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Compatibility between Molybdenum and Aluminium Nitride

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Abstract

Molybdenum and aluminium nitride sintered discs are strongly bonded after hot pressing at 1850°C under 20 MPa in flowing argon. If aluminium nitride discs are pre-sintered with lime or yttria additive, the bonding is only achieved when the dopant content is weak (1 to 3%). By comparison with the behaviour of tungsten under the same conditions, the bonding is supposed to be due to the reaction of the secondary oxide phase of molybdenum with its analogue in aluminium nitride, providing a complex interfacial phase, able to exist at the grain boundaries of both the materials near the interface, and making the bonding strong after cooling. If the interfacial phase is too great in volume and too liquid (when AlN is doped with important amounts of lime or yttria) it is expelled from the interfacial zone and no bonding is observed.

Gesinterte Molybdän- und Aluminiumnitridscheiben weisen nach dem Heißpressen in einem Argonstrom bei 1850°C und einem Druck von 20 MPa eine gute Haftung auf. Werden die Aluminiumnitridscheiben mit Kalk oder Yttriumoxid vorgesintert, ergibt sich eine gute Haftung nur bei schwacher Dotierung (1–3%). Aus einem Vergleich mit dem Verhalten von Wolfram unter den gleichen Bedingungen ist zu vermuten, daß die Haftung aufgrund der Reaktion der sekundären Oxidphase des Molybdäns mit der entsprechenden Phase des Aluminiumnitrids verursacht wird. Dies führt zu einer komplexen Grenzflächenphase, die entlang der grenzflächennahen Korngrenzen beider Materiaien existieren kann und resultiert in einer guten Haftung nach dem Abkühlen. Bei zu großem Volumen der Grenzflächenphase und wenn die Phase zu flüssig ist (wenn AlN mit beträchtlichen Mengen Kalk oder Yttriumoxid dotiert wurde), wird sie von der Grenzflächenzone abgewiesen und es findet keine Haftung statt.

Des pastilles frittées de molybdène et de nitrure d'aluminium adhèrent fortement après pressage à chaud à 1850°C sous 20 MPa en atmosphère dynamique d'argon. Si les pastilles de nitrure d'aluminium sont préalablement frittées avec de la chaux ou de l'yttria, l'adhésion n'est obtenue que lorsque le taux de dopant est faible (1 à 3%). Par comparaison avec le comportement du tungstène placé dans les mêmes conditions, on suppose que l'adhésion est due à la réaction de la phase secondaire oxyde du molybdène avec son analogue du nitrure d'aluminium, formant une phase interfaciale complexe susceptible d'exister aux joints de grains des deux matériaux au voisinage de l'interface, et rendant la jonction solide après refroidissement. Si la phase interfaciale est trop volumineuse et trop liquide (quand AlN est dopé avec d'importantes quantités de chaux ou d'yttria) elle est expulsée de la zone interfaciale et l'on n'obtient pas d'adhésion.

1 Introduction

Among the different metals able to be joined to aluminium nitride with a view to obtaining high density electronic devices, few of them allow the use of multilayer technology. Indeed in these processes, because substrate sintering and metal bonding are to be made simultaneously and aluminium nitride needs high sintering temperatures, only refractory metals can be used. The study of the behaviour of such metals in the presence of aluminium nitride is therefore of great interest.

In some previous work the compatibility[1] and the bonding conditions of tungsten on aluminium nitride[2,3] have been studied. Hence, it seemed also interesting to examine the compatibility between aluminium nitride and molybdenum, which is a refractory metal sometimes used for integrated circuits.

