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Alumina/molybdenum nanocomposites obtained in organic media

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Abstract

Alumina/molybdenum nanocomposites were obtained from a modified alumina powder in a solution of molybdenum(V) chloride in ethanol. The modified alumina powder was calcined at low temperatures to remove organic residue. A reduction step was necessary to obtain 2–10 nm metallic nanoparticles on the surface of the alumina crystals. Theoretically dense composites containing 0.69, 2.66, and 8.91 vol.% Mo were prepared by cold isostatic pressing and sintering in Ar/H_2 atmosphere. In all cases a very narrow homogeneous distribution of Mo nanoparticles was obtained. Molybdenum nanoparticles are very homogeneously distributed in the alumina matrix, with an average nanoparticle size smaller than 90 nm. The presence of such molybdenum nanoparticles drastically affects the microstructural evolution during sintering, mainly the final grain size of alumina. An important improvement in mechanical bevavior was also observed. For example, the composite containing 0.69 vol.% Mo showed a flexural strength (four-point method) of 700 MPa and a fracture toughness K_{1c} (SENB) of 6.26 MPa $m^{1/2}$.

Keywords: Alumina; Molybdenum; Nanocomposite; Processing in organic media

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1. Introduction

Ceramics have good wear resistance and high thermal and chemical stability. These important characteristics make them suitable for engineering applications. However, ceramics are brittle materials and are easily fractured as a consequence of crack propagation, which restricts their application. Many attempts have been made to increase the fracture toughness of ceramics by incorporating a second ductile phase, such as metal particles. Such ceramic–metal composites, consisting of a ceramic matrix into which metal second-phase dispersions are incorporated, are widely used as materials with important technological applications. The presence of metallic particles in these materials adds physical properties inherent to the metallic phase, such as electric and thermal conductivity or magnetic properties. In addition, they have excellent mechanical behavior, because of the action of reinforcement mechanisms due to the presence of ductile particles in the ceramic matrix. At the same time, the ceramic matrix gives them a high chemical stability and refractoriness. This combination of properties makes these materials excellent candidates for electric, optic, and magnetic devices or chemical sensors. Recent investigations in the nanotechnology field have led to the development of ceramic–metal nanocomposites, such as Al_2O_3/Mo, Al_2O_3/W, etc.,[1–8] for structural applications. These systems are usually fabricated by hot-pressing of the fine ceramic and metal powder mixtures or by reducing and hot pressing alumina and metal-oxide powders. In general, the mechanical properties of monolithic ceramics are improved by the addition of nanometer-sized metal particles homogeneously dispersed in the matrix.

In a manner similar to that described earlier, Nawa et al., [1] have prepared Al_2O_3/Mo composites by hot-pressing a mixture of Al_2O_3 and molybdenum powders. They have investigated the influence of starting alumina phase, hot-pressing temperature, and molybdenum content on the mechanical properties of the Al_2O_3/Mo composites. Considerable improvements in mechanical properties, fracture toughness, and flexural strength were observed, but these improvements were not enhanced simultaneously when the molybdenum content was increased. The particle size of spherical molybdenum particles was below 2 μm, and the smallest size of the molybdenum particles was about 1 μm.

In this work alumina/molybdenum nanocomposites were obtained starting from a modified alumina powder in a solution of molybdenum(V) chloride in ethanol. The presence of molybdenum nanoparticles drastically

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affects the microstructural evolution during sintering and, as a consequence, the mechanical properties. By means of the colliodal processing method described in this article, it is possible to obtain a very homogeneous distribution of very small molybdenum nanoparticles in an alumina matrix. The results of the present investigation (colloidal processing method) are compared with those obtained by the traditional powder-mixing method.

