# Fabrication and mechanical behaviour of $AI_2O_3/Mo$ nanocomposites

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Two types of  $AI_2O_3/Mo$  composites were fabricated by hot-pressing a mixture of  $\gamma$ - or  $\alpha$ - $AI_2O_3$  powder and a fine molybdenum powder. For  $AI_2O_3/5$  vol% Mo composite using  $\gamma$ - $AI_2O_3$  as a starting powder, the elongated molybdenum layers were observed to surround a part of the  $AI_2O_3$  grains, which resulted in an apparent high value of fracture toughness (7.1 MPa m<sup>1/2</sup>). In the system using  $\alpha$ - $AI_2O_3$  as a starting powder, nanometre sized molybdenum particles were dispersed within the  $AI_2O_3$  grains and at the grain boundaries. Thus, it was confirmed that ceramic/metal nanocomposite was successfully fabricated in the  $AI_2O_3/Mo$  composite system. With increasing molybdenum content, the elongated molybdenum particles were formed at  $AI_2O_3$  grain boundaries. Considerable improvements of mechanical properties were observed, such as hardness of 19.2 GPa, fracture strength of 884 MPa and toughness of 7.6 MPa m<sup>1/2</sup> in the composites containing 5, 7.5, 20 vol% Mo, respectively; however, they were not enhanced simultaneously. The relationships between microstructure and mechanical properties are also discussed.

## 1. Introduction

Sintered ceramics, due to their desirable properties such as high refractory capability, good wear resistance, and chemical stability, are being investigated as candidates for a wide variety of engineering applications. As opposed to metallic materials, ceramics have inherently strong covalent and ionic bonds that prohibit substantial dislocation motion or plastic deformation. Therefore, most ceramics fail to alleviate stress concentrations that occur in front of a crack tip. Consequently, ceramics are easily fractured as a consequence of crack propagation resulting from a slight surface flaw or internal flaw. Thus, ceramics exhibit poor toughness which restricts their application for structural materials.

To improve the mechanical properties, particularly fracture strength and toughness, many attempts have been made to provide ceramic matrix composites incorporating second-phase dispersions such as particulates, platelets, whiskers or fibres [1-4]. In this case, ceramic/ceramic systems are the most active field of ceramic matrix composite research. On the other hand, there are also some investigations regarding ceramic/metal composites which have incorporated secondary metal-phase dispersions such as tungsten, molybdenum, titanium, chromium, nickel, etc. [5-10]. However, for both types of composites, fracture strength and toughness have not been improved simultaneously. This is mainly due to the fact that the addition of second-phase dispersions generally causes an enlargement of the flaw size in the composites. Therefore, these composites have advanced from a micro-order dispersion to a nano-order dispersion, especially in the ceramic/ceramic systems in an attempt to alleviate this problem. In recent years, nanocomposites, in which nanometre sized second particles are dispersed within the ceramic matrix grains and at the grain boundaries, have shown significant improvements in mechanical properties, such as fracture strength, hardness and creep resistance, even at high temperatures [11-13]. However, with regard to fracture toughness, the ceramic nanocomposites have only shown slight improvement. Consequently, it is highly desirable to further improve the fracture toughness of ceramic nanocomposites so that they may combine excellent toughness with fracture strength.

The purpose of this investigation was to extend nanocomposites to other ceramic/metal composite systems containing nanometre-sized metal inclusions and to confirm the possibility for toughening and strengthening of the ceramic matrix. In the first approach,  $Al_2O_3$  and molybdenum were selected for the ceramic matrix and metal dispersions, respectively.  $Al_2O_3$  has been well examined as a structural ceramic and has been studied in ceramic/ceramic nanocomposite systems such as  $Al_2O_3/SiC$  [11, 12]. Molybdenum particles were selected as one of the refractory metals and a material having lower thermal expansion coefficient than the Al<sub>2</sub>O<sub>3</sub> matrix. A conventional powder metallurgical technique was used for preparing Al<sub>2</sub>O<sub>3</sub>/Mo composites. In the system Al<sub>2</sub>O<sub>3</sub>/ 5 vol % Mo composites,  $\gamma$ - and  $\alpha$ -phase of Al<sub>2</sub>O<sub>3</sub> were used as a starting powder for the matrix, respectively. In Al<sub>2</sub>O<sub>3</sub>/Mo composites containing above 5 vol %Mo, however, only  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder was used. In this paper, the fabrication process, microstructure and mechanical properties will be described for Al<sub>2</sub>O<sub>3</sub>/Mo composites containing up to 20 vol % Mo.

