Aluminium nitride–molybdenum ceramic matrix composites: influence of molybdenum concentration on the mechanical properties

A. A. KHAN, J. C. LABBE
Laboratoire de Matériaux Céramiques et Traitements de Surface (LMCTS), URA CNRS 320, Groupe ''Céramiques Nouvelles'', 123 Av. Albert Thomas, Faculté des Sciences, Université de Limoges, 87060 Limoges Cedex, France

Aluminium nitride–molybdenum ceramic matrix composites are produced by hotpressing a mixture of two powders. Mechanical properties of a series of samples are measured in order to study the effect of molybdenum phase on the behaviour of composite. Three-point bend strength increases from a value of 270 MPa for pure aluminium nitride to 571 MPa for a composite containing 40% by volume of metallic phase. Fracture toughness measured by the single-edged precracked beam (SEPB) technique, is also increased as a function of molybdenum concentration. From 2.3 $MPam^{1/2}$ for pure AlN we obtain a value of 6.9 $MPam^{1/2}$ in the case of composite containing 40% by volume of metallic phase. This very important increase in the mechanical properties of AlN-Mo composites is attributed to higher mechanical properties of molybdenum and an adherent interface between AlN and Mo grains.

1. Introduction

Aluminium nitride has excellent thermal and mechanical properties which makes it an attractive material for high-temperature engineering applications. Aluminium nitride has received considerable attention in recent years due to its high thermal conductivity and the material is currently exploited in thermal management applications. AlN single crystals exhibit thermal conductivity [1] values of up to 320 $Wm^{-1}K^{-1}$, whereas the thermal conductivity of polycrystalline AlN varies between 80 to 200 $W m^{-1} K^{-1}$ according to the microstructure and composition of the sintered ceramic [2, 3, 4, 5]. Its field of application is limited primarily due to its low fracture toughness. Hotpressed pure AlN [6, 7, 9] shows bend strength values of about 250 to 300 MPa and an elastic modulus ranging between 300 to 310 GPa. It presents a good thermal stability at temperatures higher than 2400 °C. Thus, aluminium nitride presents itself as a potential material for thermomechanical applications.

Attempts have been made to improve the fracture toughness of AlN by adding a dispersed second phase in the ceramic matrix, usually in the form of whiskers having a close to AlN thermal expansion. In an effort to improve the mechanical characteristics of AlN, and thereby to expand its application field, silicon carbide whiskers (SiC_w) were employed [8, 9, 10] as a dispersed second phase. Solid solution formation in the AlN–SiC_w system results not only in a chemical phase change, but also in a morphology change. Whiskers are consumed as SiC diffuses into equiaxed AlN grains, converting them into a solid solution. Bend strength of hotpressed whisker-reinforced AlN composites containing 10% SiC, increases upto 370 MPa [8]. Tensile strength is equally improved from almost 120 MPa for pure hotpressed AlN to a value around 275 MPa [9]. Results of high-temperature strength of SiC whisker-reinforced AlN composites show an improvement in its value, compared to pure aluminium nitride [10], for temperatures between 20 and 1500 °C.

Influence of a metal phase addition over the mechanical strength of AlN is studied by different authors [11, 12]. Plastic deformation of metallic grains is observed in cases where second phase is composed of a ductile metal such as aluminium [11, 12, 19]. Microcracking also helps to improve the mechanical properties of composites having a brittle matrix [20, 21]. Results [11] concerning the mechanical properties of AlN–Al composites, produced by direct nitridation of aluminium, have shown that the flexural strength of AlN can be improved upto a value of 400 MPa, mainly due to the presence of ductile residual aluminium particles which are adherent to the AlN matrix. Fracture toughness is equally increased from 3 $MPa m^{1/2}$ for pure AlN to around 7 $MPa m^{1/2}$ for a composite containing 30% Al phase [12]. Addition of TiB_2 in the form of platelets [11], can increase AlN flexural strength to a value near 500 MPa.

