen in Fig. 6.

As can be seen from the HRTEM image of the interface between Mo particles and the matrix shown in Fig. 10, no reaction phases are observed at the interface, and a comparatively compatible interface is formed. Since secondary cracks, as seen in Fig. 8c and d, are frequently observed at the interfaces between the Mo particles and the matrix, which indicates the bonding strength of interface is not very strong and is thought to act as an effective path for crack propagation. In summary, the increase in fracture toughness by dispersion of flaky Mo particles is considered to the following reasons: 1) increase in plastic energy at the time of fracture through plastic deformation of flaky Mo particles, 2) Crack deflection effects due to weak bonding strength at interfaces between the Mo particles and matrix, and 3) Pull-out effects of Mo particles from the matrix, etc.

3.5. Increase in fracture toughness by the microdispersion of flaky ductile metal particles

On the subject of the toughening method of brittle materials by crack-tip blunting by a ductile phase, Chan [12] has introduced the rule of mixtures for analyzing the HRR (Hutchinson [13], and Rice and Rosengren [14]) field, and defined the toughening ratio, λ_b, as follows: for crack-tip blunting by a ductile phase, the toughening ratio, λ_b, which is defined as the ratio of the applied stress intensity factor, Kc, to that in the matrix, Km, is given by

$$\lambda_b = \frac{Kc}{Km} = [1 + V_\beta(\Sigma - 1)]^{(n-1)/2n} \times [1 + V_\beta(\Lambda - 1)]^{(n+1)2n}\left[\frac{Ec}{Em}\right]^{(n+1)/2n} \quad (3)$$

with

$$\Sigma = \frac{\sigma_y^\beta}{\sigma_y^\alpha} \quad (4)$$

$$\Lambda = \frac{\varepsilon_f^{-\beta}}{\varepsilon_f^{-\alpha}} \quad (5)$$

$$Ec = V_m Em + V_\beta E_\beta \quad (6)$$

where V_α and V_β are the volume fractions of the matrix (α) and ductile phase (β), σ_y^α and σ_y^β are the yield stress

