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Aluminium Nitride–Molybdenum Ceramic Matrix Composites: Characterization of Ceramic–Metal Interface

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Abstract

Pure aluminium nitride can be hot pressed with an addition of molybdenum powder. With this technique we obtain a ceramic matrix composite having a dispersed metallic phase. Composites produced in this manner present a homogeneous structure with very little open porosity. Electrical resistivity measurements done over a series of composites show a sharp decrease in electrical resistivity when the molybdenum volume fraction in the material increases from 0·2 to 0·22. This value corresponds to the percolation threshold of metallic phase in the ceramic matrix. The interface between molybdenum particles and aluminium nitride grains is established through a fine oxide or oxynitride layer present at the surface of AlN grains.

Le frittage d'un mélange des poudres de nitrure d'aluminium et de molybdène est effectué sous charge. Par cette technique on obtient des composites à matrice céramique avec une phase métallique (Mo) dispersée dans la matrice de AlN. Les échantillons frittés de cette façon présentent une structure dense et homogéne. Les mesures de la résistivité électrique effectuées sur une série de mélanges montrent une chute brutale de celle-ci lorsque la fraction volumique du molybdène dans le matériau passe de 0·2 à 0·22. Cette composition correspond au seuil de percolation des grains métalliques. L'interface entre les particules de molybdène et les grains de AlN s'établit à travers une fine couche d'oxyde ou d'oxynitrure qui se trouve à la surface des grains de AlN.

1 Introduction

Aluminium nitride has many attractive properties for applications which need high thermal conductivity, good mechanical strength, low density value and a low thermal expansion coefficient. Aluminium nitride single crystals exhibit thermal conductivity[1] values of up to 320 W m^{-1} K^{-1}, whereas the thermal conductivity of polycrystalline AlN varies between 80 and 200 W m^{-1} K^{-1} according to the microstructure and composition of the sintered ceramic.[2–5] Hot pressed pure AlN[6,7] shows bend strength values of about 250 to 300 MPa and an elastic modulus ranging between 300 and 310 GPa. It presents a good thermal stability at temperatures higher than 2400°C, under normal conditions. Thus aluminium nitride presents itself as a potential material for thermomechanical applications.

On the other hand, aluminium nitride possess a brittle nature, as is the case for other ceramic materials. 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 similar thermal expansion to AlN. 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] 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, resulting in the formation of a solid solution. Bend strength of hot pressed whisker-reinforced AlN composites increases up to 370 MPa but no important change takes place in the fracture toughness.[8] On the other hand, the thermal conductivity of AlN is dramatically reduced due to Si contamination.

Another way of improving the mechanical and thermomechanical properties of AlN could be the addition of a metallic phase with higher mechanical and thermal properties. Added metallic particles should present a high melting point (in order to

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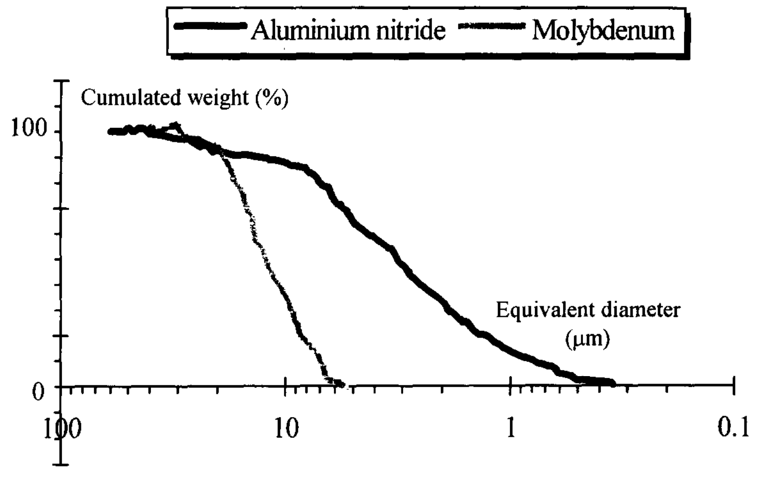

Fig. 1. Size distribution of AlN and Mo powders measured by X-ray sedigraphy technique.

preserve the refractoriness of AlN) and low solubility in the AlN lattice (to preserve high thermal conductivity), in view of high temperatures employed during the sintering of AlN. To keep the density of the composite at its optimum value, a refractory metal with relatively light weight is preferable for this purpose.