Another possible way of improving AlN mechanical strength is by the addition of a refractory metal having high mechanical and thermal properties. Molybdenum is a relatively light refractory metal ($d_{th} = 10.2$) with a melting point of 2610 °C, high thermal conductivity (138 $W m^{-1} K^{-1}$) and it presents

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good sinterability at lower temperatures (1400 °C). In a previous work [13] we have shown that hotpressed AlN–Mo mixtures present a homogeneous and dense structure, with as high as 97% densification. Aluminium nitride and molybdenum powders are co-sintered using a hotpressing cycle commonly employed for pure aluminium nitride. AlN–Mo composites are thus produced with an aim of understanding and verifying the influence of molybdenum phase on the mechanical properties of aluminium nitride matrix. Composites produced in this manner are composed of uniformly distributed molybdenum particles in an AlN matrix. Because of its relatively ductile nature, the addition of molybdenum is supposed to improve the mechanical properties as well as thermal and thermomechanical properties of aluminium nitride. In this work we study the influence of molybdenum addition on the mechanical behaviour of AlN–Mo composites.

2. Sample preparation

2.1. Starting powders

Aluminium nitride powder presents a specific surface area of 4 $m^2 g^{-1}$. Principal elements of this powder are presented in Table I where we note that oxygen is the main impurity. Size distribution of this powder (Fig. 1) studied by the sedigraphy technique show that the majority of particles have sizes varying between 0.3 to 5 μm. Molybdenum powder is 99.9% pure. Fig. 1 presents the size distribution of this powder where we note that the particle size is situated between 5 to 30 μm.

2.2. Sintering conditions

The two powders are mixed in different proportions, varying the molybdenum concentration by volume in AlN from 5 to 35%. The mixtures are prepared by dry milling for a period of 24 h. The hotpressing technique is employed, which is the most common technique for the sintering of pure AlN without any sintering aids.

TABLE I Composition of AlN powder

Element	A1	N	O	C	Fe
%weight	>64.5	33.2	1.8	0.05	0.01

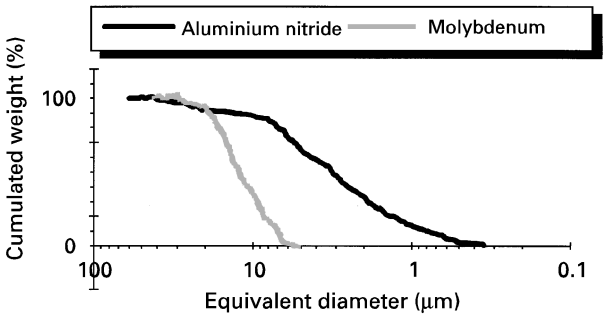

Figure 1 Size distribution of AlN and Mo powders measured by X-ray sedigraphy technique.

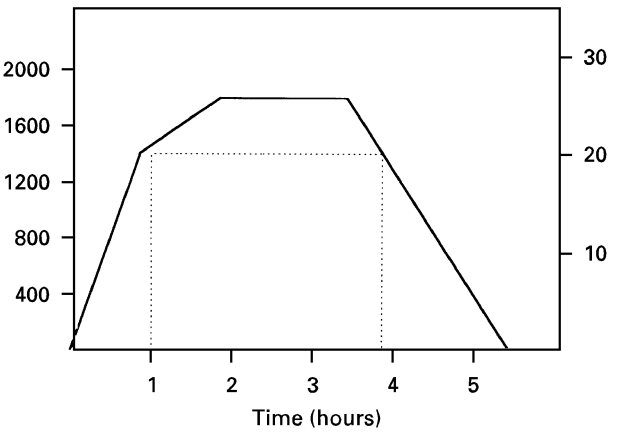

Figure 2 Temperature and pressure cycles used during the hotpressing of AlN–Mo mixtures. (————) temperature (°C); (- - - - -) pressure (MPa).