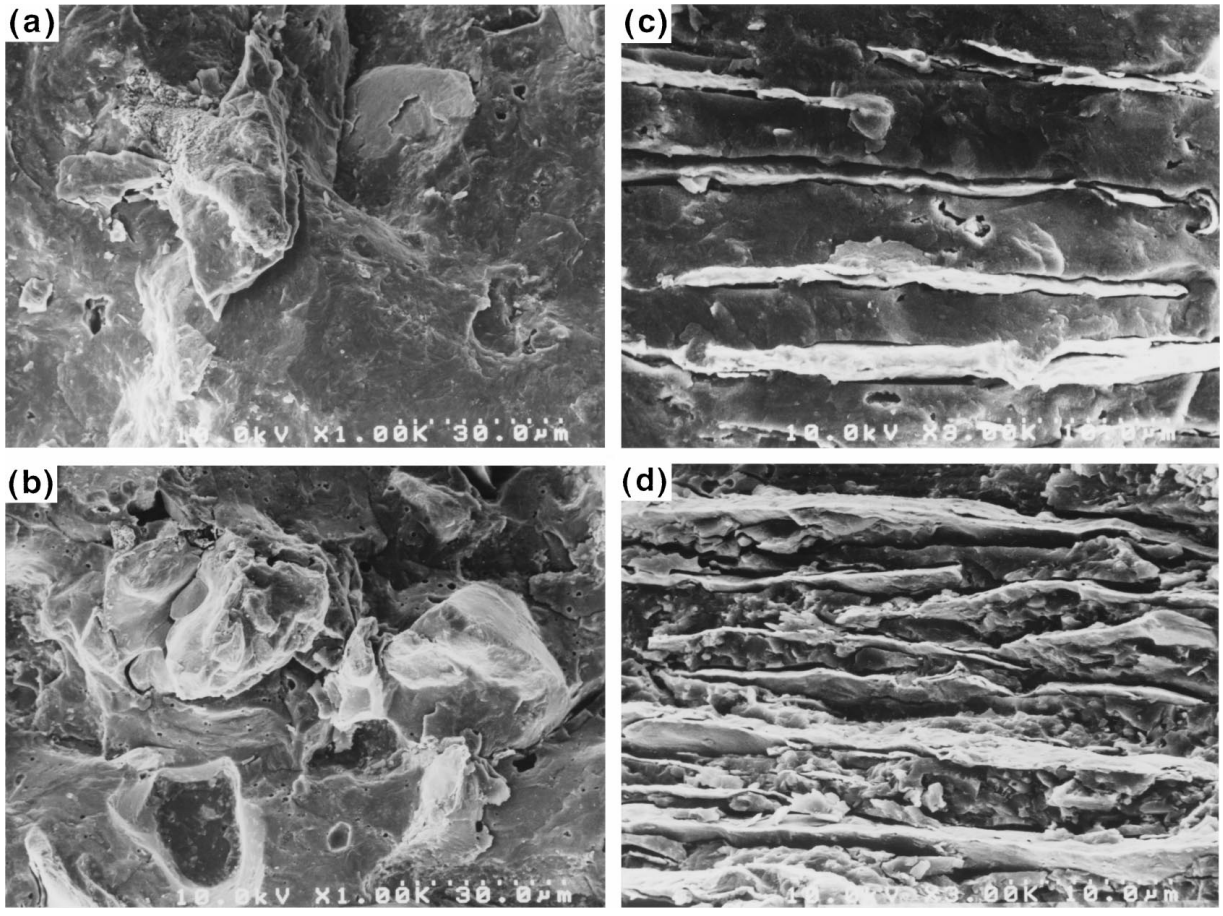

Figure 8 SEM photographs of fracture surfaces of tested for fracture toughness in the L direction: (a, b) MAS glass/massive Mo particle composites, (c, d) MAS glass/flaky Mo particle composites: (a, c) 20 vol% Mo, (b, d) 50 vol% Mo.

of the matrix (α) and ductile phase (β), $\varepsilon_f^{-\alpha}$ and $\varepsilon_f^{-\beta}$ are the effective fracture strain of the matrix (α) and ductile phase (β), n is the inverse of the strain hardening exponent, N, and Ec and Em are Young's moduli of the composite and matrix, respectively.

The dependence of toughening ratio on volume fraction of Mo particles for MAS glass/flaky Mo particle composites obtained in this study, for Al_2O_3/flaky Mo particle composites [7], and calculated results using Equation 3 are shown in Fig. 11. Here the Young's moduli of the composites was calculated from the rule of mixtures, using Young's modulus of MAS glass, Al_2O_3 and Mo particles as 120 GPa, 350 GPa and 343 GPa, respectively. For the calculations, Σ and Λ were taken as 3.81 (= 500 MPa/130 MPa) and 20 (= 0.2/0.01), respectively, for the case of MAS glass composites, and 1.43 (= 500 MPa/350 MPa) and 20 (= 0.2/0.01), respectively, for the case of Al_2O_3 composites, and n as 20. In the case of Al_2O_3/flaky Mo particle composites, the measured values agree with the calculated values but, in the case of a MAS glass/flaky Mo particle composite, measured values are apparently higher than the calculated values. In the case of the MAS glass/flaky Mo particle composites, numerous debonding at interfaces between the flaky Mo particles and the matrix, and secondary cracks are observed as seen in Figs 8c, d and 9b. It is presumed that the higher fracture toughness than those calculated in the MAS glass/flaky Mo particle composites may be due to shielding effect, pull-out effect, crack deflection effect in addition to restraining effect on crack propagation through plastic deformation of flaky Mo particles.

