

# Aluminium Nitride–Molybdenum Ceramic Matrix Composites. Influence of Molybdenum Addition on Electrical, Mechanical and Thermal Properties

Amir Azam Khan and Jean Claude Labbe

Laboratoire de Matériaux Céramiques et Traitements de Surface, URA CNRS N° 320, Faculté des Sciences, Université de Limoges, 123 Av. Albert Thomas, 87060 Limoges CEDEX, France

## Abstract

*Aluminium nitride–molybdenum ceramic matrix composites are produced by hot pressing a mixture of two powders without any sintering aids. Sintered samples show homogeneous and dense structure. Electrical resistivity measurements conducted over a series of samples show a rapid decrease in its value once the molybdenum volume fraction in AlN matrix is increased from 0.2 to 0.22. The interface between AlN matrix and Mo particles is found to be devoid of any secondary phases. Mechanical thermal and thermomechanical properties of these composites are then studied in a way to investigate the influence of molybdenum addition on the behaviour of AlN. An important increase in the fracture toughness, bend strength and thermal shock resistance of the composites is observed as a function of Mo concentration. Thermal conductivity measured at room temperature and thermal diffusivity measured at temperatures between 400 and 1000°C also show an improvement when molybdenum concentration in the AlN matrix is increased from 0 to 40%. This improvement in mechanical thermal and thermomechanical behaviour of composites is attributed to a clean adherent AlN–Mo interface deprived of low melting and low thermal conductivity secondary phases as well as better mechanical properties and good thermal conductivity of Mo. Molybdenum has a thermal expansion coefficient near the AlN one which allows to minimise the residual and thermal stresses at the AlN–Mo interface. © 1997 Elsevier Science Limited.*

## 1 Introduction

Aluminium nitride has received considerable attention in recent years due to its high thermal

conductivity and good mechanical properties, which makes it an attractive material for thermal management and high temperature engineering applications. It presents a good thermal stability at temperatures higher than 2400°C, whereas thermal conductivity of polycrystalline AlN varies between 80 and 200 W m<sup>-1</sup> K<sup>-1</sup>, according to the microstructure and composition of the sintered ceramic.<sup>1–4</sup> Its field of application is limited primarily due to its low fracture toughness and thermal shock resistance. Attempts were made to improve its mechanical properties, either by incorporating a ductile metal phase<sup>5,6</sup> (Al) or ceramic whiskers<sup>7,8</sup> (SiC) in AlN matrix. AlN–SiC interface studies showed presence of secondary phases which degrade thermal and thermomechanical properties. With a goal to improve thermal, mechanical and thermomechanical properties of AlN, addition of a refractory metal, such as molybdenum, was supposed to be helpful in order to improve the overall thermal and mechanical behaviour of AlN. Molybdenum was chosen due to its sufficiently high melting point (2610°C), high thermal conductivity (138 W m<sup>-1</sup> K<sup>-1</sup>), good mechanical properties and close to AlN thermal expansion coefficient ( $\sim 7 \times 10^{-6}$  K<sup>-1</sup> between 300 and 1200 K, against  $\sim 6.5 \times 10^{-6}$  K<sup>-1</sup> for pure AlN in the same range of temperature). Meanwhile, the properties of such a dispersed phase composite would strongly depend upon the nature and properties of AlN–Mo interface and possible interface reactions at the sintering temperature. Earlier studies<sup>9</sup> prove that a strong bonding is produced between sintered AlN and molybdenum plates, heat treated for 4 h at 1850°C under 20 MPa pressure. The objective of this work was to produce and characterise AlN-based composite materials with molybdenum as a dispersed metallic phase having better than AlN

thermal, mechanical and thermomechanical properties.

## 2 Sintering

Aluminium nitride–molybdenum ceramic matrix composites (CMC) were produced by hot pressing a mixture of two powders. AlN powder was supplied by Hermann C. Starck Berlin (grade B), with specific surface area of about  $4\text{ m}^2\text{ g}^{-1}$  and with oxygen as the principal impurity (1.8 wt%). Molybdenum was supplied by Prolabo, having a total impurity content of less than 0.01 wt%. The two powders were mixed in different proportions, varying the molybdenum concentration in AlN from 5 to 40 vol%. The mixtures were prepared by dry milling for a period of 24 h. Since AlN formed a continuous majority phase (matrix), sintering conditions were kept similar to those commonly employed for hot pressing of pure aluminium nitride. Sintering was performed under controlled nitrogen atmosphere, under pressure of 20 MPa and at  $1800^\circ\text{C}$  for a dwell time of  $1\frac{1}{2}$  h. Samples produced under these conditions showed an open porosity of less than 1.5% and the microstructure showed a uniform distribution of Mo grains without any preferential orientation. Details concerning sintering conditions and sintered samples microstructure can be found elsewhere.<sup>10</sup>