2. Experimental procedure

2.1. Processing of alumina/molybdenum nanocomposites

Alumina/molybdenum nanocomposites were prepared using α-alumina (Al_2O_3) powder (HPA0,5, Condea, Hamburg, Germany) with $d_{50} = 0.46$ μm, a specific surface area of 9.9 m^2/g, and 99.98% purity, and a solution of molybdenum(V) chloride (Sigma-Aldrich, Spain) in anhydrous 99.97% ethanol. In a typical experiment to synthesize alumina/molybdenum nanocomposites, alumina powder was dispersed in anhydrous 99.97% ethanol, and a solution of molybdenum(V) chloride in ethanol was added dropwise. Powder mixtures containing 0.69, 2.66, and 8.91 vol.% Mo were prepared. The slurries were first heated under magnetic stirring at 70 °C and subsequently in air at 120 °C for 24 h in order to start the nucleation and eliminate any traces of alcohol. Dried powders were thermally treated at 450 °C for 2 h in order to remove organic residuals and then were reduced under Ar/H_2 atmosphere at 850 °C for 2 h to obtain metallic nanoparticles. Finally, the powders were attrition-milled for 1 h, dried, and sieved under 45 μm. The powders obtained in this way were cold isostatically pressed (CIP) at 200 MPa, and finally sintered in Ar/H_2 atmosphere at 1600 °C for 2 h.

2.2. Characterization techniques

The phase evolution of the samples was studied by X-ray diffraction (XRD) (D5000, Siemens, Germany) using Cu*K*α radiation. Diffraction patterns were recorded in step-scan mode (3 s/0.2°; 2θ) in the 0–65° 2θ range.

The microstructure of the different samples was characterized with a scanning electron microscope (SEM) (Zeiss DSM 942) equipped with a Link energy-dispersive X-ray system. Grain-size distributions on the polished samples were measured by using image-analysis software.

Fracture toughness and bending strength measurements were made in an Instron 8562 testing machine by using a four-point bending fixture with an outer span of 21 mm and an inner span of 10 mm. For fracture toughness measurements, the single-edge-notched-beam (SENB) technique ($a/w = 0.4$) was used.

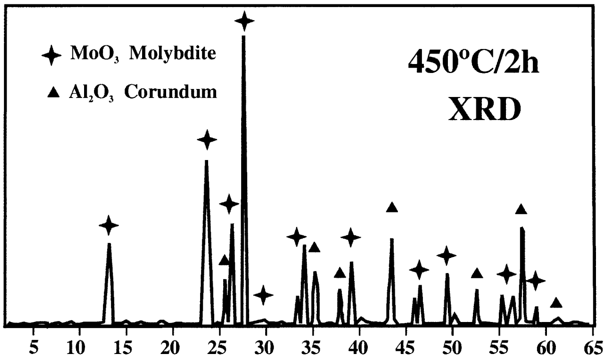
Alumina/molybdenum nanoparticles were studied by transmission electron microscopy (TEM) in a Philips CM200FEG with a field-emission lens operated at 200 kV, 2.35 Å resolution, and XEDS detector.

3. Results and discussion

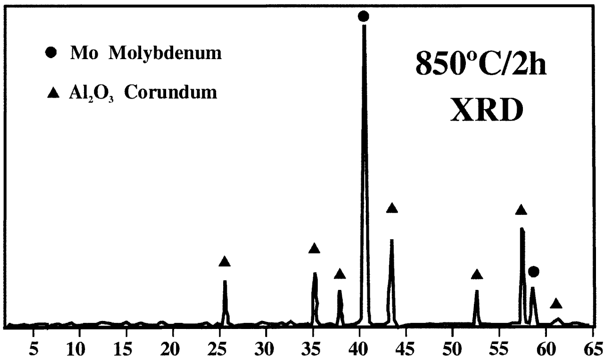
3.1. Nanocomposite powders

3.1.1. Phase identification

Fig. 1 shows the XRD patterns of alumina/8.91 vol.% Mo powder after calcination at 450 °C for 2 h and after reduction in Ar/H_2 atmosphere at 850 °C for 2 h. When the powder is heated in air at 450 °C for 2 h, α-Al_2O_3 and MoO_3 are detected. After the reduction step, the mixture is composed only of α-Al_2O_3 and Mo particles. A detailed microstructural characterization was made by TEM. In Fig. 2 a TEM image corresponding to the alumina/0.69 vol.% Mo nanocomposite powder is shown. It can be observed that molybdenum nanoparticles have an average grain size of about 20 nm.



Calcined modified powder at 450ºC/2 h



Reduced modified powder at 850ºC/2 h

Fig. 1. X-ray diffraction patterns of calcined modified powder at 450 °C/2 h and reduced modified powder at 850 °C/2 h.