## 2. Experimental procedure

#### 2.1. Fabrication

γ-Al<sub>2</sub>O<sub>3</sub> powder (Asahi Chemical Co.) with a specific surface area of  $100 \text{ m}^2 \text{ g}^{-1}$  and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder (Taimei Chemical Co.) with an average particle size below 0.3 µm were used as starting materials for the matrix, respectively. Molybdenum powder (Japan New Metals Co.) with an average particle size of 0.65 µm was used as reinforcing metal particles, but it had a bimodal distribution with the particle size below 0.2 µm and above 1 µm. The powder mixtures, containing 5, 7.5, 10, 15, 20 vol % Mo, were ball milled using zirconia milling media in acetone for 24 h. These slurries were dried and passed through a 250 µm screen. Then the mixtures were hot-pressed in carbon dies of 40 mm diameter. The hot-pressing conditions were 1400°-1700 °C with an applied pressure of 30 MPa for 1 h under a vacuum of less than  $10^{-4}$  torr (1 torr = 133.322 Pa).

## 2.2. Characterization

Phase identification of the composite was determined by X-ray diffraction analysis on the surfaces of the specimens. The densities of the specimens were obtained by the Archimedes method using toluene as the medium. The microstructure of the composites and the crack propagation behaviour were observed by scanning electron microscopy (SEM). More detailed microstructural characteristics were examined by transmission electron microscopy (TEM). The grain size was estimated by the line intercept method.

## 2.3. Mechanical properties

The hot-pressed specimens were cut by a diamondblade saw, and ground with a 600-grit diamond wheel. The specimens had the dimensions of  $3 \text{ mm} \times 4 \text{ mm} \times 35 \text{ mm}$  for the mechanical properties measurement, and  $3 \text{ mm} \times 1 \text{ mm} \times 38 \text{ mm}$  for the elastic modulus measurement. The elastic modulus was determined by the resonance vibration method with first-mode resonance. The fracture strength was measured by a three-point bending test at room temperature. The span length and crosshead speed were 20 mm and 0.5 mm min<sup>-1</sup>, respectively. The tensile surfaces of the specimens were perpendicular to the hot-pressing axis and were polished with a diamond liquid suspension. The fracture toughness was estimated by the indentation fracture (IF) method using the following equation of Marshall and Evans [14]

$$K_{\rm IC} = 0.036 E^{0.4} P^{0.6} a^{-0.7} (c/a)^{-1.5}$$
 (1)

Where E is the elastic modulus and P is an applied load. Here a and c are characteristic dimensions of the Vickers impression and the radial/median crack, respectively. The polished surfaces were used for the Vickers indentation with a load of 196 N and a loading duration of 15 s. The Vickers hardness of the composite was determined separately with a load of 9.8 N.

#### 3. Results and discussion

#### 3.1. Phase identification

In the system of  $Al_2O_3/5$  vol % Mo composite hotpressed at 1600 °C using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a starting powder, mainly  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and molybdenum were found, but  $MoO_2$  phase was detected as an oxidized phase. To investigate the cause of the MoO<sub>2</sub> formation during sintering, reduction under hydrogen up to  $1200\,^\circ\mathrm{C}$ was attempted before hot-pressing for the composite using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as the starting powder. In this case, the composite hot-pressed in vacuum after hydrogen reduction was composed of only  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and molybdenum but no MoO<sub>2</sub>. From this result, it was assumed that the formation of MoO2 was derived from the y-Al<sub>2</sub>O<sub>3</sub> powders possessing high reactivity and hydroxyl groups absorbed on the surfaces of the powder due to the extremely large specific surface area. The relative density of the composite was only 98.5%, probably due to the formation of the  $MoO_2$  phase possessing a lower density than molybdenum.