## 3 AlN–Mo Interface

Study of sintered samples surface by X-ray diffraction and by EDAX technique does not reveal any secondary phase. Earlier studies have shown<sup>11</sup> that a very fine oxide or oxynitride layer (Al–O–N) exists at the surface of AlN powder particles, which depends upon the powder production process and the quantity of oxygen present in the initial powder (1.8 wt% in our case). The presence of this layer is helpful in the densification process during sintering, but the quantity of formed secondary oxide phase must be limited to a strict minimum in order to preserve the thermal and mechanical properties of AlN. It could, therefore, be concluded that oxygen is present in the form of a very thin oxynitride layer which, perhaps, is in amorphous state and thus difficult to detect by classical investigation techniques.

Electrical resistivity measurements were conducted<sup>10</sup> over a series of samples with varying molybdenum concentration, using the four-point Valdes technique. Variation of the electrical resistivity was observed as a function of molybdenum concentration (Fig. 1) and results showed a sharp decrease in

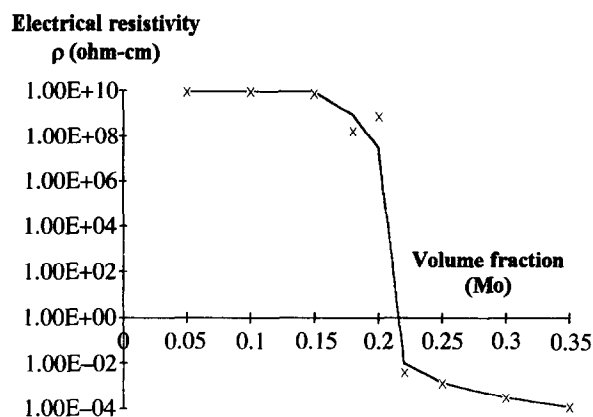


Fig. 1. Electrical resistivity  $\sigma$  of different AlN–Mo composites, as a function of molybdenum volume fraction.

Table 1. Mean values of electrical resistivity of different AlN–Mo sintered samples obtained using the four-point Valdes method

Reference	Volume fraction (AlN)	Volume fraction (Mo)	Electrical resistivity $\rho$ ( $\Omega\text{ cm}$ )
AM5	0.95	0.05	$8.6 \times 10^9$
AM10	0.9	0.1	$8.85 \times 10^9$
AM15	0.85	0.15	$6.98 \times 10^9$
AM18	0.82	0.18	$0.16 \times 10^9$
AM20	0.8	0.2	$0.75 \times 10^9$
AM22	0.78	0.22	$3.95 \times 10^{-3}$
AM25	0.75	0.25	$1.41 \times 10^{-3}$
AM30	0.7	0.3	$3.14 \times 10^{-4}$
AM35	0.65	0.35	$1.25 \times 10^{-4}$

its value when the Mo volume fraction in the composite increased from 0.2 to 0.22 ( $0.75 \times 10^9$  ohm cm and  $3.95 \times 10^{-3}$  ohm cm, respectively). This important decrease in electrical resistivity was attributed to the percolation phenomena, responsible for electric conduction in the absence of a real contact between the metal grains. This behaviour, observed in the case of ceramic–metal composites,<sup>12,13</sup> is a result of a space charge layer present at the ceramic–metal interface.

## 4 Mechanical Properties

Addition of a dispersed second phase could equally improve as well as deteriorate the mechanical resistance of a CMC. Metal phase particles could behave as defects in the presence of undesirable reaction products or in the absence of adequate adherence at the particle–matrix interface and, therefore, could facilitate crack propagation in the composite material. Knowing that no detectable phase is formed at the AlN–Mo interface<sup>10</sup> and that sintered AlN and Mo plates show respectable adherence and compatibility,<sup>9</sup> addition of molybdenum was supposed to improve the mechanical