Since AlN forms the continuous majority phase, the sintering conditions are kept similar to those employed commonly for the hotpressing of pure aluminium nitride [14, 15]. Sintering powder is placed inside a graphite mould with its inner walls coated with a BN slurry to avoid any interaction between the powder and graphite and also to facilitate the demoulding process.

Hotpressing furnace is LPA 2000 which allows one to keep 20 MPa pressure on the mould during heating. Sintering is performed under a dynamic nitrogen atmosphere, at a temperature of 1800 °C and for a dwell time of $1\frac{1}{2}$ h. Pressure is applied once the temperature reaches 1400 °C. The sintering cycle can be visualized with the help of Fig. 2. Sintered samples are in the form of discs with 30 mm diameter and 4 mm thickness. All samples produced in the given conditions showed a densification rate of more than 95% and an open porosity content of less than 1.5%.

3. Bend strength measurement

3.1. Experimental procedure

Sintered discs are cut in the form of rectangular bars with dimensions $4 \times 4 \times 22$ m. Samples are polished to a fineness of 1000 on SiC paper and the face which receives the maximum tensile stress is polished upto 1 μm with a diamond paste. The three-point bend test has the advantage of being easy because it does not require any particularly complex equipment. The rupture strength is measured on a traction-compression machine. The samples are tested at a descending rate of 0.2 mm min^{-1} while the distance between the supports is kept at 19 mm. The force is directly given in kN and the flexural strength can be calculated, knowing the dimensions of the sample, with the help of a simple formula

$$\sigma_{\text{maxi}} = \left(\frac{3PL}{2bh^2}\right) \quad (1)$$

where p, L, b, h, are the force, distance between the supports, width and height of the sample, respectively.

TABLE II Mean values of three point bend strength (σ_f), for different AlN–Mo hotpressed samples

Reference	Volume fraction (AlN)	Volume fraction (Mo)	Bend strength σ_f (MPa)
AlN	1	0	270
AM5	0.95	0.05	330
AM10	0.9	0.1	424
AM15	0.85	0.15	409
AM18	0.82	0.18	439
AM20	0.8	0.2	420
AM22	0.78	0.22	453
AM25	0.75	0.25	437
AM30	0.7	0.3	471
AM35	0.65	0.35	527
AM40	0.6	0.4	571

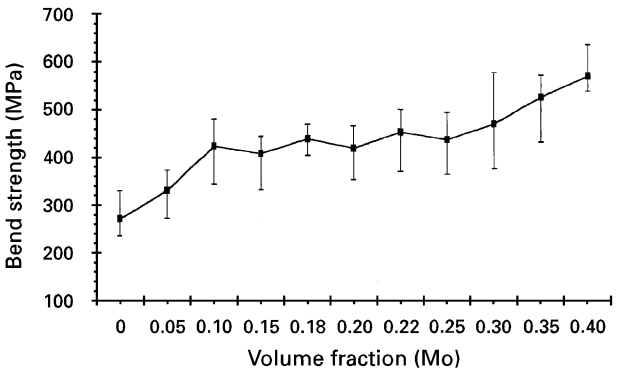

Figure 3 Variation of three point bend strength (σ_f) of different AlN–Mo mixtures after sintering, as a function of molybdenum concentration.

3.2. Results and discussion

Variation of the bend strength as a function of molybdenum volume fraction in the composite is presented in Table II and Fig. 3. We note a remarkable increase in the bend strength of the composite as a function of metal phase concentration (from 270 MPa for pure AlN up to 571 MPa for sample referenced as AM40). This increase can be attributed to a good quality metal–ceramic interface. We note also that the samples show a rapid increase in the bend strength value for molybdenum concentrations of 10% or more (by volume).