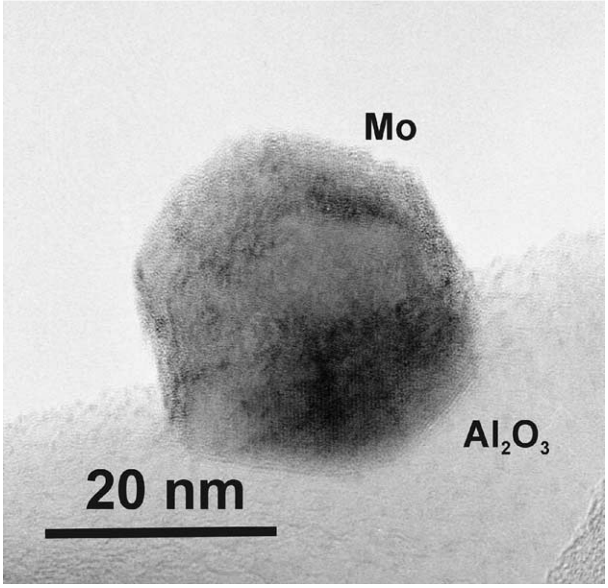


Fig. 2. TEM image of reduced modified powder at 850 °C/2 h of the composite alumina/0.69 vol.% molybdenum.

3.2. Dense nanocomposites

3.2.1. Microstructure

Figs. 3 and 4 show a SEM general view of the microstructure of the different composites (0.69, 2.66, and 8.91 vol.% Mo after sintering at 1600 °C for 2 h) obtained on polished surfaces, as well as the corresponding fracture surfaces. In all cases, a homogeneous distribution of Mo particles was observed. Alumina grain size is affected by the presence of Mo. This can be clearly observed in Fig. 3, where the microstructure of monolithic alumina and alumina/Mo nanocomposites is compared. Spherical molybdenum nanoparticles are located mainly at triple points. This metal acts as a grain-growth inhibitor, as can be seen in Fig. 5, which shows the variation of alumina grain size as a function of vol.% Mo content . Small amounts of Mo (0.69 vol.%) clearly inhibit alumina grain growth. When higher amounts of Mo are added, the Mo particle size increases (Fig. 6).

3.2.2. Mechanical properties

The fracture surfaces in Fig. 4 show that the presence of small Mo nanoparticles at grain boundaries promotes a transgranular crack path even in the case of smaller alumina grain sizes. When Mo grain size increases (higher vol.% Mo), the crack path changes to an intergranular mode, as can be seen in Fig. 4.

Fig. 7 shows the variation of fracture toughness as a function of molybdenum content for alumina/Mo composites obtained by conventional processing (powder mixtures)[1] and the colloidal processing method used in this report. From this figure, it can be deduced that small amounts of Mo lead to important improvements