On the other hand, in the system using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a starting powder, only  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and molybdenum were observed for the composites containing up to 20 vol % Mo hot-pressed at 1400°-1700 °C. These composites obtained relative densities above 99.5%.

#### 3.2. Microstructures

Fig. 1 shows scanning electron micrographs of the fracture surface for  $Al_2O_3/5$  vol % Mo composite hot-pressed at 1600 °C for 1 h under a vacuum, using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a starting powder. The elongated molybdenum layers, having an approximate length of  $10 \,\mu m$ , were observed to surround a part of the Al<sub>2</sub>O<sub>3</sub> grains. The formation of the elongated molybdenum layers was estimated to be related to the formation of  $MoO_2$ phase. It is considered that, during sintering, the surfaces of molybdenum particles are oxidized by hydroxyl groups absorbed around the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles to produce molybdenum oxides. In the phase diagram of the Mo-O system [15], molybdenum oxides are known to have various oxide valence levels between  $MoO_3$  and  $MoO_2$  such as  $Mo_4O_{11}$  and  $Mo_9O_{26}$ . In addition, there are many liquid phases that coexist such as  $MoO_2$  + liquid,  $MoO_3$  + liquid,  $Mo_4O_{11}$ + liquid, and  $Mo_9O_{26}$  + liquid. In particular, the  $MoO_2$  + liquid phase has a wide range above 818 °C. Therefore, it seems reasonable to assume that the formation of the elongated molybdenum layers was derived from a liquid phase, such as  $MoO_2 + liquid$ .



Figure 1 Scanning electron micrographs of the fracture surface for  $Al_2O_3/5$  vol% Mo composite fabricated using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a starting powder: (a) hot-pressed at 1660 °C, (b) back-scattered electron image of (a).

The  $Al_2O_3$  grains grew to columnar form having an approximate length of 15 µm and an average grain size of 8–9 µm, probably due to the formation of a liquid phase associated with the formation of the MoO<sub>2</sub>. The particle size of spherical molybdenum was less than 2 µm. Smaller sized molybdenum particles, less than 1 µm, were observed within the  $Al_2O_3$  matrix grains.

Fig. 2 shows scanning electron micrographs of the fracture surface for Al<sub>2</sub>O<sub>3</sub>/5 vol % Mo composite hotpressed at 1600 °C for 1 h under a vacuum, using α- $Al_2O_3$  as a starting powder. The fine microstructure of  $Al_2O_3/Mo$  composite was determined to have an average grain size of less than 1 µm. This was much smaller than the grain size of the composite which used  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a starting powder. The variation of the average grain size with hot-pressing temperature is shown in Fig. 3. It was shown that the addition of molybdenum particles, which served as inclusions, resulted in grain-growth inhibition of the Al<sub>2</sub>O<sub>3</sub> matrix. However, with increasing molybdenum content and rising sintering temperature, slight grain growth of Al<sub>2</sub>O<sub>3</sub> and the coalescence of molybdenum particles at the  $Al_2O_3$  grain boundaries were observed.

Typical TEM image of  $Al_2O_3/5$  vol % Mo composite hot-pressed at 1500 °C, using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a starting powder, are shown in Fig. 4. The nanometresized molybdenum particles were confirmed to be dispersed within the equiaxed  $Al_2O_3$  matrix grains and at the grain boundaries. In addition, the larger



Figure 2 Scanning electron micrographs of the fracture surface for  $Al_2O_3/5$  vol % Mo composite fabricated by using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a starting powder: (a) hot-pressed at 1600 °C, (b) back-scattered electron image of (a).



