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The Direct Bonding Between AlN Ceramics and CaO-doped Tungsten

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Abstract

The bonding of AlN ceramic substrates with tungsten can only be achieved by incorporating CaO into the metallic powder. This oxide improves the sintering process of W and leads to calcium aluminates at the AlN/W interface, whose enrichment in CaO through the metal gives compositions CA, $C_{12}A_7$ and C_3A with decreasing eutectic temperatures and viscosity. This allows a liquid phase to diffuse at firing temperatures. A good adhesion needs: (i) a CaO content threshold to form substantial amounts of liquid phase, which depends on the amount of alumina available from the nitride surface; and (ii) temperatures above 1490°C, a eutectic temperature in the system CaO/WO_3, because the solid Ca tungstate film simultaneously formed near the W/AlN interface may prevent Ca aluminate from diffusing when not displaced towards the metal core by means of a dissolution–precipitation mechanism.

Eine Haftung zwischen einem AlN-Werkstoff und Wolfram kann nur dann erreicht werden, wenn dem Wolframpulver CaO zugegeben wird. Dieses Oxid verbessert das Sinterverhalten von Wolfram und führt an der AlN/W-Grenzfläche zu Calziumaluminaten deren Anreicherung an CaO durch das Metall die Verbindungen CA, $C_{12}A_7$ und C_3A mit abnehmenden eutektischen Temperaturen und Viskositäten ergibt. Dies resultiert bei der Brenntemperatur in einer gut benetzenden flüssigen Phase. Für eine gute Haftung ist folgendes nötig: (i) ein gewisser Mindestanteil CaO, der vom Al_2O_3-Anteil an der Oberfläche des AlN abhängt, um eine ausreichende Menge an Schmelze zu bilden; und (ii) eine Temperatur über 1490°C, was im CaO/WO_3-System einer eutektischen Temperatur entspricht. Dies ist nötig, da der an der W/AlN-Grenzfläche sich spontan bildende $CaWO_4$-Film die weitere Diffusion des Calziumaluminats verhindert, falls er nicht über einen Auflösungs-Ausscheidung-Prozeß zum Metallkern hin verschoben wird.

La métallisation de substrats AlN par le tungstène ne peut être obtenue qu'avec des poudres métalliques additionnées de chaux. Celle-ci améliore le frittage du tungstène et forme à l'interface AlN/W des aluminates de calcium qui s'enrichissent en chaux dans le métal pour donner des composés CA, $C_{12}A_7$ et C_3A de températures eutectiques et de viscosité décroissantes, ce qui permet la diffusion d'une phase liquide. Pour avoir une bonne adhérence, il faut: (i) une teneur en chaux minimale conduisant à une quantité suffisante de phase liquide qui dépend évidemment de l'alumine disponible sur le nitrure; et (ii) opérer au-dessus de 1490°C, température eutectique du système CaO/WO_3. En effet, le tungstate de calcium, simultanément formé à l'interface W/AlN peut former un film protecteur qui empêche l'aluminate de diffuser s'il n'est pas déplacé vers le coeur du metal par un mécanisme de dissolution–précipitation.

1 Introduction

AlN has drawn attention from the electronics industry in the past few years because of its remarkable properties, such as a thermal conductivity over 10 times that of alumina, a high electrical resistivity and low dielectric constant and loss, as well as a thermal expansion coefficient close to that of silicon. All these properties make AlN attractive as a heat spreader in integrated circuits for higher voltage and power electronic devices.

Such an application, however, requires reliable bonding methods with metallic conductors. In the multilayer ceramic technology devoted to alumina, the conventional method consists in metallizing ceramic substrates with a screen-printable thick film of refractory metals such as Mo or W.

As far as aluminium nitride is concerned, tungsten seems to be quite suitable, since it has similar thermal expansion to AlN at any temperature.[1,2] One of the major problems to tackle, however, is the metallization adhesion between AlN and W. It has indeed been shown that there is no diffusion of either W or Al[3,4] and no reaction resulting in a secondary phase[4,5] at the AlN/W interface. In fact, a mechanical interlocking of AlN and W grains at this interface can only explain[3] the adhesion observed after special conditions of cofiring.