Since AlN is a covalent compound, limited atomic mobility prevents complete densification of pure AlN at temperatures lower than 1700°C. At higher temperatures (1700 to 1800°C), pressures or sintering aids are required to achieve respectable densification rates. The hot pressing technique helps to obtain more than 97% densification of AlN, where pressure plays a very important role during sintering. Samples obtained by hot pressing show better mechanical properties than those obtained by pressureless sintering because of the absence of low melting point secondary phases at the grain boundaries and a fine microstructure. Sintering cycles during hot pressing are relatively shorter and hot pressed sample dimensions are closer to the finished product dimensions due to better shrinkage control during hot pressing. But at the same time, this technique remains difficult to apply in the case of large-sized samples and for those having complex shapes because of the high pressures necessary to obtain the required densification.

In this work, aluminium nitride is co-sintered with molybdenum using a hot pressing cycle commonly employed for pure aluminium nitride. AlN–Mo composites are produced with the aims of understanding and verifying the influence of the molybdenum phase on the aluminium nitride ceramic matrix. Molybdenum is a relatively light refractory metal (theoretical density = 10·2 g.cm^{-3}) with a melting point of 2610°C. Earlier studies[9] have shown the presence of adequate bonding between plates of sintered pure AlN and Mo, heat-treated under pressures of 20 MPa at 1850°C for 4 h. Molybdenum equally shows high thermal conductivity (138 W m^{-1} K^{-1}). Because of its ductile nature, the addition of molybdenum is supposed to improve the mechanical as well as the thermomechanical properties of aluminium nitride, whereas better thermal conductivity can be expected in the case where the AlN–Mo interface is clean and devoid of any secondary phases. In this work we study the influence of molybdenum addition on the electrical properties of AlN–Mo composites in order to investigate the percolation threshold, the composition for which the material becomes an electrical conductor, and to verify the state of the metal–ceramic interface in the as-sintered samples.

2 Experimental Procedure

2.1 AlN and Mo powders

Aluminium nitride powder from H. C. Starck (Berlin), with a specific surface area of 4 m^2 g^{-1}, was used. Principal elements of this powder are presented in Table 1 where we note that oxygen is the main impurity. The size distribution of this powder, as studied by the sedigraphy technique (Sedigraph 5000 D, Micromeritics), is presented in Fig. 1. We observe in this figure that the majority of particles have sizes varying between 0·3 and 5 μm. This result is confirmed by the scanning electron micrograph shown in Fig. 2(a).

Molybdenum powder was supplied by Prolabo. This powder is 99·9% pure showing a size distribution of 5 to 30 μm (Fig. 1). Figure 2(b) presents

Table 1. Composition of AlN powder as given by H. C. Starck (Berlin)