Figure 3 Variation of average grain size with hot-pressing temperature for  $Al_2O_3/Mo$  composites. ( $\bigcirc$ ) Monolithic  $Al_2O_3$ , ( $\bigcirc$ )  $Al_2O_3/5$  vol % Mo, ( $\blacktriangle$ )  $Al_2O_3/7.5$  vol % Mo, ( $\bigstar$ )  $Al_2O_3/10$  vol % Mo, ( $\bigstar$ )  $Al_2O_3/10$  vol % Mo, ( $\bigstar$ )  $Al_2O_3/20$  vol % Mo.

molybdenum particles, above 1  $\mu$ m, appeared to be located at the grain boundaries. Furthermore, as shown in Fig. 5, no reaction phase was observed at the interface between Al<sub>2</sub>O<sub>3</sub> and molybdenum within the



Figure 4 TEM image of the microstructure for  $Al_2O_3/5$  vol % Mo composite fabricated by hot-pressing under a vacuum.



Figure 6 A line of piled up dislocation observed within the  $Al_2O_3$  for  $Al_2O_3/5$  vol % Mo composite.



Figure 5 High-resolution TEM image of the interface between  $Al_2O_3$  matrix and molybdenum within the  $Al_2O_3$  grain.

 $Al_2O_3$  grain. The composite prepared in this work, therefore, had a mixed morphology composed of both intragranular and intergranular microstructural features. Consequently, it was confirmed that ceramic/ metal nanocomposite was successfully fabricated in the  $Al_2O_3/Mo$  composite system when  $\alpha$ - $Al_2O_3$  was used as a starting powder.

Fig. 6 shows what seems to be a line of piled up dislocations within the  $Al_2O_3$  grain for  $Al_2O_3/5$  vol % Mo composite. The formation of a dislocation might be regarded as one argument in support of the existence of localized internal stresses within the  $Al_2O_3$  grains and/or around the molybdenum particles caused from their thermal expansion mismatch.

#### 3.3. Mechanical properties

For  $Al_2O_3/5$  vol% Mo composite hot-pressed at 1600 °C, using  $\gamma$ - $Al_2O_3$  as a starting powder, fracture strength was 306 MPa which was much lower than that of the monolithic  $Al_2O_3$  prepared under the same conditions. As shown in Fig. 7, characteristic crack-





Figure 7 Scanning electron micrographs of the crack-type morphology around the Vickers indentation for  $Al_2O_3/5$  vol % Mo composite fabricated by using  $\gamma$ -Al\_2O<sub>3</sub> as a starting powder: (a) entire indentation, (b) isolated cracks.

type morphology around the Vickers indentation was observed. It was shown that many cracks branched and propagated between various Al<sub>2</sub>O<sub>3</sub> grains and the interfaces of the elongated molybdenum layers. These results suggest that the grain boundaries of Al<sub>2</sub>O<sub>3</sub> and interfaces of elongated molybdenum layers are fairly weak. In addition, for the composite containing coalesced and elongated molybdenum particles in the Al<sub>2</sub>O<sub>3</sub> matrix composed of developed columnar microstructure, there is a fear of the production of microcracking due to the crystal anisotropy of the thermal expansion coefficient of Al<sub>2</sub>O<sub>3</sub> and the thermal expansion mismatch between Al<sub>2</sub>O<sub>3</sub> and molybdenum, in the case where the dimension of the molybdenum particles exceeds the critical particle size for microcracking. However, it was ascertained that there were no traces of microcracks by SEM observations. Hence, the lower fracture strength of the composite was supposed to be contributed to the weak grain boundaries between the interfaces of elongated molybdenum layers and Al<sub>2</sub>O<sub>3</sub> grains, along with the grain growth of Al<sub>2</sub>O<sub>3</sub> matrix.

On the other hand, in the composite having a microstructure described above, fracture toughness could not be evaluated by the IF method; therefore, the single-edge precracked beam (SEPB) method [16] was tried to estimate an approximate value. In the SEPB method, the half size specimens from the fracture strength test were used in a three-point bending test with a span length of 16 mm. Fracture toughness evaluated by the SEPB method was 7.1 MPa  $m^{1/2}$ . In addition, as shown in Fig. 7b, there was some evidence that cracks propagated through the elongated molybdenum layers. Therefore, it was supposed that fracture toughness was improved by incorporating metal phase associated with a relaxation of stress intensity derived from bridging of the crack tip by the elongated molybdenum layers, although the contribution of microcrack toughening could not be completely excluded.