So, the bonding between pure tungsten and AlN ceramics bodies cannot be achieved whatever kind of additives (Al_2O_3, Y_2O_3, CaO) may be used for the nitride densification.[4] A potential solution, as shown recently,[4] is to use CaO-doped tungsten which becomes active at firing temperatures and forms a eutectic melt that can help interfacial bonding.

This paper describes the influence of CaO contents in the metal and that of the firing temperature in order to get a better understanding of the adhesion mechanism.

2 Experimental Procedure

The AlN powder from Stark Ltd (grade C) was hot-pressed without any sintering additive at 1800°C under 20 MPa for 90 min in flowing N_2. The fully dense ($d = 3{\cdot}23$) disks so obtained were 4 mm thick and 20 mm in diameter.

The tungsten powder (from Eurotungstene Ltd) was mixed with different amounts of calcium oxide (1 to 13 wt%) and compacted on the AlN disks. These specimens were introduced into an electric furnace through a graphite die coated with a thin layer of BN to avoid any carbon diffusion. They were hot-pressed for 4 h under 20 MPa in an argon flow at temperatures between 1450 and 1650°C.

After cooling, the samples were cut with a diamond saw into parallelepipedic bars for characterization, which allowed appreciation of the adhesion strength: the metal to ceramic bonding was considered as achieved when undamaged during cutting. Cross-sections were then polished for scanning electron microscopy (SEM). Energy dispersion X-ray (EDX) analysis of the metal/ceramic interface and of rectangular bands ($4 \times 125\,\mu m$) parallel to this interface gave access to Ca, Al or W elemental concentrations. These were then plotted as a function of the distance from the interface to determine elemental profiles at each temperature. Cross-sectional X-ray analysis was also performed.

3 Results

3.1 Influence of CaO contents

Tungsten powder mixed with CaO, in amounts varying from 1 to 13 wt%, were cold-pressed in a floating steel die using a hydraulic press. Compacts were then hot-pressed at 1600°C, as described in Section 2, on dense disks of 'pure' AlN first obtained at 1800°C by hot-pressing the as-received powder including some alumina as an impurity.

In all cases a ceramic-to-metal bonding occurred, but when tungsten contained less than 3 wt% CaO the adhesion strength was not strong enough to sustain the mechanical strains developed through the cutting. Furthermore, the densification of the metal layer increased with CaO content, especially between 1 and 3 wt%, as shown in Table 1, where relative densities of the W/CaO 'composites' have been calculated assuming that no reaction occurred between tungsten and lime.

When no successful bond was achieved (for CaO contents below 3 wt%), X-ray analysis of both sides of metal/ceramic interface showed the formation of the aluminate CA_2, i.e. $CaO.2Al_2O_3$, on the nitride surface and nothing but W on the metal surface.

In the case of CaO additives with concentrations > 3 wt%, the polished sections showed (Fig. 1) two different areas in tungsten (lower part of the micrographs). The samples shown in Fig. 1, whose thickness is about 50 μm independently of CaO contents (compare Fig. 1(a) and 1(b)), displayed

Table 1. Density of the metal layer after hot-pressing (1600°C, 4 h, 20 MPa) as a function of CaO contents in tungsten

	CaO (wt%) in W						
	1	*3*	*5*	*7*	*9*	*11*	*13*
Density (exp.)	17·05	16·35	15·20	14·10	13·25	12·30	11·70
Relative density, % (calc.)	92·5	97	98	98	98·5	98	99