3.6. Comparison with other strengthening methods

Fig. 12 shows comparisons of the relationships between flexural strength and fracture toughness for MAS glass/Mo composites, with those for other strengthening methods by the microdispersion of SiC whiskers [2], SiC platelets [4], SiC particles [4] and ZrO_2 particles [5]. From Fig. 12, dispersion of ceramic materials, such as SiC whiskers, SiC platelets, SiC particles and ZrO_2 powders is effective in increasing strength, but not very effective in increasing fracture toughness. It can be seen that dispersion of massive Mo particles, similarly to the ceramic materials, is not very effective in increasing toughness. That is to say, in cases where the dispersed phase shows almost no plastic deformation, and the main mechanisms of toughness increase are crack deflection effect, crack shielding effect, crack bridging effect, etc., strength is increased effectively, but no drastic effect of increase in toughness can be expected. By contrast, microdispersing the flaky Mo particles is effective in simultaneously increasing strength and fracture toughness, and can be considered to be a new toughening technique for brittle materials, such as glass and ceramics. Fracture toughness is, in particular,

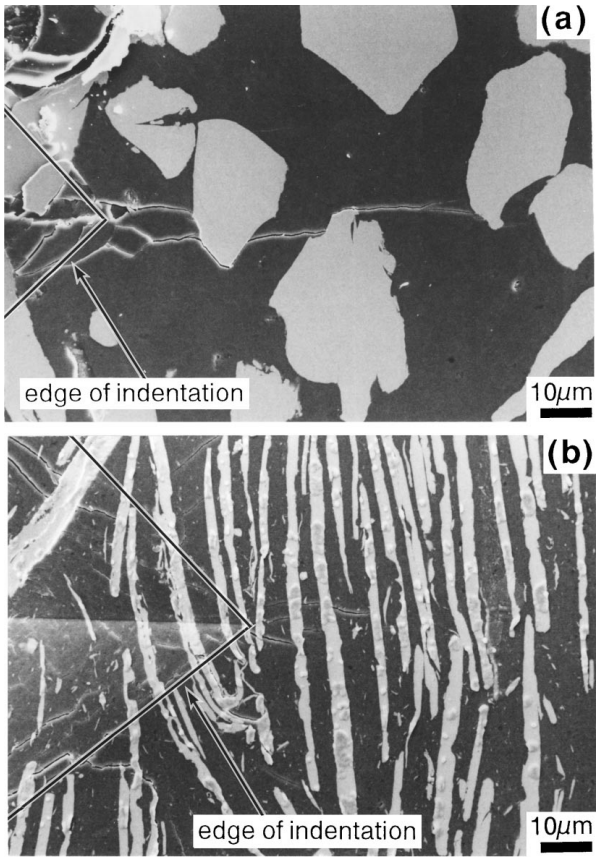

Figure 9 SEM micrographs of representative crack propagation around the Vickers indentation for the composites with 30 vol% Mo: (a) MAS glass/massive Mo particle composites, (b) MAS glass/flaky Mo particle composites.

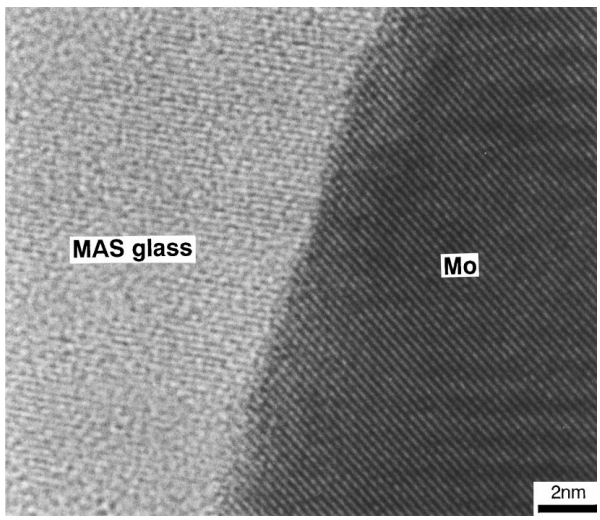

Figure 10 HRTEM image of the interface between flaky Mo particle and MAS glass.

increased by microdispersion of the flaky Mo particles as shown Fig. 12. This is thought to be due to increased plastic energy by plastic deformation, and additional effects such as crack deflection effect, crack shielding effect, crack bridging effect, etc. In the case where plastic deformation is observed in the reinforcing phase, the relationship between toughening ratio and volume fraction of reinforcing phase can be considered to lie between the straight line for MAS glass/flaky Mo particle composites and the curve for MAS glass/ceramic materials composites shown in the Fig. 12, depending on the extent of plastic deformation and bonding strength at interfaces.