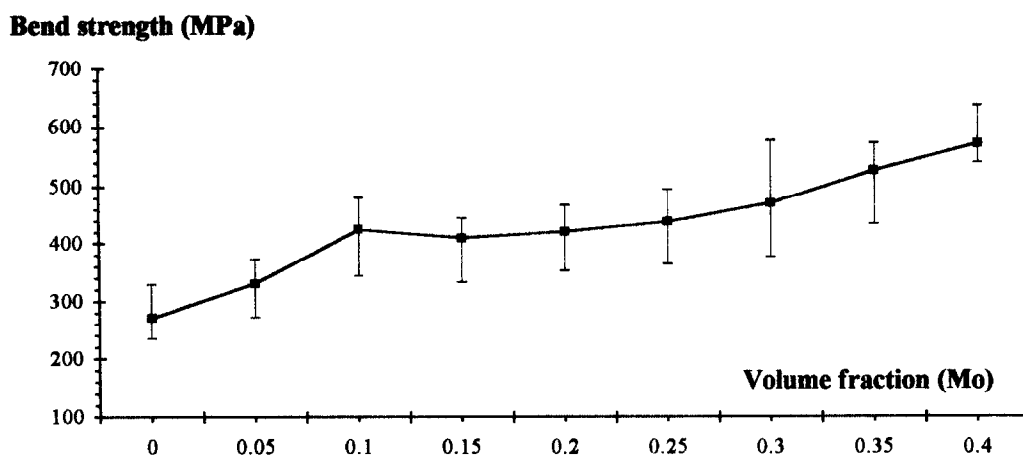


Fig. 2. Three-point bend strength ( $\sigma_f$ ) for different hot pressed AlN–Mo mixtures, as a function of molybdenum volume fraction.

resistance of the composite. Anyhow, bend strength and fracture toughness of sintered composites containing different volume fractions of molybdenum were measured in order to observe and verify this phenomenon.

Bend strength was measured using the classical three-point test. Samples were in the form of rectangular bars with dimensions  $4 \times 4 \times 22 \text{ mm}^3$ , were polished and tested for rupture strength at a rate of  $0.2 \text{ mm min}^{-1}$ . Figure 2 shows the variation of three-point bend strength as a function of molybdenum volume fraction in the composite, where it could be seen that the bend strength increases from a mean value of 270 MPa for pure AlN to almost 571 MPa for a composite containing 40 vol% of molybdenum. Fracture toughness measurements were carried out using the single edge precracked beam (SEPB) test. This technique, initially developed by Warren *et al.*<sup>14</sup> and employed to measure the fracture toughness of ceramics such as  $\text{Al}_2\text{O}_3$ ,  $\text{Si}_3\text{N}_4$  and SiC by Nose *et al.*<sup>15</sup>, uses precracked samples to measure the fracture toughness. The advantage of this method over

those commonly employed is the fact that the produced crack is large enough ( $> 1 \text{ mm}$ ) compared to the zone containing residual stresses, and thus the influence of the latter present at the crack tip could be considered as negligible. Figure 3 gives the variation of fracture toughness as a function of molybdenum concentration where it could be observed that fracture toughness increases from  $2.3 \text{ MPa.m}^{1/2}$  measured for pure hot pressed AlN to almost  $7 \text{ MPa.m}^{1/2}$  for a composite containing 30 vol% of molybdenum (AM30).

Elastic constants (Young's modulus, shear modulus and Poisson's coefficient) were measured using ultrasonic technique. No important change in their values was observed which, however, improved slightly as the molybdenum concentration in AlN matrix was increased. This explains, knowing that AlN and molybdenum have near to each other elastic constants, an absence of microcracking at the particle–matrix interface and an excellent interface contact. A description of results concerning mechanical properties can be found elsewhere.<sup>16</sup>