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Table 1. Main impurities of the molybdenum powder

	Impurity					
	O	*W*	*K*	*Fe*	*N,C*	*Ca, Cr, Na, Ni, Pb, S, Si, V, Zr*
Content (ppm)	1 500	< 100	< 60	< 50	< 30	< 10

2 Experimental

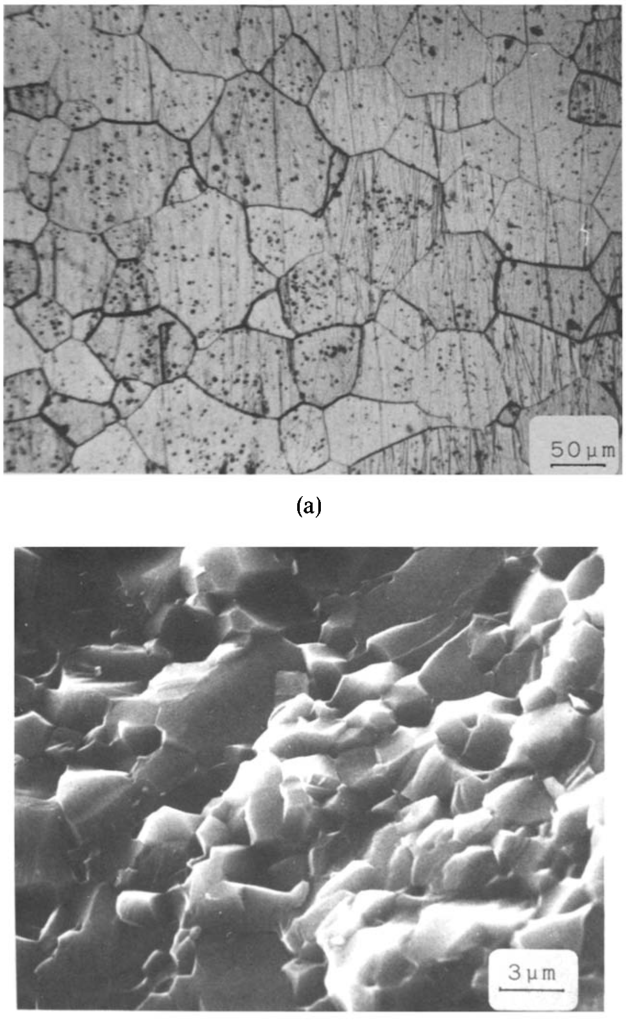
Aluminium nitride and molybdenum samples are discs (diameter $\phi = 20\,mm$, thickness $t = 4\,mm$) obtained by hot pressing of commercial powders. For aluminium nitride powder (Starck Ltd, grade C), sintering conditions with Y_2O_3 or CaO or without additive are presented elsewhere[1] leading to products nearly fully dense ($\rho = 3{\cdot}16$–$3{\cdot}24\,g\,cm^{-3}$). Molybdenum powder is provided by Aldrich Ltd and its main impurities are listed in Table 1. It is hot pressed under 20 MPa in flowing argon. Characteristics of the sintered discs according to the experimental conditions are presented in Table 2.

Even with a significant increase of temperature molybdenum densification is only slightly improved.

Table 2. Characteristics of molybdenum discs according to sintering conditions

Temperature (°C)	*Time (min)*	*Relative density (%)*	*Mean grain size (μm)*
1 400	90	95	9
1 500	90	96·3	14
1 850	90	97·5	30
1 850	120	97·8	40

For the compatibility tests the densest discs, obtained after 90 to 120 minutes of treatment at 1850°C, were chosen. Figure 1(a) shows their microstructure with coarse grains, after polishing and etching, to be compared with the fine texture of sintered aluminium nitride (Fig. 1(b)).



(a)

(b)

Fig. 1. Microstructure of (a) sintered molybdenum and of (b) sintered aluminium nitride.

3 General Results

3.1 Compatibility tests

Aluminium nitride and molybdenum discs, put one on the other, were hot pressed under 20 MPa at 1850°C for 4 h in flowing argon. After cooling they were cut with a diamond saw and the cross-sections were polished to observe the interface.

In some cases this mechanical action induced the debonding of the discs, so that it constituted a first bonding test. The quality of the bonding estimated by this means strongly depended on the sintering additives in the aluminium nitride and Table 3 summarizes these results.

When AlN was sintered without additive or with small amounts of Y_2O_3, debonding was never observed. It sometimes occurred during cutting or polishing when AlN was previously sintered with lime (1 wt%), but no bonding was achieved when using large amounts of additives, yttria or lime, in AlN during its sintering.