Next, the mechanical properties of Al<sub>2</sub>O<sub>3</sub>/Mo composites, using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a starting powder, are described below. Fig. 8 shows the variation of fracture strength with hot-pressing temperature for the  $Al_2O_3/Mo$  composites containing up to 20 vol % Mo. On the whole, fracture strength was increased by the addition of molybdenum particles; however, it decreased with increasing hot-pressing temperature for both monolithic Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>/Mo composites containing molybdenum content. Fracture strength of the Al<sub>2</sub>O<sub>3</sub>/7.5 vol % Mo composite hot-pressed at 1400 °C exhibited a maximum value of 884 MPa, which was 1.5 times larger than that of the monolithic  $Al_2O_3$  prepared under the same conditions. When the hot-pressing temperature was increased to 1700 °C, strength decreased to around 450 MPa, which corresponded to the grain growth of Al<sub>2</sub>O<sub>3</sub> matrix. Thus, in the Al<sub>2</sub>O<sub>3</sub>/Mo composites, strengthening was assumed to be mainly attributed to the inhibition of grain growth of Al<sub>2</sub>O<sub>3</sub> matrix in the presence of nanometre-sized molybdenum particles. Scanning electron micrographs of fracture surfaces for monolithic Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>/7.5 vol % Mo com-



Figure 8 Variation of fracture strength with hot-pressing temperature for Al<sub>2</sub>O<sub>3</sub>/Mo composites. ( $\bigcirc$ ) Monolithic Al<sub>2</sub>O<sub>3</sub>, ( $\bigcirc$ ) Al<sub>2</sub>O<sub>3</sub>/5 vol % Mo, ( $\blacktriangle$ ) Al<sub>2</sub>O<sub>3</sub>/7.5 vol % Mo, ( $\blacktriangledown$ ) Al<sub>2</sub>O<sub>3</sub>/ 10 vol % Mo, ( $\blacklozenge$ ) Al<sub>2</sub>O<sub>3</sub>/15 vol % Mo, ( $\blacksquare$ ) Al<sub>2</sub>O<sub>3</sub>/20 vol % Mo.



Figure 9 Scanning electron micrograph of the fracture surface for monolithic  $Al_2O_3$  sample hot-pressed at 1500 °C.

posites are shown in Figs 9 and 10, respectively. As shown in Fig. 10, the microstructure of the Al<sub>2</sub>O<sub>3</sub>/7.5 vol % Mo composites, hot-pressed at any temperature, was composed of relatively equiaxed Al<sub>2</sub>O<sub>3</sub> matrix grains. However, many voids were observed, in which relatively large molybdenum particles seemed to be pulling out from the grain boundaries or triple junctions of the Al<sub>2</sub>O<sub>3</sub>. This result suggests that the bonding strength of the interfaces between  $Al_2O_3$ grains and molybdenum particles is not strong. On the other hand, the fracture mode of monolithic Al<sub>2</sub>O<sub>3</sub> was mainly intergranular, as shown in Fig. 9, but in the case of a large grain size, transgranular fracture mode was observed. On the contrary, the fracture mode of the composites were predominantly transgranular even in the case of a small grain size. This significant change in fracture mode from intergranular



*Figure 10* Scanning electron micrographs of the fracture surfaces for  $Al_2O_3/7.5$  vol% Mo composite hot pressed at (a) 1400 °C, (b) 1500 °C, (c) 1600 °C, (d) 1700 °C.

for the monolithic  $Al_2O_3$  to transgranular for the Al<sub>2</sub>O<sub>3</sub>/Mo composites, may be associated with the internal stresses supposed to be developed during cooling from the sintering temperature because of the thermal expansion mismatch between Al<sub>2</sub>O<sub>3</sub> and molybdenum. In the case where molybdenum has a lower thermal expansion coefficient than Al<sub>2</sub>O<sub>3</sub>, it is proposed that hydrostatic pressures are produced within the molybdenum particle and radial compressive and tangential tensile hoop stresses are also produced around molybdenum particles. Therefore, transgranular fracture for the Al<sub>2</sub>O<sub>3</sub>/Mo composites was assumed to be derived from crack attraction towards the inner part of the Al<sub>2</sub>O<sub>3</sub> grains which is caused by the tangential tensile hoop stresses around the molybdenum particles within the Al<sub>2</sub>O<sub>3</sub> grains.