Element	*Al*	*N*	*O*	*C*	*Fe*
% weight	>64·5	33·2	1·8	0·05	0·01

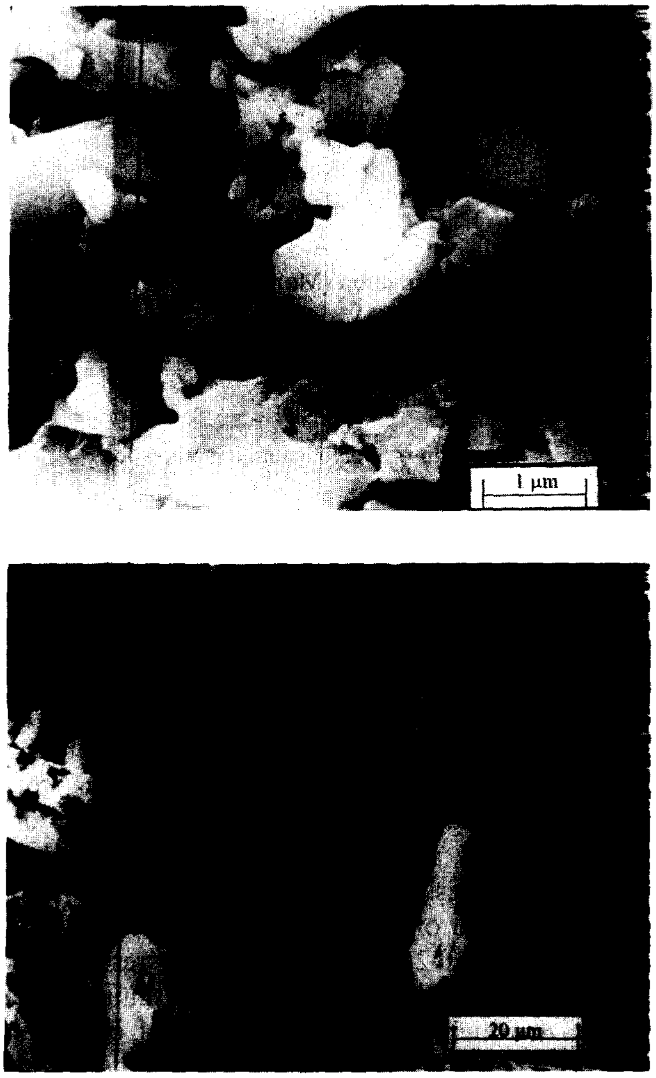

Fig. 2. SEM photomicrographs of AlN (a) and Mo (b) powders, showing size distribution and particle form.

the structure of powder particles which is relatively uniform compared with that of AlN.

2.2 Sintering conditions

Powders were mixed in different proportions, varying the molybdenum concentration by volume in AlN from 5 to 35%. The mixtures were prepared by dry milling for a period of 24 h. Since AlN forms the continuous majority phase (molybdenum concentration never exceeds 35% by volume) and the molybdenum particles are supposed to be embedded inside the AlN matrix, the sintering conditions are kept similar to those commonly employed for the hot pressing of pure aluminium nitride,[10,11] in order to obtain a dense composite.

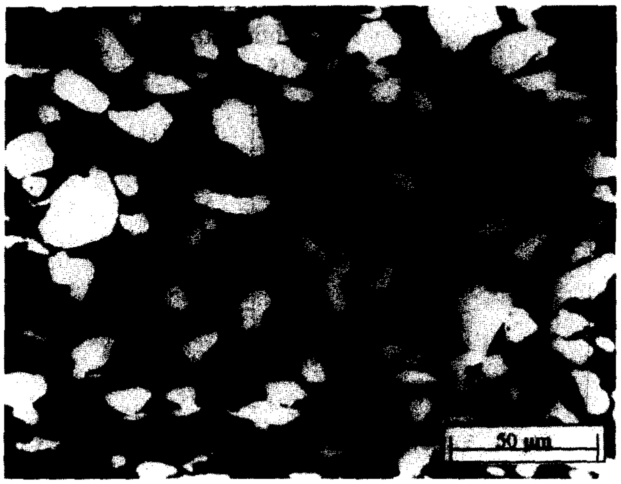

Fig. 3. Microstructure of hot-pressed AM25 (25% Mo and 75% AlN by volume).

Sintering powder was 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. An LPA 2000 (La Physique Appliquée) hot pressing furnace was used, which allowed 20 MPa pressure on the mould during the sintering cycle to be obtained. Sintering was performed under a dynamic nitrogen atmosphere, at a temperature of 1800°C and for a dwell time of 1·5 h. Pressure was applied once the temperature reached 1400°C. Sintered samples were in the form of discs with 30 mm diameter and were rectified to a 4 mm thickness.

The mercury penetration technique was employed to measure the density and open porosity content. Results concerning five compositions are presented in Table 2, where it is found that all the samples presented show a densification rate of more than 94% and an open porosity content of less than 1·5%. Figure 3 illustrates the structure of a hot pressed AlN–Mo sample containing 25% molybdenum by volume. The structure is relatively homogeneous, showing metal particles almost the same size as the powder particles and only traces of porosity in the AlN matrix.