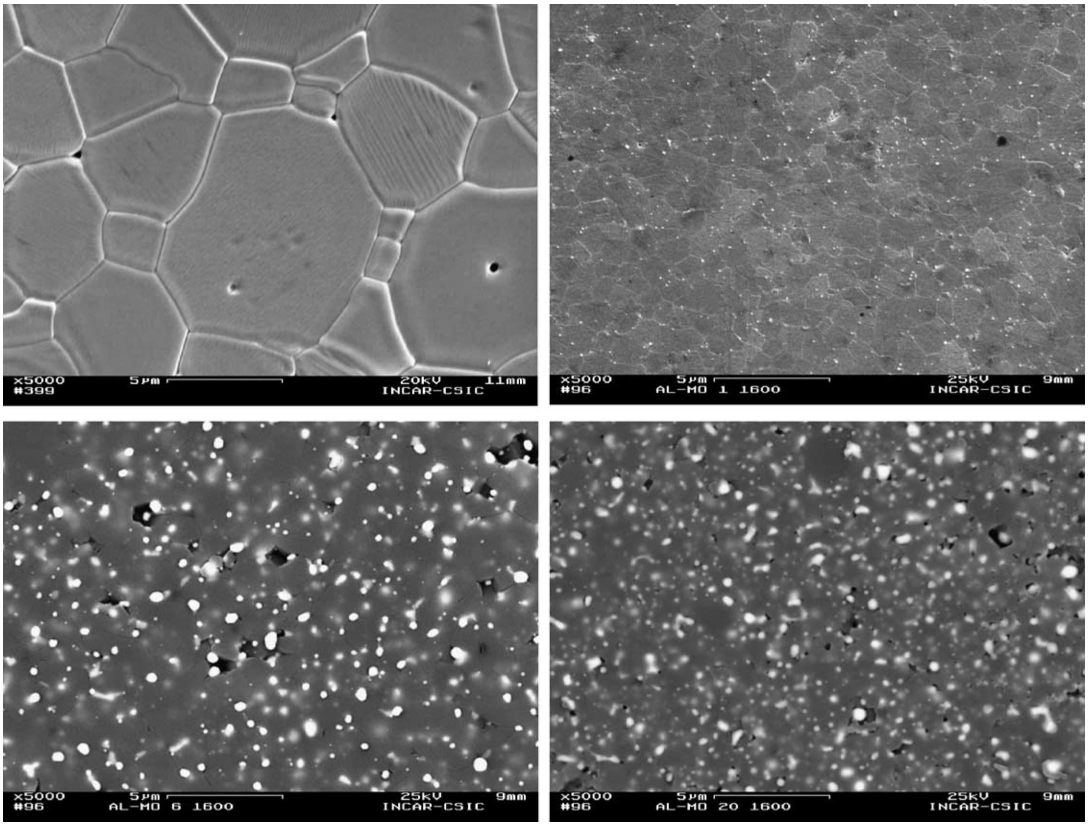


Fig. 3. SEM micrograph of monolithic alumina and alumina/molybdenum nanocomposites.

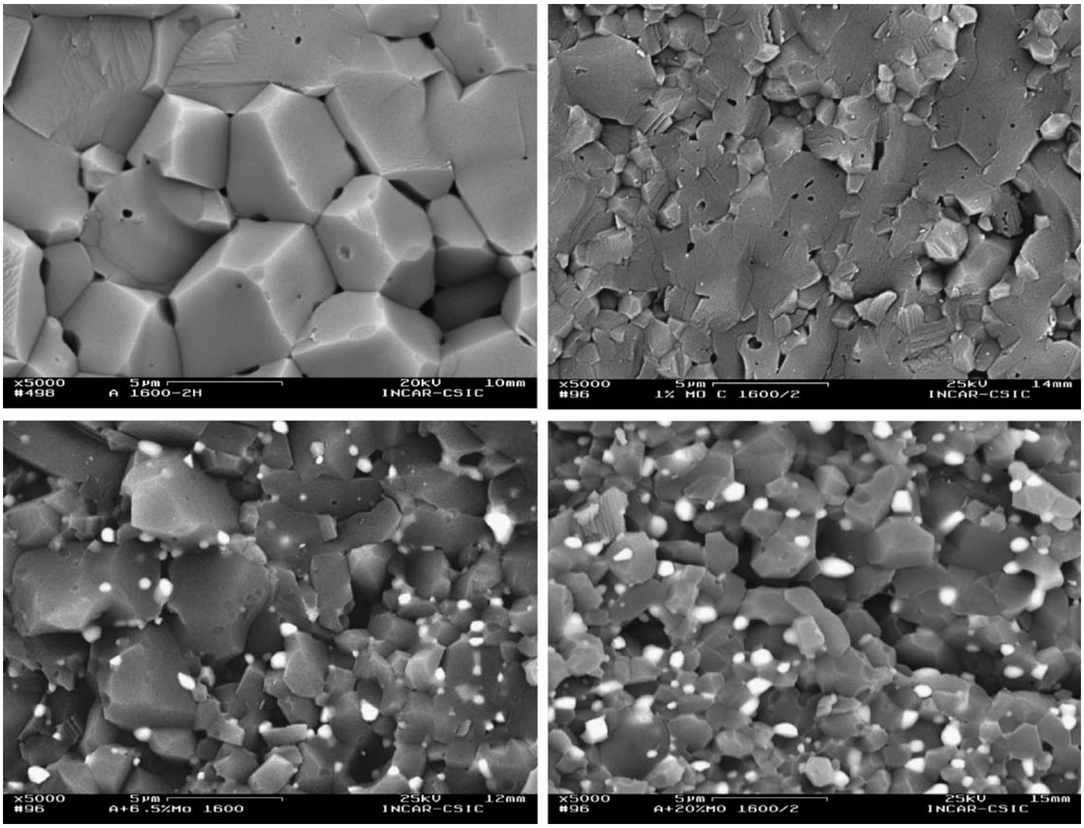


Fig. 4. Fracture surfaces at room temperature of pure alumina and all the nanocomposites studied.