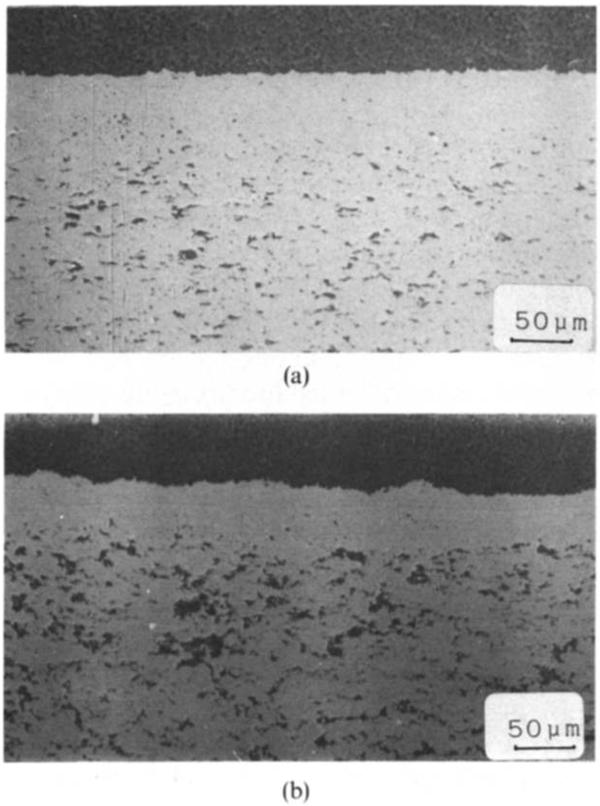


Fig. 1. SEM micrographs of polished cross-sections for specimens hot-pressed 4 h at 1600°C with CaO-doped tungsten: (a) 5 wt% and (b) 13 wt%.

a lot of small spots and large dark areas. As far as aluminium nitride is concerned, there is no apparent change in microstructure with increasing amounts of CaO added to tungsten.

A more precise observation of these spots by microanalysis allowed their identification. Near the W/AlN interface (X_1, Fig. 2(a)) Al, Ca and O elements are found, with very small amounts of W (Fig. 2(b)). This is a calcium diffusion area as will be shown later. The larger spots of the second zone towards the metal core (X_2, Fig. 2(a)) contain only unreacted CaO (Fig. 2(c)).

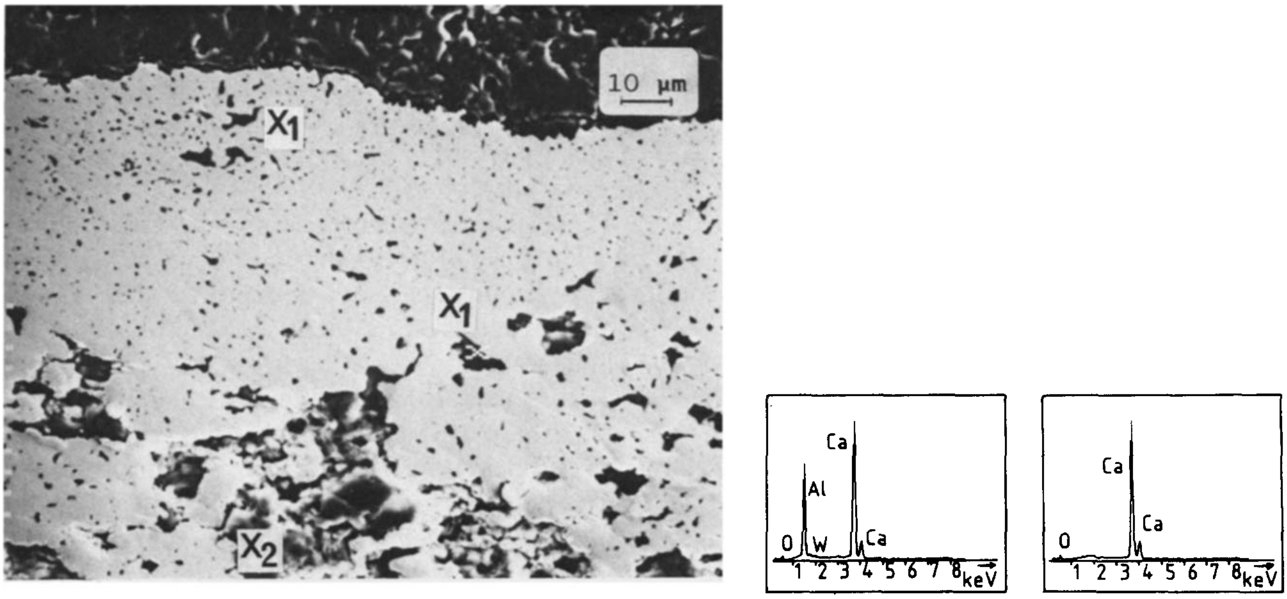
3.2 Influence of temperature

Green bodies of tungsten containing CaO (13 wt%) were hot-pressed under 20 MPa on dense AlN substrates for 4 h at different temperatures ranging from 1400 to 1650°C.