We know that addition of ductile metals like aluminium [11, 12] improves the mechanical properties of AlN. Aluminium being a ductile metal, the reinforcement is mainly obtained through the plastic deformation of Al grains inside the AlN matrix. Molybdenum grains are supposed to influence the mechanical properties of AlN–Mo composites in the same manner. Values of bend strength as high as 570 MPa, obtained in the case of samples containing 40% of molybdenum by volume, could be explained by the fact that molybdenum possesses superior mechanical properties compared to those of aluminium and aluminium nitride. These results can also be explained on the basis of a good adherence between the matrix and molybdenum particles.

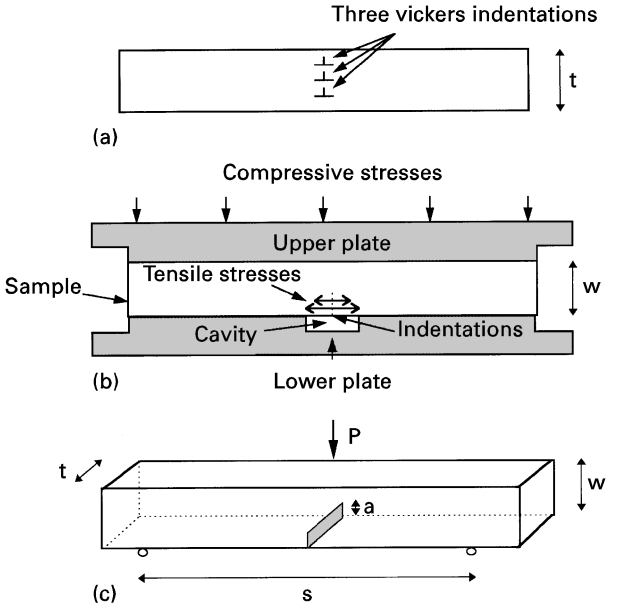

Figure 4 SEPB method shown in three steps. (a) Sample preparation and Vickers indentation. (b) Precracking. (c) Three-point bend test.

4. Fracture toughness measurement

4.1. Experimental procedure

Different methods employed for the fracture toughness measurement are composed generally of two steps. Initially a crack of known form and size is produced at the sample surface and finally the sample is tested under flexural stress to obtain the value of critical stress intensity factor (K_{1c}). In almost every technique the measurement of crack size and the presence of residual stresses at the crack tip complicate the material behaviour. Warren *et al.* [16] recently adopted a new technique named as "bridge indentation" (B1). The principal characteristics of this technique reside in a macroscopic crack obtained at the tip of a Vickers notch, which reduces the effect of residual stresses on the measured fracture toughness. Nose *et al.* [17] employed the same apparatus to measure the fracture toughness of ceramic materials and named it "single edge precracked beam test" (SEPB). They measured, with excellent reproducibility, the fracture toughness of Al_2O_3, Si_3N_4 and SiC. This technique, illustrated with the help of the simplified diagram in Fig. 4, is briefly described in the following paragraph.

Three equidistant Vickers indentations are produced on the surface of polished samples in the form of rectangular bars ($4 \times 3 \times 20$ mm), which serve as crack initiating source during the precracking operation. Precracking of the samples is performed using a specially designed press which allows the creation of a crack of uniform size and shape, which is afterwards impregnated with a liquid penetrant (Ardox 970P2) in order to facilitate the crack size measurement after the test. Samples are then tested to measure the flexural strength. Crack size measurement is performed with the help of an optical microscope linked with a monitoring screen. The fracture toughness is finally calculated using Strawley's

TABLE III Mean values of fracture toughness of AlN–Mo composites, measured by SEPB method, as a function of molybdenum concentration.