Table 3. Quality of the bonding of aluminium nitride and molybdenum discs according to the sintering additive of aluminium nitride

	Without additive	*Additive (wt%)*			
		Y_2O_3 *(3%)*	*CaO (1%)*	Y_2O_3 *(15%)*	*CaO (10%)*
Estimated bonding	Good	Good	Weak	Poor	Poor

Table 4. Relations between secondary phases and bonding

	Secondary phase of the nitride	*Estimated viscosity of the interfacial liquid phase*	*Estimated volume of the interfacial liquid phase*	*Apparent bonding*
AlN alone	Aluminium oxynitride	High	Very small	Good
AlN + 3% Y_2O_3	Yttrium aluminate	Low	Small	Good
AlN + 1% CaO	Calcium aluminate	Very low	Small	Weak
AlN + 15% Y_2O_3	Yttrium aluminate	Low	Important	Poor
AlN + 10% CaO	Calcium aluminate	Very low	Important	Poor

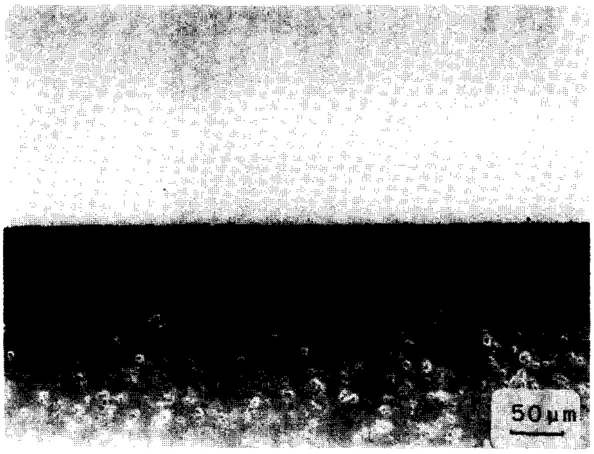


Fig. 2. SEM micrograph of cross-section of bonded discs of molybdenum (upper part) and aluminium nitride (lower part).

The SEM micrograph of Fig. 2 provides an example of the appearance of the interface, that is plane and very regular, whether the aluminium nitride had been doped or not.

3.2 Examinations of the interface

When the debonding was easy, it was possible to observe and analyse the interface. The case examined here is that of the interface between molybdenum and 15% yttria-doped aluminium nitride. Figure 3 shows that the surface of the molybdenum disc which was in contact with aluminium nitride retains the imprint of the aluminium nitride grain boundaries, appearing smaller by far than those of molybdenum.

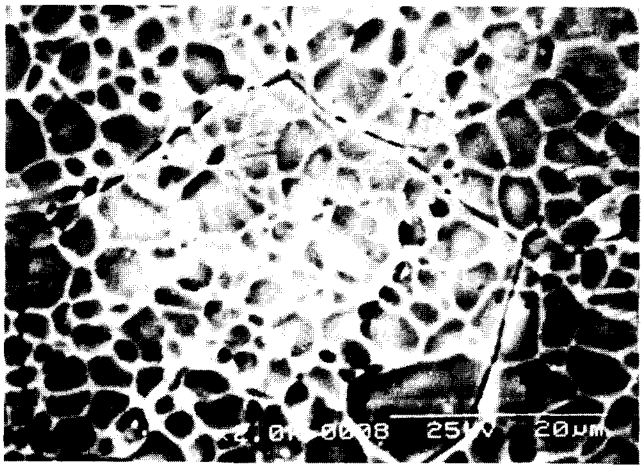


Fig. 3. Marks of the grain boundaries of Y_2O_3-doped aluminium nitride on molybdenum after unsticking.

When the additive was lime (10 wt%) the grain boundaries of molybdenum seemed to be etched and widened by a secondary phase (Fig. 4(a)). The corresponding X-ray maps of aluminium (Fig. 4(b)), calcium (Fig. 4(c)) and molybdenum (Fig. 4(d)) show that this phase contains mainly aluminium and calcium and only a small amount of molybdenum. These three X-ray maps are not exactly complementary, and compared with Fig. 4(a), it is probable that the composition of the secondary phase is not absolutely constant and is constituted of various calcium aluminates containing molybdenum traces. These phases could not be identified by X-ray diffraction.