Adhesion was observed in all cases after cooling but the bonding obtained at temperatures lower than 1500°C was easily ruptured during cutting. Then X-ray analysis of both sides of the interface detected the presence of the calcium aluminate $C_{12}A_7$ at 1450°C and that of CA at 1500°C.

A real bonding occurred from 1500°C onwards, as shown in Fig. 3, where the tungsten duplex microstructure can be seen on cross-sectional micrographs. The fine homogeneous layer close to the interface grows thicker with increasing temperature, especially between 1500 and 1550°C. This layer, which allows the direct bonding between CaO-doped tungsten and aluminium nitride, corresponds to a zone of low calcium content, as shown in Fig. 4 by the concentration profiles.

It is worth noting that this zone is followed towards the metal core by another one where Ca concentration becomes far higher than that originally introduced in tungsten before hot-pressing (Fig. 4). Such a phenomenon whose intensity roughly decreases with increasing temperatures vanishes at 1650°C; it looks as if calcium has been pulled back



(a) (b) (c)

Fig. 2. (a) Cross-sectional SEM image; EDX analysis of (b) the X_1 and (c) the X_2 spots.

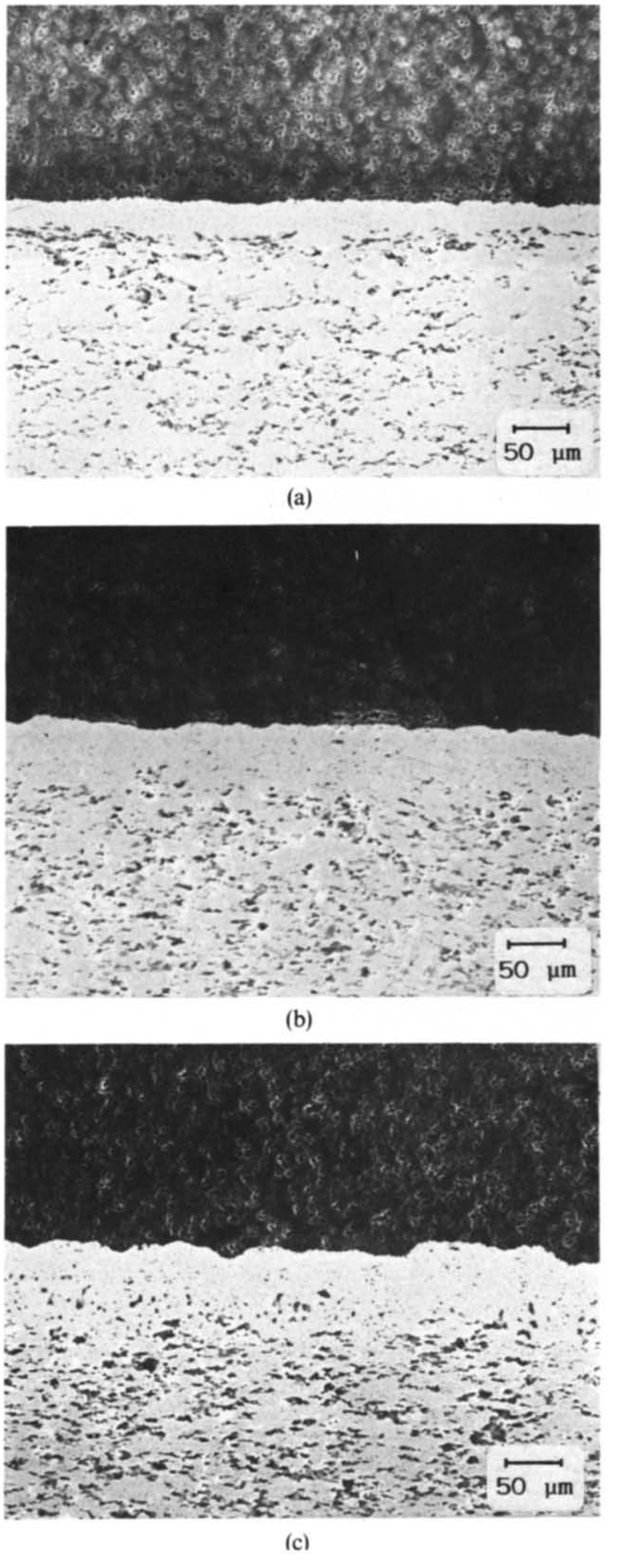


Fig. 3. SEM of polished cross-sections of CaO-doped W (13 wt%) hot-pressed (20 MPa, 4 h) on dense AlN substrate at temperatures (a) 1500°C; (b) 1550°C; (c) 1650°C.

from the W/AlN interface. However, at the same time, the concentration profiles show that small amounts of Ca have also diffused through AlN as far as a depth of 50–60 μm. Again, it clearly appears from Fig. 4 that the Ca depletion zone exceeds the enrichment area at each temperature but 1500°C. So, there are some calcium losses during hot-pressing, which is consistent with the extrusion of a liquid phase along the graphite dies as observed after cooling.