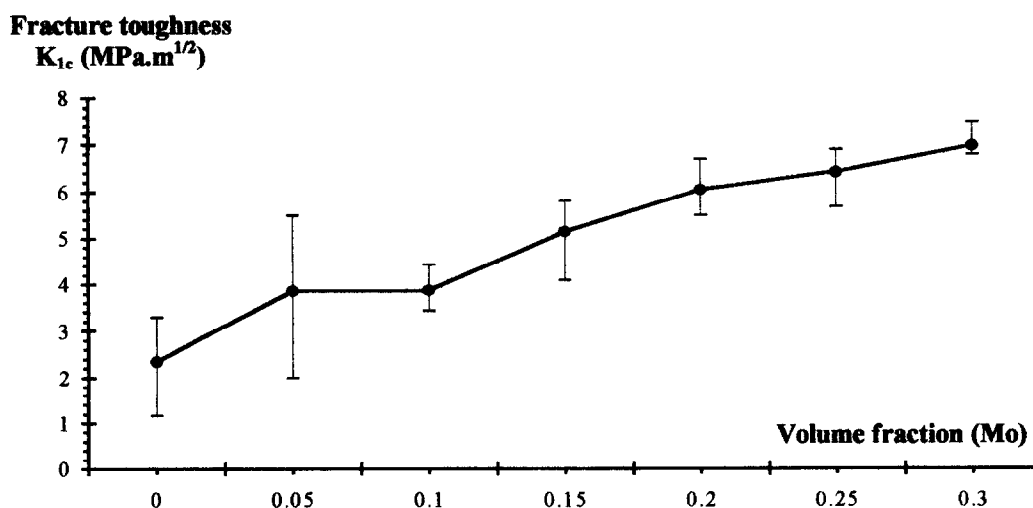


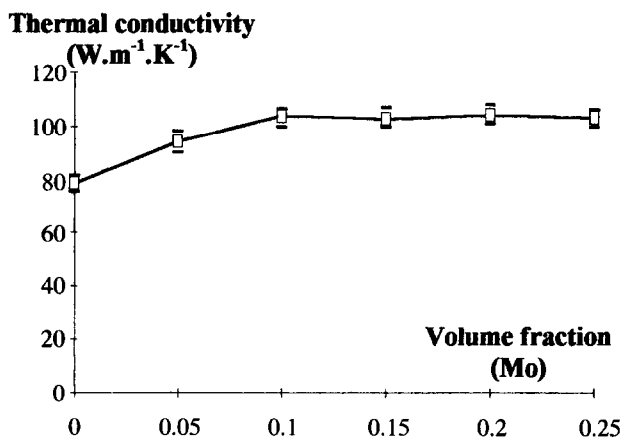
Fig. 3. Fracture toughness ( $K_{1c}$ ) of AlN–Mo composites, measured by S.E.P.B. method, as a function of molybdenum concentration.

**Table 2.** Elastic constants of different AlN–Mo composites, measured by ultrasonic technique

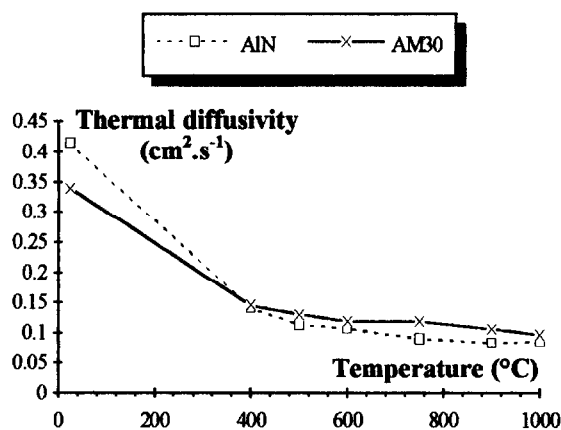
Samples	Volume fraction (AlN)	Volume fraction (Mo)	Young's modulus $E$ (GPa)	Shear modulus $G$ (GPa)	Poisson's ratio ( $\nu$ )
AlN	1	0	313	126	0.24
AM5	0.95	0.05	314	126	0.243
AM10	0.9	0.1	319	127	0.25
AM15	0.85	0.15	305	121	0.25
AM20	0.8	0.2	319	127	0.25
AM25	0.75	0.25	323	128	0.257
AM30	0.7	0.3	320	127	0.26
Mo	0	100	322	123	0.30

## 5 Thermal Properties

Mean values of room temperature thermal conductivity of AlN–Mo composites, as a function of molybdenum concentration, are presented in Fig. 4. It could be observed that from almost  $78 \text{ W m}^{-1} \text{ K}^{-1}$  for pure AlN, its value increases to about  $104 \text{ W m}^{-1} \text{ K}^{-1}$  for a composite containing more than 20% molybdenum by volume. Thermal diffusivity at high temperature was measured using flash laser technique. Figure 5 shows that AM30 presents higher than AlN thermal diffusivity between 400 and  $1000^\circ\text{C}$ . More details about the