Reference	Volume fraction (AlN)	Volume fraction (Mo)	Fracture toughness (MPa m$^{1/2}$)
AlN	1	0	2.3
AM5	0.95	0.05	3.8
AM10	0.9	0.1	3.8
AM15	0.85	0.15	5.1
AM20	0.8	0.2	6.0
AM25	0.75	0.25	6.4
AM30	0.7	0.3	6.9

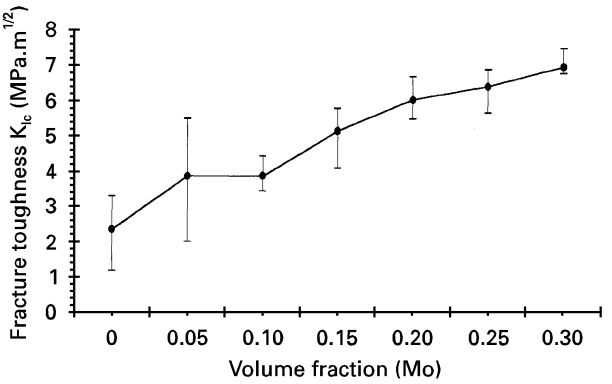

Figure 5 Fracture toughness (K_{Ic}) of AlN–Mo composites, measured by SEPB method, as a function of molybdenum concentration.

formula [18]

$$K_{Ic} = \left(\frac{3SP}{2tw^2}\right) a^{1/2} F(x) \tag{2}$$

where S = the distance between the supports; P the pressure applied; w is the height of the rectangular bar; t the width of the rectangular bar; a the crack depth, and where $x = a/w$ and $F(x)$ is Strawley's function [18], given by the following relation

$$F(x) = \left[\frac{(1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2))}{(1+2x)(1-x)^{3/2}}\right] \tag{3}$$

This method is relatively more precise and results are more reproducible compared to classical methods such as single-edge notched beam (SENB), due to the crack size which is large enough (> 1 mm) compared to the zone containing the residual stresses. Thus the influence of residual stresses present at the crack tip can be considered as negligible.

4.2. Results and discussion

Variation of the fracture toughness of a series of AlN–Mo composites, sintered in the given conditions, is studied as a function of metal phase concentration. The results are presented in Table III and Fig. 5 where we observe that an important improvement is obtained in the fracture toughness of AlN–Mo composites, as the Mo content in the ceramic matrix is increased from 5 to 30% by volume. Pure hotpressed AlN shows a mean value of K_{Ic} around 2.3 MPa m$^{1/2}$ whereas this value increases to 6.9 Mpa m$^{1/2}$ in the case of composite containing 30% molybdenum by volume. For comparison sake we give, in Table IV, the values of fracture toughness and bend strength, found in the literature for different known ceramics. We note that AlN–Mo composites containing 25% or more metal phase show mechanical properties which are superior to those obtained for the best ceramic materials. This important increase in the fracture toughness could be attributed to different mechanisms which are active in the presence of a metallic phase reinforcement.

TABLE IV Bend strength and fracture toughness values of different known ceramics. Values for AM20 and AM40 are given for comparison

Ceramic	Bend strength σ_f (MPa)	Fracture toughness K_{Ic} (MPa m$^{1/2}$)
Si_3N_4	320–400	3.3–4.2
TiN	300–350	–
SiC	370–440	3.0–5.0
Al_2O_3	200–250	1.9–2.4
ZrO_2 (8% CaO)	450–500	5.5–6.5
TiC	300–500	2.4–3.5
SiAlON(β)	350–450	3.5–4
AM20	420	6*
AM40	571	6.9*