The variation of fracture toughness with molybdenum content for the  $Al_2O_3/Mo$  composites is shown in Fig. 11. When hot-pressed at a lower sintering temperature of 1400 °C, fracture toughness for the  $Al_2O_3/Mo$  composites was around 4.4 MPa m<sup>1/2</sup>, nevertheless, with increasing molybdenum content up to 20 vol %, which was nearly equal to that of the monolithic  $Al_2O_3$ . On the contrary, significant improvement of fracture toughness was observed with increasing molybdenum content and rising hot-pressing temperature. Fracture toughness of the  $Al_2O_3/20$  vol % Mo composite hot-pressed at 1700 °C exhibited a maximum value of 7.6 MPa m<sup>1/2</sup>,



Figure 11 Variation of fracture toughness with molybdenum content for  $Al_2O_3/Mo$  composites hot-pressed at ( $\bullet$ ) 1400 °C, ( $\blacktriangle$ ) 1500 °C, ( $\blacktriangledown$ ) 1600 °C, ( $\blacklozenge$ ) 1700 °C.

which was 1.8 times larger than that of the monolithic  $Al_2O_3$  hot-pressed at 1600 °C. The crack propagation behaviour around the Vickers indentation for the  $Al_2O_3/15$  vol % Mo composites hot-pressed in the



*Figure 12* Scanning electron micrographs of the crack propagation behaviour around the Vickers indentation for  $Al_2O_3/15 \text{ vol }\%$  Mo composites hot-pressed at (a) 1400 °C, (b) 1500 °C, (c) 1600 °C, (d) 1700 °C.

range 1400°-1700 °C, is shown in Fig. 12. At a lower hot-pressing temperature of 1400 °C, the crack propagated straight with small deviations around relatively small-sized molybdenum particles, which corresponded to the low fracture toughness. While, with increasing hot-pressing temperature, the coalescence of molybdenum particles and the formations of elongated molybdenum particles, which were formed due to the necking of molybdenum particles, were observed at the  $Al_2O_3$  grain boundaries. As a whole, cracks propagated with large deflection around coalesced molybdenum particles. In addition, predominant evidence of crack penetration behaviour through the elongated molybdenum particles and crack-bridging by the metal phase were observed, which corresponded to the significant improvement of fracture toughness. These interactions between crack tip and metal phase were assumed to be due to the stress shielding effect acting as a toughening mechanism, which is based on the relaxation of stress intensity derived from blunting and/or bridging of crack tip by the metal phase, and plastic deformation which occurs when cracks penetrate through the elongated molybdenum particles.

Fig. 13 shows the variation of the Vickers hardness with molybdenum content for the  $Al_2O_3/Mo$  composites. The dotted line represents hardness calculated by the linear rule of mixtures, where the hardness of monolithic  $Al_2O_3$  and molybdenum polycrystal is



Figure 13 Variation of Vickers hardness with molybdenum content for Al<sub>2</sub>O<sub>3</sub>/Mo composites hot-pressed at ( $\textcircled{\bullet}$ ) 1400 °C, ( $\bigstar$ ) 1500 °C, ( $\textcircled{\bullet}$ ) 1600 °C, ( $\bigstar$ ) 1700 °C.