Table 2. Values of theoretical density, measured density, total porosity and open porosity obtained by the mercury penetration technique, for five different mixtures after hot pressing

Ref.	*Volume fraction of AlN*	*Volume fraction of Mo*	*Theoretical density,* d_{th}*(g.cm⁻³)*	*Apparent density,* d_a*(g.cm⁻³)*	*Total porosity (%)*	*Open porosity (%)*
AM5	0·95	0·05	3·605	3·4	5·93	0·75
AM10	0·9	0·1	3·954	3·77	4·66	1·31
AM15	0·85	0·15	4·301	4·2	2·88	0·47
AM20	0·8	0·2	4·648	4·42	4·91	0·98
AM25	0·75	0·25	4·995	4·85	2·93	0·32

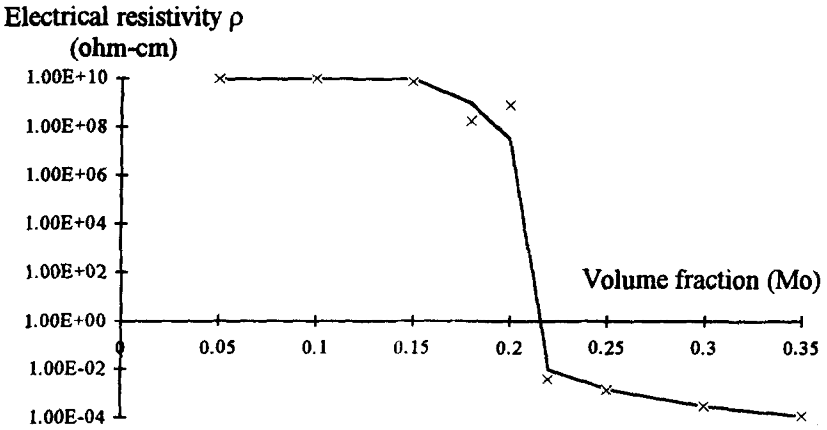

Fig. 4. Variation of the electrical resistivity ρ of Aln–Mo composites, as a function of molybdenum concentration.

Molybdenum particle growth is prohibited due to the high pressures employed during sintering and the absence of sufficient contact between the molybdenum particles at sintering temperatures, whereas the angular structure of initial molybdenum powder particles is not preserved in the sintered structure. The particles have a tendency to acquire rounded forms which are thermodynamically more stable and the particle size is increased wherever a contact is established.

3 Electrical Resistivity Measurement

Electrical resistivity measurements were performed with the help of four-point Valdes method. In this method we employed four fine needle-shaped points in line, 1 mm apart, which were brought in contact with the sample surface. Two outer contacts were used to inject current I into the sample and inner contacts gave the potential difference v between the given points. The electrical resistivity ρ is calculated using a simple Valdes relation which can be written in the case of four points in line, separated through a distance d, as:

$$\rho = 2\,\pi d(v/I) \qquad (1)$$

Samples were prepared under conditions similar to those mentioned in Section 2.2. Molybdenum concentration in the samples was varied from 5 to 35% by volume. Samples, in the form of discs having 30 mm diameter and 4 mm thickness, were rectified and polished to obtain a clean parallel surface.

Table 3 gives the values of current intensity I, potential difference v and electrical resistivity ρ, measured by the above-mentioned technique, for samples having different volume fractions of metallic phase. The results show that the value of electrical resistivity falls rapidly when the volume fraction of molybdenum in the composite increases from 0·2 to 0·22. The same results are illustrated in the form of a semilogarithmic curve in Fig. 4, which shows the variation of electrical resistivity of AlN–No composites as a function of molybdenum volume fraction. This insulator to conductor transformation can be attributed to a percolation phenomenon due to the presence of metal particles in the ceramic matrix. Earlier studies[12,13] showed the same type of results in the case of composites containing Ni, Pd, Cu and Ag particles dispersed in NiO matrix. As can be seen in Fig. 3, the metal particles for a 25% volume concentration are not in contact with each other. Electron conduction in this case can only take place through a modification in AlN matrix properties, produced by the presence of a ceramic–metal interface.