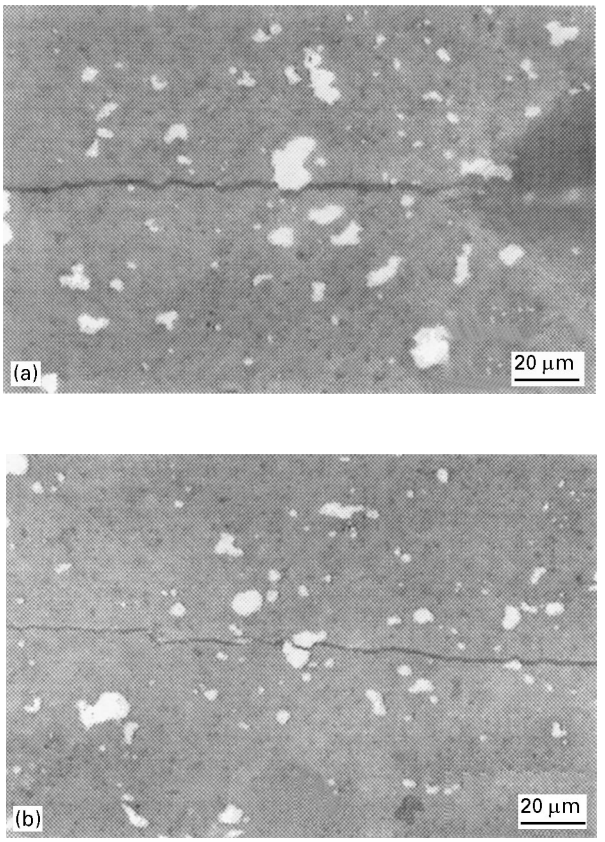

Figure 6 Micrograph illustrating the form of a crack initiated through a Vicker's indentation, in a sample containing 5% Mo by volume. (a) Crack follows the AlN–Mo interface; (b) rupture of Mo grain.

The most commonly observed reinforcement mechanisms in ceramic matrix composites are crack bridging, crack deflection, particle pull-out, microcracking and plastic deformation of the metallic phase (in the case where a metallic phase is present as reinforcement). Observation of fractured samples (Figs 6a and b) allows us to confirm the presence of crack bridging and crack deflection phenomena in the AlN–Mo composites.

Molybdenum possesses mechanical properties which are relatively superior compared to aluminium nitride (Young's modulus = 322 GPa, Tensile strength > 700 MPa) and thus deformation of molybdenum grains needs a large quantity of work which results in proportional energy loss. When the crack tip approaches a metallic particle, depending upon the size and the form of the particle, it is either deviated towards the interface or it passes through the metallic grain. In the case where the adherence at the interface is high, a large amount of energy is lost in order to propagate the crack through the composite material. Figs 6a and b describe the form of crack introduced inside an AlN matrix containing 5% molybdenum (AM5) by a Vickers indentation. According to the size and form of Mo particle, a pull-out (Fig. 6a) or metal phase rupture (Fig. 6b) can be observed in this figure. It is evident that these two processes are active and participate at the same time to improve the mechanical properties.

5. Conclusions

An attempt is made to improve the mechanical properties of AlN through the addition of a refractory metal (Mo). Two powders are mixed in different proportions and hotpressed under conditions defined for pure aluminium nitride. Mechanical properties of a series of samples are studied in order to understand the influence of metal phase on the fracture behaviour of the composite.

Results obtained for the three-point bend strength show that pure aluminium nitride presents a flexural resistance of 270 MPa. An improvement in flexural resistance is observed as a function of molybdenum concentration and a value of 571 MPa is measured in the case of a composite containing 40% Mo by volume. Fracture toughness measurements performed by the SEPB technique show almost the same type of result. K_{1c} value of 2.3 MPa $m^{1/2}$ is observed for pure hotpressed aluminium nitride, whereas this value increases to 6.9 MPa $m^{1/2}$ for a composite containing 30% molybdenum by volume.

These results, attributed to the presence of a metal phase, could be due to different reinforcement mechanisms. Commonly active reinforcement mechanisms in ceramic matrix composites are crack bridging or pull-out and crack deflection. The process of pull-out and bridging can exist at the same time. Composite materials generally present a mixed fracture mode, in which all type of processes take part at the same time. Microscopic analysis of the fracture surface shows that the AlN–Mo composites present two types of fracture. When the crack tip approaches a metallic particle, depending upon the size and the form of the particle, it is either deviated towards the interface or it passes through the metallic grain. Due to its better mechanical properties, molybdenum participates in arresting the crack propagation through the material. In the case where the crack follows the metal–ceramic interface, it slows down as a result of an adherent AlN–Mo interface.

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