As far as aluminium is concerned, it also diffuses in small quantities through tungsten at distances increasing with temperature but not exceeding 60–65 μm from the interface in the most favourable conditions (1650°C). Its concentration in tungsten has been correlated to that of Ca at any temperature and plotted against the distance from the interface in Fig. 5. It can be seen that the diffusing phase corresponds to a calcium aluminate whose composition is enriched with CaO from CA, just by the W/AlN interface, to composition limit C_3A.

4 Discussion

These results clearly show that the bonding is achieved by fulfilling experimental conditions allowing the formation of a liquid calcium aluminate. Its diffusion through tungsten, which is partly responsible for the bonding, leads to a thin calcium depletion zone (about 50 μm deep) close to the W/AlN interface.

The formation of calcium aluminate is not surprising as CaO can easily react with traces of alumina on the nitride surface or with the γ-AlON phase present at superficial grain boundaries.[6] It should be recollected that AlN was hot-pressed without any other additive than alumina, which is practically unavoidable as an impurity in starting nitride powders. So, because of a high alumina content at the W/AlN interface, the aluminate primarily formed must be CA_6 or CA_2, as checked by X-ray analysis and illustrated by the equilibrium diagram of the CaO/Al_2O_3 system (Fig. 6). Such phases are crystalline in nature at working temperatures (≤ 1650°C).

These aluminates produce a compositional gradient in the nitride so that calcium is allowed to diffuse through the grain boundaries by means of cation vacancies of the AlON phase.[8] And since this volume diffusion is rather slow, AlN eventually contains just a little bit of calcium, as observed.

On the opposite side of the interface, the situation is quite different because further reactions can take place involving extra CaO in tungsten and aluminate(s) located at this interface. It results in the formation of Ca-enriched aluminates: CA, $C_{12}A_7$, then C_3A, as illustrated in Fig. 5. According to the phase diagram of the CaO/Al_2O_3 system (Fig. 6),