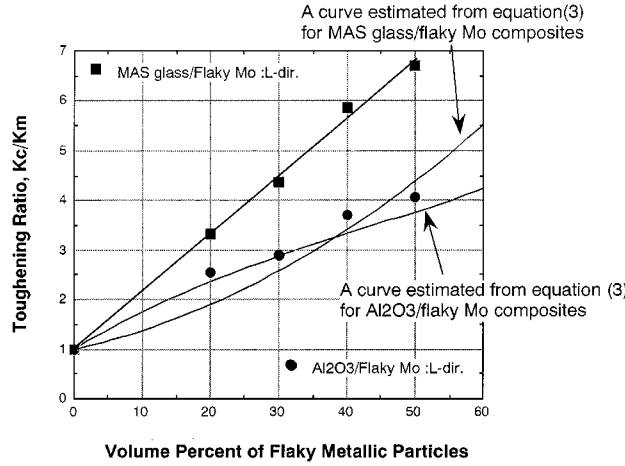

Figure 11 Comparison of measured and calculated values for relationships between toughening ratio, λ_b, and volume percent of Mo particles for MAS glass/massive Mo particle and MAS glass/flaky Mo particle composites.

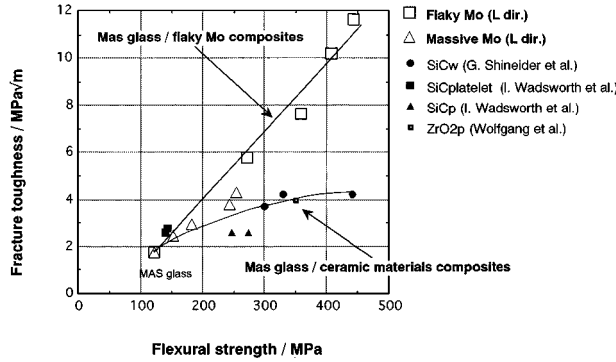

Figure 12 Comparison of relationships between flexural strength and fracture toughness for MAS glass/massive Mo particle and MAS glass/flaky Mo particle composites, and composites using other strengthening techniques.

4. Conclusions

As a result of the investigation of the effect of shape and volume fraction of Mo particle on the strength and fracture toughness for MAS glass/Mo composites, the followings were found.

(1) It is possible to obtain mixed powder of massive Mo particles and MAS glass powder by directly removing the ethyl alcohol from a slurry of MAS glass and Mo powder. Through wet ball milling of the slurry, mixed powder of flaky Mo particles and MAS glass powder can be obtained. It is possible to fabricate composites using these powders by hot pressing.

(2) The strength of the composites depends heavily on Mo particle shape and volume fraction. The ratio of improvement of flexural strength is greater for flaky Mo particles than for massive Mo particles. In the case of flaky Mo particles, the flexural strength of the composites at 50 vol% Mo is increased by 3.4 times that of MAS glass from 131 MPa to 450 MPa.

(3) Fracture toughness differ greatly depending on Mo particle shape. The ratio of improvement of fracture toughness is conspicuously greater for flaky Mo particles than for massive Mo particles. Hence, controlling the shape of particles to be flaky is extremely effective for increasing fracture toughness, because plastic energy increases substantially due to conspicuous plastic deformation of flaky particles.

(4) The increase in fracture toughness of the composites reinforced with flaky Mo particles is greater than that reinforced with SiC whiskers, SiC platelets, SiC particles or ZrO_2 particles. The effect of massive Mo particles on fracture toughness is to be similar with the effect of SiC whiskers, SiC platelets, SiC particles or ZrO_2 particles.

(5) The microdispersion of flaky Mo particles in brittle materials such as ceramic and glass is an effective toughening technique for the simultaneous improvement of strength and fracture toughness.

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