4 Discussion

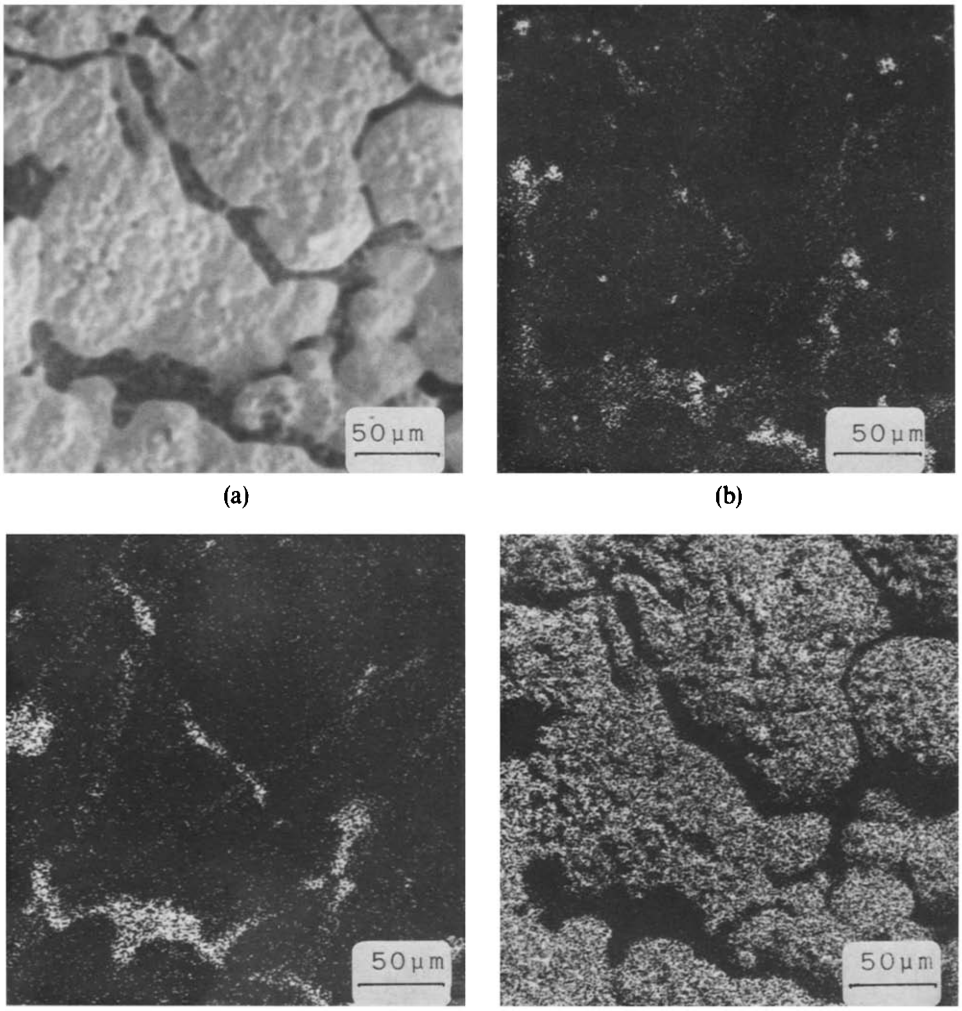
It is clear that the bonding between aluminium nitride and molybdenum discs may be related to the nature and the quantity of secondary phases in the aluminium nitride. When this phase was not fusible and in low quantity, such as when AlN was sintered without additive (i.e. only with an aluminium oxynitride phase at the grain boundaries[4,5]) a good bonding was achieved.

At the opposite extreme, when aluminium nitride was doped with 10 wt% lime, the secondary phase was composed of calcium aluminates,[3] liquid at the experimental temperature (1850°C): It is highly probable that the traces of molybdenum identified in this phase made it even more fusible.[6]

The quantities of sintering additive also plays a role in the quality of the bonding, since, for low contents of yttria or lime it was good, but not when there were important amounts of additives.

Table 4 summarizes all the results with the secondary phase present in aluminium nitride with its estimated viscosity and volume. This presentation makes coherent all the experimental results.