Table 3. Values of electrical resistivity for different AlN–Mo composites, measured by the four-point Valdes method

Ref.	*Volume fraction of AlN*	*Volume fraction of Mo*	*Current intensity,* I *(A)*	*Potential difference,* v *(V)*	*Electrical resistivity,* ρ *(Ω cm)*
AM5	0·95	0·05	$0{\cdot}1 \times 10^{-9}$	0·8	$8{\cdot}6 \times 10^{9}$
AM10	0·9	0·1	$0{\cdot}1 \times 10^{-9}$	0·824	$8{\cdot}85 \times 10^{9}$
AM15	0·85	0·15	$0{\cdot}1 \times 10^{-9}$	0·65	$6{\cdot}98 \times 10^{9}$
AM18	0·82	0·18	$0{\cdot}1 \times 10^{-9}$	0·026	$0{\cdot}16 \times 10^{9}$
AM20	0·8	0·2	$0{\cdot}1 \times 10^{-9}$	0·12	$0{\cdot}75 \times 10^{9}$
AM22	0·78	0·22	0·1	$6{\cdot}3 \times 10^{-4}$	$3{\cdot}95 \times 10^{-3}$
AM25	0·75	0·25	0·1	$2{\cdot}2 \times 10^{-4}$	$1{\cdot}41 \times 10^{-3}$
AM30	0·7	0·3	0·1	5×10^{-5}	$3{\cdot}14 \times 10^{-4}$
AM35	0·65	0·35	0·1	2×10^{-5}	$1{\cdot}25 \times 10^{-4}$

3.1 Percolation through a space charge layer

When two surfaces having different work functions are in contact, a charge transfer takes place in such a manner that the surface having higher value of work function is enriched in electrons. This transfer of charge at the interface between a metallic particle and the ceramic matrix is responsible for the formation of a space charge layer[12] at the particle surface. The electrical resistivity in such a system depends upon the electronic concentration in the space charge layer, the thickness of the space charge layer and the distance between the two particles.

When the distance between metal phase particles in the solid material is decreased due to an increase in the metal phase concentration, the free electron population in the region between the two particles is increased. Critical concentrations corresponding to electronic conduction in ceramic–metal composites depend essentially on the nature of the interface. Any type of interaction at the interface or the presence of a secondary phase between the two surfaces, formed during sintering, will modify to a large extent the nature of the interface and consequently the electrical and thermal properties of such a material will be modified. Results of electrical resistivity measurements for the AlN–Mo composites show, knowing that the percolation threshold is situated around 22% of metallic phase, that no reaction takes place between molybdenum grains and the AlN matrix during sintering that is capable of modifying the interface properties, and thus the electrical properties, in a significant manner.

4 AlN–Mo Interface

The physical and chemical conditions of adhesion between AlN and molybdenum metal have been studied by Quèriaud and Lefort.[9] Their samples were obtained by placing two discs, one of molybdenum and the other of aluminium nitride, one on top of the other and treating under pressures of 20 MPa for 4 h under flowing argon atmosphere at 1850°C. Adhesion studies at the interface showed that only AlN samples sintered without additives and those with 3% Y_2O_3 remained attached with molybdenum. Samples of aluminium nitride sintered in the presence of CaO showed very little adhesion to molybdenum. In all cases, AlN samples with higher additive content (10 to 15% by weight) do not show any adhesion to molybdenum. According to these results,[9,14] we can say that the presence of oxide secondary phases is undesirable for a good quality AlN–Mo interface.

EDAX (energy dispersion analysis by X-rays) at the AlN–Mo interface, performed by Quèriaud[14] on the samples mentioned previously, after treatment at 1850°C, showed the diffusion of a small quantity of aluminium (less than 4 at%) over a thickness of a few μm inside the molybdenum layer. In cases where a secondary phase was present, molybdenum diffused into the liquid oxide phase with concentrations up to 9 at%. However, no molybdenum traces were found inside the AlN grains. These results can be explained by the fact that the diffusion either takes place after slight decomposition of AlN, which is possible under conditions described by Quèriaud,[9,14] or in the presence of an oxide phase present at the grain boundaries.