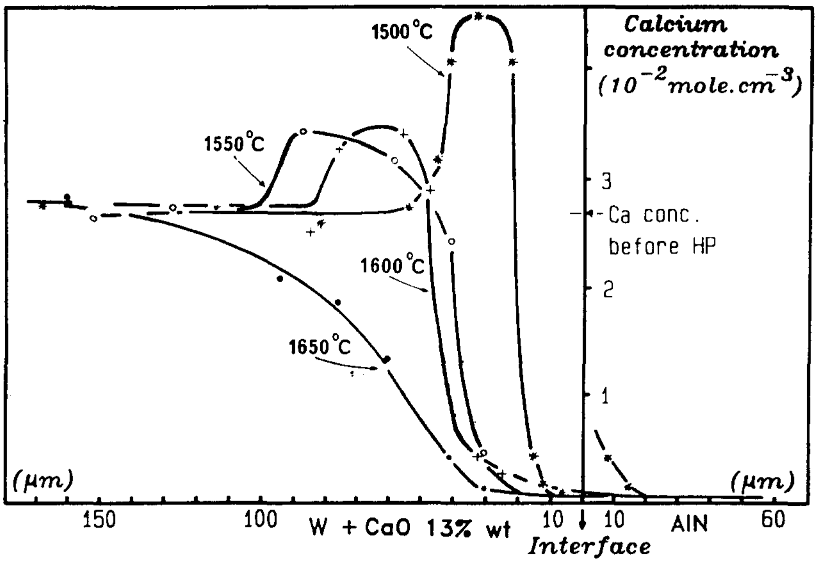


Fig. 4. Ca concentration profiles near the W + CaO 13 wt%/AlN interface at different temperatures.

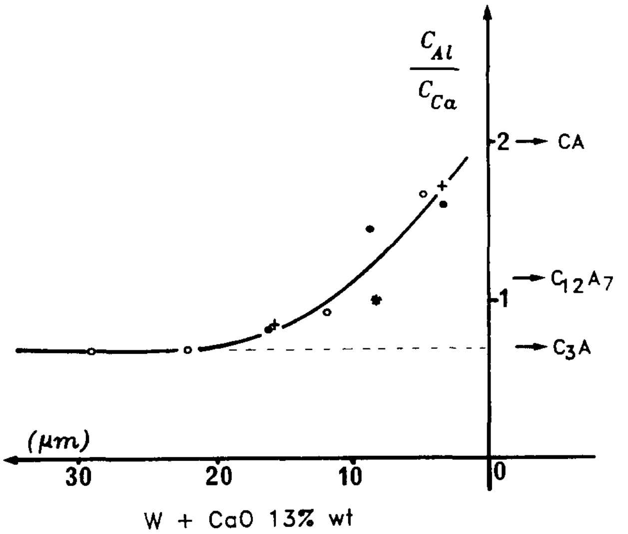


Fig. 5. Al/Ca atomic ratios in tungsten as a function of the distance from the interface. ●, 1500°C; +, 1550°C; *, 1600°C; ○, 1650°C.

this compositional shift promotes a liquid phase by lowering eutectic temperatures, so that diffusion can take place through tungsten when suitable conditions of temperature are achieved.

At this point, it should be noted that CaO must be present in sufficient amounts in tungsten to form the diffusing Ca-enriched aluminates, thus explaining the observed limit in CaO content (3 wt%) necessary to achieve the bonding. However, it is easy to predict that this limit, which depends on the amount of the reacting calcium aluminate initially formed at the W/AlN interface, will vary with the oxygen impurity levels of the nitride surface. Purer AlN would obviously need less CaO to react and achieve the bonding.

As suggested by the phase diagram (Fig. 6), the liquid-phase diffusion and subsequent bonding should be possible from temperatures above 1400°C