When the secondary phase of aluminium nitride was liquid and a little viscous (calcium aluminate) it was quickly driven out towards the side of the mould, slightly dissolving some molybdenum at the



(a) (b)

(c) (d)

Fig. 4. Micrograph of (a) molybdenum surface after a 4 h contact at 1850°C with a lime-doped aluminium nitride disc and corresponding X-ray maps of (b) aluminium, (c) calcium and (d) molybdenum.

metallic grain boundaries during its passage, and it only remains at the interface, in the furrows thus made.

In contrast, when the secondary phase is viscous and in a small quantity it may remain in the nitride and simultaneously diffuse to the grain boundaries of the molybdenum, performing, after cooling, a good bonding through a complex aluminate in the same way as described for tungsten–aluminium nitride bonding.[1,2] However, contrary to the case of tungsten which must be doped, with lime for instance, only traces of secondary phase in aluminium nitride were sufficient for obtaining the bonding, so their diffusion (for instance by EDAX) could not be followed and hence, an experimental proof of the proposed bonding mechanism can not be found.

How can it be explained that tungsten alone can never be bonded with aluminium nitride[1] when it is easy with molybdenum using the same process? It is assumed that in both cases the impurities inside the metal are located at the grain boundaries and are mainly constituted of metallic oxides. However, firstly, tungsten powder contained less oxygen (1000 ppm) than molybdenum powder (1500 ppm) and, secondly, tungsten oxides are less fusible than molybdenum oxides. Thus the contact and the reaction between the secondary phase of the metal with that of aluminium nitride could be more difficult in the case of tungsten. This hypothesis might justify the difference of behaviour of the two metals.

5 Conclusion

A central role seems to be played by the secondary oxide phase in the molybdenum which is certainly responsible for the bonding with aluminium nitride. Its presence might lead to the formation of a secondary mixed molybdenum–aluminium oxide phase at the ceramic–metal interface, whose diffusion through the grain boundaries of both the materials might justify the bonding after cooling.

The effect of the molybdenum oxide, even in small quantities, on the secondary calcium[6] or yttrium[7] aluminate phase inside the nitride (when added with lime or yttria) lowers the viscosity of the fusible interfacial phase, facilitating even more its expulsion by the effect of pressure.

The results open interesting fields of research into obtaining a good bonding between aluminium nitride and molybdenum at low temperatures: the inevitable presence of oxide in molybdenum may be cleverly turned into an advantage if aluminium nitride is sintered with a convenient additive in a suitable proportion. Then, one may expect the formation of an interfacial secondary phase leading to a good bonding after a short thermal treatment.

References

1. Quériaud, R., Lefort, P. & Billy, M., Compatibility between tungsten and aluminium nitride. In *Proceedings of the 1st European Conference on Advanced Materials and Process, Euromat 89*, Vol. 2, ed. H. E. Exnev. DGM, Oberursel, 1990, p. 903.
2. Quériaud, R., Lefort, P. & Billy, M., The direct bonding between AlN ceramics and CaO-doped tungsten. *J. Eur. Ceram. Soc.*, **8** (1991) 319.
3. Denoirjean-Deriu, P. & Lefort, P., Evolution of the secondary phase AlON in AlN during its bonding with CaO-doped tungsten. *J. Eur. Ceram.*, **11** (1993) 359.
4. Ado, G., Bernache, D., Billy, M., Han, K. S. & Lefort, P., Mécanisme de frittage sous charge du nitrure d'aluminium et de l'oxynitrure AlON. *Rev. Chimie Minérale*, **22** (1985) 473.
5. Sakai, T. & Iwata, M., Effect of oxygen on sintering of aluminium nitride. *J. Mat. Sci.*, **12**(8) (1977) 1659.
6. Yanushkevich, T. M. & Zhukovskii, V. M., Phase diagram of the molybdenum trioxide–calcium oxide system. *Zh. Neorg. Khim.*, **18**(8) (1973) 2234.
7. Antonova, S. S., Shakhoro, I. V. & Phyushchev, V. E., Reaction of samarium, yttrium and erbium oxides with molybdenum trioxide. *Izv. Vyssh. Ucheb. Zaved. Khim. Technol.*, **14**(1) (1971) 17.