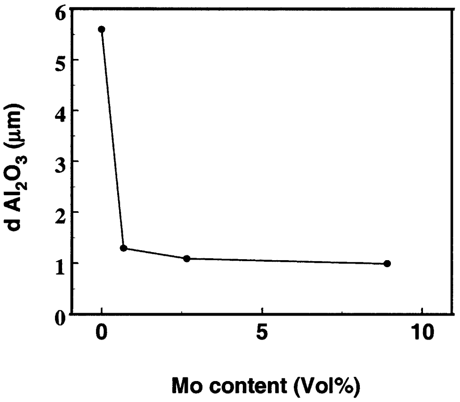


Fig. 5. Variation of average grain size of alumina as a function of molybdenum content.

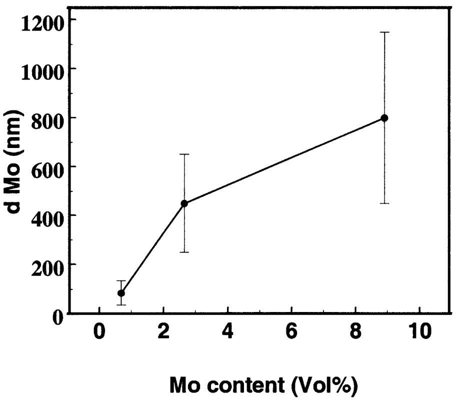


Fig. 6. Variation of molybdenum particle size as a function of molybdenum content.

in fracture toughness when the colloidal processing method is employed. For example, fracture toughness for alumina/0.69 vol.% Mo is 6.26 MPa $m^{1/2}$, whereas for pure alumina it is 4 MPa $m^{1/2}$. In the work of Nawa et al.,[1] improvements in fracture toughness are only significant when the molybdenum content is as high as 10%, and even in this case, the K_{1c} value is lower than the maximum K_{1c} obtained in organic media. The reason for this result is that both materials show different reinforcement mechanisms. For materials obtained by mechanical mixing of powders, the reinforcement is due to the plastic deformation of the elongated molybdenum grains, which are formed at higher molybdenum content.[1] However, in the present work, the spherical molybdenum grains are smaller (about 80 nm), and the reinforcement in this case is caused by the thermal stresses appearing at grain boundaries during cooling, due to the mismatch of the thermal expansion coefficients of alumina and Mo ($Al_2O_3 \cong 8\times10^{-6}$ K^{--1}, Mo $\cong 5\times10^{-6}$ K^{-1}). When the Mo particle size is smaller

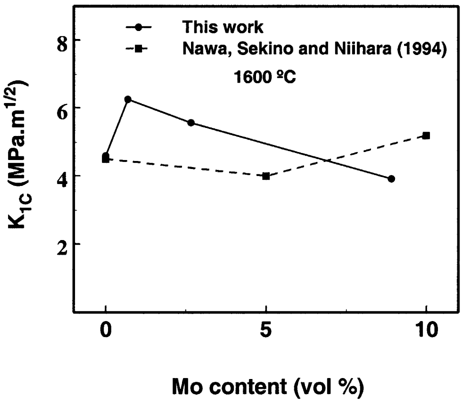


Fig. 7. Variation of fracture toughness as a function of molybdenum content.