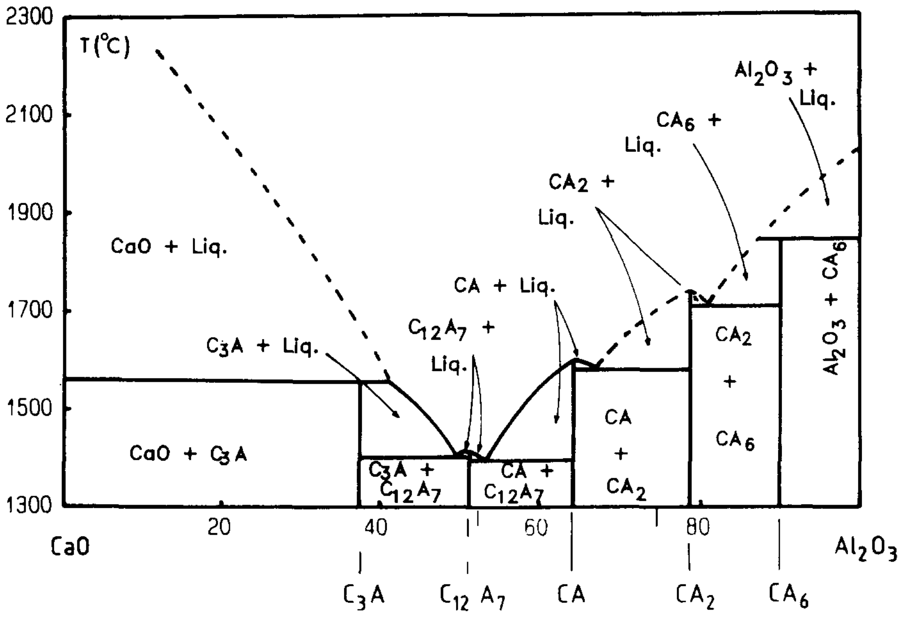


Fig. 6. Phase diagram for the pseudo-binary system CaO/Al_2O_3 (after Ref. 7).

or so. In fact, the observed critical temperature for achieving the bonding was about 100°C more. Many other observations are also in contradiction with a single model of calcium aluminate diffusion:

(i) First is the Ca-enriched area observed on concentration profiles (Fig. 4), which obviously results from precipitation of a liquid phase containing calcium.
(ii) The aluminium diffusion front never reaches the calcium-enriched region at any temperature.
(iii) The extent of the Ca precipitation or Ca depletion areas is incompatible with the low volume fraction of C_3A carried out by liquid diffusion.

For all those reasons, it must be concluded that precipitation of the Ca-containing liquid phase does result from a tungstate and not only from an aluminate. The presence of tungstate as an impurity within the metal is confirmed by the fact that CaO-enhanced densification of tungsten, as pointed out earlier; the reason for this can be understood if it is borne in mind that metal powders have been milled with CaO before being hot-pressed.

Considering now the phase diagram for the CaO/WO_3 system (Fig. 7), it appears that there is no liquid phase allowing migration when extra CaO is present in the metal core. But the situation changes near to the interface where CaO is consumed during reaction with calcium aluminates. This gives rise to compositional shifts along the CaO/WO_3 basic line and to the formation of a tungstate liquid phase (Fig. 7) for $T \geq 1490°C$. It is precisely the approximate critical temperature observed for achieving the bonding. As a result, the outward migration of calcium may be interpreted as follows.

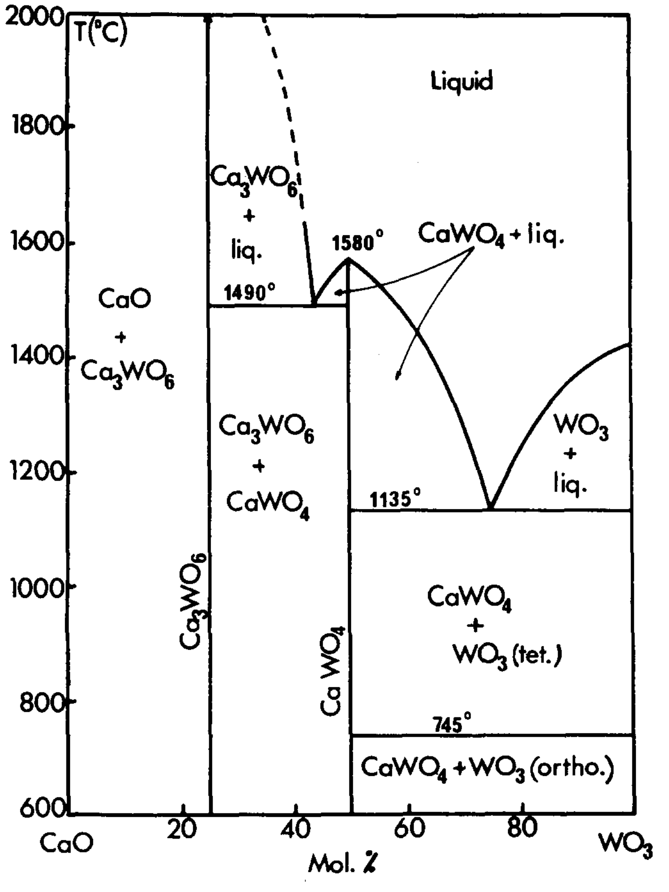


Fig. 7. The CaO/WO_3 system.[9]