18.5 and 2.1 GPa [17], respectively. On the whole, the hardness of the  $Al_2O_3/Mo$  composites decreased with increasing molybdenum content, which approximately obeyed the rule of mixtures. In addition, a

decrease of hardness was also observed with increasing hot-pressing temperature for both monolithic Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>/Mo composites containing individual molybdenum contents. This decrease in hardness was thought to be attributable to the coalesced and elongated molybdenum particles at the Al<sub>2</sub>O<sub>3</sub> grain boundaries and the grain growth of Al<sub>2</sub>O<sub>3</sub> matrix. However, for the composites containing 5-15 vol % Mo hot-pressed at lower sintering temperatures, higher values of hardness than those predicted by the rule of mixtures were observed. Furthermore, the  $Al_2O_3/5$  vol % Mo composites exhibited obvious hardening and obtained a maximum value of 19.2 GPa when hot-pressed at 1400 °C. This hardening is supposed to be accounted for by the contributions of the fine-grained microstructure of Al<sub>2</sub>O<sub>3</sub> matrix [18] and/or the intergranular nanostructure of Al<sub>2</sub>O<sub>3</sub>/Mo composites, in which nanometre-sized molybdenum particles are dispersed within the  $Al_2O_3$ grains and at the grain boundaries. In fact, the monolithic  $Al_2O_3$  prepared in this work showed a negative dependence of grain size on the hardness, as clearly seen in Fig. 13 and the nanometre-sized metal particle will cause the hardening itself [19]. In another aspect related to the intergranular nanostructure, the radial compressive stresses around molybdenum particles within the Al<sub>2</sub>O<sub>3</sub> grains, which are assumed to be generated by their thermal expansion mismatch, might cause the hardening of Al<sub>2</sub>O<sub>3</sub> grains. Therefore, it is proposed that these contributions will result in the higher hardness values observed.

## 4. Conclusions

Two types of  $Al_2O_3/Mo$  composites were fabricated by hot-pressing a mixture of  $\gamma$ - or  $\alpha$ - $Al_2O_3$  powder and a fine molybdenum powder under a vacuum using a conventional powder metallurgical process. The microstructure and mechanical properties were examined for both  $Al_2O_3/Mo$  composites. The results are summarized as follows.

1.  $Al_2O_3/5$  vol % Mo composite using  $\gamma$ - $Al_2O_3$  as a starting powder was composed of mainly  $\alpha$ - $Al_2O_3$ and molybdenum, but MoO<sub>2</sub> was detected as an oxidized phase. The composite had a microstructural feature in which the elongated molybdenum layers, that were assumed to be formed due to the formation of liquid phase, surrounded a part of the  $Al_2O_3$  grains. Many cracks were observed branching and propagating between various  $Al_2O_3$  grains and interfaces of the elongated molybdenum layers. Fracture toughness exhibited an apparently high value, although no enhancement of fracture strength was observed.

2.  $Al_2O_3/5-20$  vol % Mo composites using  $\alpha$ - $Al_2O_3$  as a starting powder were composed of only  $\alpha$ -Al\_2O\_3 and molybdenum. In these composites, nanometre-sized molybdenum particles were dispersed within the  $Al_2O_3$  grains and relatively large molybdenum particles, above 1 µm, were located at the grain boundaries. Thus, it was confirmed that ceramic/metal nanocomposites were successfully fabricated. TEM observation revealed that no reaction phases were present at the interfaces between the  $Al_2O_3$  and molybdenum within the  $Al_2O_3$  grains.

3. The addition of molybdenum particles resulted in the grain-growth inhibition of the  $Al_2O_3$  matrix. The fracture strength of  $Al_2O_3/7.5$  vol % Mo composite hot-pressed at 1400 °C was 884 MPa, which was 1.5 times larger than that of the monolithic  $Al_2O_3$ . The fracture mode of the composites was confirmed to be predominantly transgranular. Higher values of hardness than those predicted by the rule of mixtures were observed for the composites hot-pressed at lower sintering temperatures.

4. With increasing molybdenum content and rising hot-pressing temperature, the coalescence of molybdenum particles and the formation of the elongated molybdenum particles were observed at the  $Al_2O_3$ grain boundaries. Predominant evidence of crack penetration behaviour through the elongated molybdenum particles and crack-bridging by the metal phase were observed. The fracture toughness of  $Al_2O_3/20$  vol % Mo composite hot-pressed at 1700 °C was 7.6 MPa m<sup>1/2</sup>, which was 1.8 times larger than that of the monolithic  $Al_2O_3$ .

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