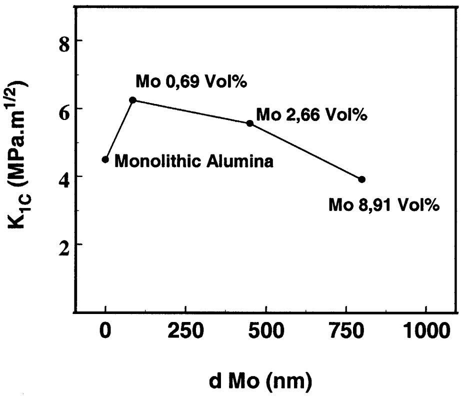


Fig. 8. Variation of flexural strength as a function of molybdenum content.

than about 100 nm, it seems that the alumina–Mo interface is strong enough to retain the stress field generated during cooling. Thus, Mo nanoparticles are in compression and, as a consequence, cracks never propagate through these interfaces; instead, they go across alumina grains. This is also the reason why only a few Mo nanoparticles can be observed on the fracture surface of the composite with only 0.69 vol.% Mo.

For higher amounts of Mo, the Mo grains grow in size, and the shear stresses generated during cooling at alumina/Mo grain boundaries cannot be retained at the interface. As a consequence, alumina/Mo interfaces becomes weaker, cracks propagate in a transgranular mode, and the reinforcement becomes less important.

Fig. 8 shows the variation of flexural strength of the alumina/molybdenum nanocomposites as a function of Mo content. The same figure shows the results of Nawa et al.[1] using conventional mechanical mixing to prepare the alumina/molybdenum composites.

In all cases, the presence of molybdenum nanoparticles improves the flexural strength of alumina, and this improvement is more important when the vol.% of Mo is lower. For example, the flexural strength of the alumina/0.69 vol.% Mo is >700 MPa. By comparison, the best flexural strength values obtained by Nawa et al.,[1] when the composites were prepared by mechanical mixing, is $\approx$600 MPa, corresponding to a composite with 5 vol.% Mo. Therefore, preparation of alumina/Mo composites by colloidal processing leads to higher improvements in flexural strength, while the amount of Mo necessary to reach the maximum flexural strength is lower. This improvement in flexural strength is related directly to the smaller alumina grain size (smaller defect size) and the higher fracture toughness value.

As can be seen in Fig. 9, for composites obtained in organic media, the lower the molybdenum grain size, the higher the K_{1c} value. In the work of Nawa et al.[1] flexural strength and fracture toughness as a function of molybdenum content show opposite trends. In our work, both properties change in the same direction with molybdenum content, which means that when the composites are prepared following colloidal processing, the flaw size in the composites remains almost constant. This fact may be related to the different sintering processes. Nawa et al.[1] used a hot uniaxial press; in this process, Mo particles deform and are linked perpendicularly to the direction of the applied load. The size of metallic agglomerates obviously depends on the molybdenum content.

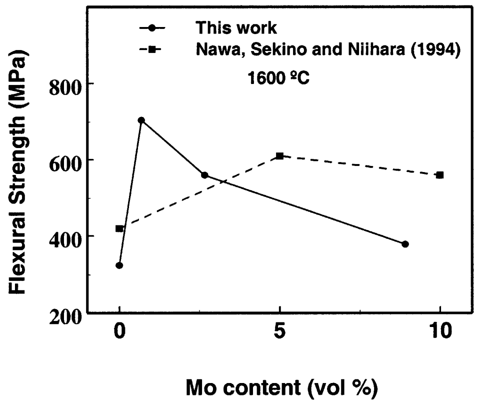


Fig. 9. Variation of fracture toughness as a function of molybdenum particle size.

4. Conclusion

Colloidal processing has been shown to be an effective way to produce alumina/Mo composites. This processing method gives a very homogeneous and narrow distribution of metallic nanoparticles at the alumina grain boundaries. The presence of very small amounts of Mo nanoparticles (<100 nm) clearly improves flexural strength and fracture toughness of monolithic alumina.

This improvement is related to the stress field generated at grain boundaries, due to the mismatch of the thermal expansion coefficient of alumina and molybdenum.

It is clear that the mechanical properties are affected by the Mo grain size, which depends strongly on Mo concentration. As a consequence, it is necessary to reach an equilibrium between grain size and maximum concentration to find the optimal composition.

The fracture surfaces clearly show that the presence of Mo at grain boundaries promotes a transgranular crack path, even for alumina smaller grain sizes. When the Mo content increases, the final Mo grain size also increases, and the crack path changes to an intergranular mode.

Acknowledgements

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