At the very beginning of the HP treatment, after a thin layer of CA_2 (or CA_6) has been formed at the W/AlN interface, solid tungstate in the form of Ca_3WO_6 (or C_3W) coexists with excess CaO throughout the tungsten, according to the phase diagram of Fig. 7. During the subsequent formation of Ca-enriched aluminates and of their corresponding liquid phases, illustrated in Fig. 8, CaO is no longer in excess. So, another liquid phase, now containing the calcium tungstate C_3W, can be formed near the interface region. But it precipitates farther on in contact with unreacted CaO (Fig. 8). And, since this phenomenon is repeated again and again as the diffusion of Ca-enriched aluminates proceeds outwards, C_3W is running as a self-refining pure zone in front of the aluminate migration band, the rate of movement being related to that of dissolution of CaO into the liquid aluminate.

Such a mechanism, which results in a calcium peak on the concentration profile, has certain similarities to chromatographic separations in the specific case of displacement development: the aluminate plays the role of a mobile phase having more affinity than the tungstate for the CaO solid sites.

This model explains that the C_3W dissolution precipitation process cannot occur for temperatures lower than 1490°C, the nearest eutectic temperature in the CaO/WO_3 system (Fig. 7). At these temperatures, moreover, the C_3A containing liquid-phase precipitates (Fig. 6), so that diffusion remains located

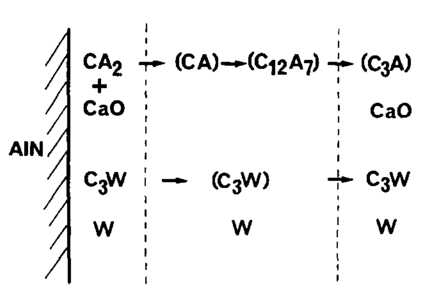


Fig. 8. A schematic diagram showing the evolution of the calcium compounds in tungsten. Brackets are representative of existing liquid phases.

at a few microns from the interface. No calcium depletion is then observed and the bonding between W and AlN is not successful.

At 1500°C, dissolution of C_3W becomes effective, but the extent of the calcium depletion zone remains limited, since the C_3A containing liquid still precipitates.

Such a limitation will no longer occur at 1550°C and over (Fig. 6). Then, the increased fluidity of the liquid phases and their subsequent losses by extrusion under compressive stresses lead to more extended calcium depletion zones. These losses, which result from a competitive process, explain that the Ca peak observed on concentration profiles decreases with increasing temperatures and even disappears at 1650°C when extrusion of the liquid phase becomes predominant.

5 Conclusions

By incorporating CaO into tungsten, a direct bonding between W and AlN ceramics could be achieved because of the intermediate formation of calcium aluminates, such as CA_2, resulting from the reaction between CaO and alumina on the nitride surface. This aluminate allows calcium to migrate through grain boundaries of the nitride according to a volume diffusion process.

The role of CaO in tungsten is to further react with the aluminate previously formed at the interface and to produce calcium-enriched aluminates with lower eutectic temperatures which provide a liquid phase allowing migration. A limited content of CaO is thus necessary to form substantial amounts of diffusing species and thus to achieve the bonding. This limit, however, obviously depends on the oxygen amount at the nitride surface and varies with the degree of purity of AlN.

It has also been shown that temperatures over 1490°C, the nearest eutectic temperature in the CaO/WO_3 system, are needed for promoting a good adhesion. In such conditions, indeed, the solid film of calcium tungstate, which is presumably formed near the W/AlN interface, cannot prevent the liquid calcium aluminate from diffusing as it moves toward the metal core according to a dissolution–precipitation mechanism.

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