**Fig. 4.** Room temperature thermal conductivity of composites as a function of molybdenum volume fraction.

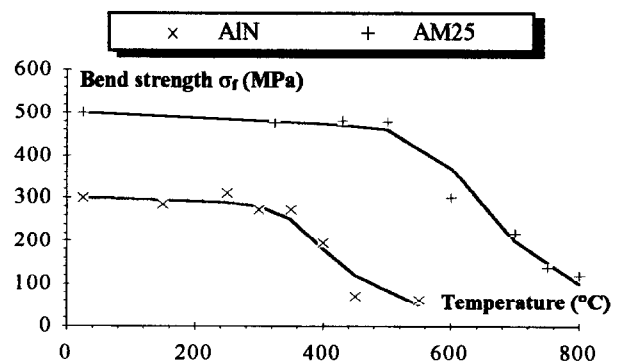


**Fig. 5.** Thermal diffusivity measured by a flash laser method, of AlN and AM30, as a function of temperature.

influence of molybdenum addition on thermal properties of composites could be found in a separate publication.<sup>17</sup>

## 6 Thermal Shock Resistance

Thermal shock resistance was measured using a vertical furnace provided with a pneumatic system to assure constant quenching conditions. Samples were cut from sintered discs, in the shape of rectangular bars with dimensions of  $3 \times 4 \times 22 \text{ mm}^3$ . All six surfaces were polished to a finesse of  $1 \mu\text{m}$  and five samples were tested for each temperature. After initial examination under ultraviolet light using a liquid penetrant technique, the three-point bend strength of thermally treated samples was measured in order to determine the critical temperature difference for thermal shock ( $\Delta T_c$ ). Figure 6 gives the variation of three-point bend strength after thermal treatment at different temperatures, of pure hot pressed AlN and a composite containing 25 vol% molybdenum (AM25). It can be seen in this figure that AM25 presents a critical temperature difference for thermal shock situated between 500 and  $550^\circ\text{C}$  much higher than that of AlN situated between  $300$  and  $350^\circ\text{C}$ . This net improvement in thermal shock resistance could be attributed to better mechanical resistance and thermal conductivity of AM25 knowing that  $\Delta T_c$



**Fig. 6.** Mean values of three-point bend strength after thermal shock treatment at different temperatures, of pure AlN and AM25.

is directly related to mechanical resistance of a material:

$$\Delta T_c = \frac{\sigma_f(1 - \nu)}{E_\alpha} \quad (1)$$

where  $E$  and  $\alpha$  are the Young's modulus and linear thermal expansion coefficient of the material. Meanwhile, a high thermal conductivity  $\kappa$  reduces the intensity of thermal shock expressed by  $\beta = r_m h / \kappa$ .  $\beta$  is the Biot's modulus, whereas  $r_m$  and  $h$  represent the sample size and heat exchange coefficient respectively.

## 7 Conclusion

AlN–Mo ceramic matrix composites were sintered with molybdenum concentration varying from 5 to 40 vol% using a hot pressing cycle generally employed for pure aluminium nitride. Good densification ( $\sim 97\%$ ) was obtained in all cases and the composite presented a homogeneous microstructure with no preferential orientation of molybdenum particles. Electrical resistivity of composites with different molybdenum concentration was measured using the four-point Valdes technique. A rapid decrease in its value was observed as the volume fraction of molybdenum increased from 0.2 to 0.22, which could be explained by the phenomenon of percolation between the metallic grains.<sup>10</sup> Observation of the AlN–Mo interface allowed one to state that a good adhesion exists between ceramic matrix and metal grains.

Mechanical properties were measured for a series of samples containing 5 to 40 vol% of molybdenum. Bend strength increased from a mean value of 270 MPa for pure aluminium nitride to almost 570 MPa for a composite containing 40 vol% of metallic phase. Fracture toughness measured by the S.E.P.B. technique also increased as a function of molybdenum concentration. From 2.3 MPa.m<sup>1/2</sup> measured for pure AlN a value of 6.9 MPa.m<sup>1/2</sup> was obtained in the case of a composite containing 40% by volume of metallic phase. These important results were associated to the excellent compatibility between the two phases and absence of residual stresses at the interface due to a close match between the thermal expansion coefficients of AlN and molybdenum ( $6.5 \times 10^{-6} \text{K}^{-1}$  and  $7 \times 10^{-6} \text{K}^{-1}$  between 300 and 170 K for AlN and Mo, respectively). Moreover, an adherent interface devoid of any brittle reaction products, relatively ductile nature and better mechanical properties of molybdenum compared to AlN<sup>16</sup>, were considered to be equally responsible for such an improvement in the composite properties.