Microanalysis EDAX studies undertaken in the case of AlN–Mo composites obtained after hot pressing under conditions specified in the earlier part of this work, do not show the presence of free aluminium. Aluminium signalled by Quèriaud[14] is provided by a slight decomposition of AlN under argon at 1850°C signalled by different authors.[15] This difference in results can be explained by the difference in sintering conditions of AlN–Mo composites and those employed by Quèriaud during his experimentation (sintering under nitrogen and at 1800°): the latter prevents AlN decomposition and, as a result, the diffusion of free aluminium inside molybdenum grains is prohibited.

X-ray diffraction analysis of the sintered AlN–Mo surface does not show any extra peaks except those attributed to AlN and Mo. The presence of a stable oxide layer at the AlN grain surface, belonging to the Al–O–N system and being favourable for good densification of AlN in the absence of sintering additives, has been shown by many authors.[10,16] This phase cannot be identified on the X-ray diffraction pattern because it exists superficially in very small quantity and perhaps in the amorphous state, which makes it impossible to be identified by this technique. Its formation can be explained by the presence of oxygen (1·8% by weight), the majority of which is found at the surface of AlN powder particles in the form of aluminium oxide. Under these conditions we can admit that the adhesion between the molybdenum grains and the AlN matrix is produced through a fine oxide or oxynitride layer. We thus find a complex three-phase system which is composed of:

1. a nitride phase (AlN), which is the majority phase and which forms the matrix;
2. a metallic phase (Mo), which is dispersed in the matrix, having particle sizes between 5 and 45 μm; and
3. a secondary phase of the Al–O–N system, in the form of a fine superficial layer, whose quantity and composition depend on the quantity of oxygen in the starting powder and the sintering conditions.

The presence of a small quantity of oxygen is helpful in the sintering process[16] but, on the other hand, a high oxygen content can produce negative effects which could result in modification of the AlN–Mo interface due to the presence of an interphase and in eventual degradation of electrical and thermal properties. Studies[15] on the properties of sintered aluminium nitride have shown that good densification during sintering is obtained for oxygen concentrations in AlN powder of around 0·6 to 1·4% by weight.

5 Conclusions

In an attempt to improve the mechanical, thermal and electrical properties of pure aluminium nitride, it is found useful to add a refractory metal dispersed phase in the AlN matrix. Molybdenum seems to be the best choice as a refractory metal, due to its good thermal and electrical properties, its melting point of 2610°C and its thermal expansion coefficient close to that of aluminium nitride. Powder mixtures of AlN–Mo were sintered with AlN as the majority phase, varying the molybdenum concentration between 5 and 35% by volume. Hot pressing was performed under conditions similar to those employed for pure AlN powders. Samples sintered under these conditions present a homogeneous structure, very little open porosity and more than 94% densification rate.

Electrical resistivity measurements were performed using the four-point Valdes technique. Results have shown that the electrical resistivity varies as a function of molybdenum concentration and that the material becomes an electrical conductor in the case of molybdenum volume fractions of more than 0·22. This insulator to conductor transformation is attributed to a percolation phenomenon in the metal phase. The presence of a space charge layer at the AlN–Mo interface modifies the electronic structure in the region closer to the interface and thus participates in the conduction of electrons between the metal phase. Consequently, the material becomes a conductor with concentrations of metallic phase for which the metallic particles are not really in contact.

X-ray studies of the sintered AM25 surface have shown the absence of any secondary phase at the interface between AlN matrix and molybdenum particles. Phase studies undertaken for the ternary system Mo–Al–N are in conformity with these results.[17] The presence of a very fine oxynitride layer at the AlN grain boundaries, which has been verified by earlier studies, aids in the densification of AlN grains during sintering and is probably helpful in obtaining an adherent interface between AlN grains and Mo particles. The presence of this layer does not affect, in a notable manner, the interface properties, the electrical conductivity or the critical metal phase concentration corresponding to the percolation threshold. In any case, a secondary oxide phase present in higher quantities would be expected to modify the AlN–Mo interface to a large extent, and degrade the electrical and thermal properties.

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