Thermal conductivity at room temperature was measured in order to understand the influence of molybdenum addition on the AlN matrix, which showed an increase as a function of Mo concentration. Its value increased from 78 W m<sup>-1</sup> K<sup>-1</sup> for pure hot pressed AlN to almost 104 W m<sup>-1</sup> K<sup>-1</sup> for a composite containing 20 vol% of Mo. Thermal diffusivity at high temperature (between 20 and 1000°C) measured by flash laser technique, for pure AlN and a composite containing 30% Mo by volume (AM30), also showed that the presence of Mo was favourable at temperatures between 400 and 1000°C. These results could be explained by the fact that no secondary oxide phases were produced at the interface between AlN and Mo grains, and that a perfect contact was established which reduced to the minimum, the thermal contact resistance (TCR) between the two grain surfaces.<sup>17</sup> Critical temperature difference of thermal shock, for which the mechanical properties of the material decrease rapidly, was found to be almost two times higher ( $\sim 550^\circ\text{C}$ ) for the composite containing 25 vol% of Mo compared to that of pure AlN ( $\sim 300^\circ\text{C}$ ). This net improvement in thermal shock resistance was attributed to better mechanical resistance and thermal conductivity of composites, compared to pure AlN.

## References

1. Partridge, G., Ceramic materials possessing high thermal conductivity. *Adv. Mater.*, 1992, 1, 51–54.
2. Böcker, D. G., Hamminger, R. W., Heinrich, J., Humber, J. and Roosen, A., Covalent high performance ceramics. *Adv. Mater.*, 1992, 131, 169–178.
3. Slack, G. A., Tanzilli, R. A., Pohl, R. O. and Vandersande, J. W., The intrinsic thermal conductivity of AlN. *Journal Phys. Chem. Solids*, 1987, 48(7), 641–647.
4. Sheppard, L. M., Aluminium nitride: a versatile but challenging material. *Am. Ceram. Soc. Bull.*, 1990, 69(11), 1801–1812.
5. Aghajanian, M. K., Biel, J. P., Smith, R. G. and Kennedy, C. R., Microstructure and properties of AlN matrix composites produced by the direct nitridation of molten aluminium. *Journal Mat. Sci. Letts.*, 1994, 13, 293–296.
6. Huang, J. L. and Li, C. H., Microstructure and mechanical properties of aluminium nitride–aluminium composites. *Journal Mat. Res.*, 1994, 9(12), 3153–3159.
7. Mroz, T. J. and Groat, E. A., Fabrication and properties of AlN–SiC whisker composites. *Advances in Ceramic Matrix Composites, Ceram. Trans.*, 1993, 38, 375–382.
8. Unni, C. K. and Gordon, D. E., Mechanical properties of monolithic AlN and SiCw/AlN composites. *Journal Mat. Sci.*, 1995, 30, 1173–1179.
9. Lefort, P. and Queriaud, R., Compatibility between molybdenum and aluminium nitride. *Journal Eur. Ceram. Soc.*, 1994, 13, 329–333.
10. Khan, A. A., and Labbe, J. C., Aluminium nitride–Molybdenum ceramic matrix composites: characterisation of ceramic–metal interface. *Journal Eur. Ceram. Soc.*, 1996, 16, 739–744.
11. Ado, G., Bernache, D., Billy, M., Han, K. S. and Lefort, P., Mécanisme de frittage sous charge du niture

- d'aluminium et de l'oxynitrure (AlON). *Rev. Chim. Minér.*, 1985, **22**, 473-483.
12. Dudney, N. J., Effect of interfacial space charge polarisation on the ionic conductivity of composite electrolytes. *Journal Am. Ceram. Soc.*, 1985, **68**(10), 538-545.
  13. Kieffer, J. and Wagner, J. B., Electrical conductivity of metal-metal oxide composites. *Journal Electrochem. Soc.*, 1988, **135**(1), 198-205.
  14. Warren, R. and Johannesson, B., Creation of stable cracks in hard metals using bridge indentation. *Powder Metall.*, 1984, **27**(1), 25-29.
  15. Nose, T and Fujii, T., Evaluation of fracture toughness for ceramic materials by a single edge precracked beam method. *Journal Am. Ceram. Soc.*, 1988, **71**(5), 328-333.
  16. Khan, A. A. and Labbe, J. C. Aluminium nitride-molybdenum ceramic matrix composites: influence of molybdenum concentration on the mechanical properties. *Journal Mat. Sc.* (submitted).
  17. Khan, A. A. and Labbe, J. C., Influence of molybdenum concentration on thermal properties of aluminium nitride-molybdenum ceramic matrix composites. *Am. Ceram. Soc. Bull.*, 1996, **75**(8), 52-56.