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AlN Dispersed Reinforced Aluminum Composite

C. Troadec,[a] P. Goeuriot,[b] P. Verdier,[b] Y. Laurent,[b] J. Vicens,[c] G. Boitier,[c] J. L. Chermant[c] and B. L. Mordike[c]

[a]Département Céramiques Spéciales, Ecole des Mines, 158 cours Fauriel, 42023 Saint-Etienne Cedex 2, France
[b]Laboratoire Verres et Céramiques, URA CNRS 1496, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes, France
[c]LERMAT, URA CNRS 1317, ISMRA, 6 Bd du Maréchal Juin, 14050 Caen Cedex, France

Abstract

In this paper the first results are presented on nitriding of aluminium powder and the fabrication of Al-AlN composites after milling and hot-pressing. Nitriding appears to follow a complex process. High energetic milling of these powders is an important factor in obtaining homogeneous materials with AlN nanometric grains. TEM and EDX nanoanalyses have shown that Al grains are surrounded by AlN nanocrystals, with some Al_2O_3 needles and AlON crystals. Physical properties — thermal expansion, thermal conductivity, electrical conductivity, hardness, Young's modulus, fracture strength — of these composites change with the AlN content, and the values for 0 vol.% AlN (process powders) always correspond to higher or lower values than for pure Al (unprocessed powders), reflecting the fact that processing introduces impurities. A comparison of composites fabricated from composite powders and from a mixture of Al-AlN commercially available powders is interesting. Generally these new composites exhibit better properties than those for Al-SiC or Al-Al_2O_3 composites with an apparently similar reinforcement content. © 1997 Elsevier Science Limited.

Résumé

Dans cet article, nous présentons les premiers résultats d'une étude portant sur la nitruration de poudres d'aluminium et l'obtention de composites Al-AlN par frittage sous charge. La nitruration de poudres d'aluminium paraît suivre une évolution complexe. Le broyage hautement énergétique de ces poudres est un facteur déterminant pour l'obtention de matériaux homogènes avec des grains nanométriques d'AlN. Les études en MET et nanoanalyse EDX ont révélé la microstructure de ces matériaux: présence de grains d'aluminium entourés de nanocristaux d'AlN, avec des aiguilles d'Al_2O_3 et quelques cristaux d'AlON. Les propriétés physiques:dilatation thermique, conductivité thermique et électrique, et mécaniques: dureté, module d'Young, contrainte à la rupture, de ces matériaux évoluent avec la teneur en AlN et les valeurs obtenues pour 0% d'AlN correspondent toujours à des valeurs supérieures ou inférieures à celles de l'aluminium pur, mettant en évidence l'introduction d'impuretés par ce procédé. La comparaison des propriétés de ces composites avec ceux élaborés à partir de mélanges de poudres industrielles Al+AlN est intéressante. Dans l'ensemble ces nouveaux composites ont, à teneur en renfort similaire, des propriétés superiéures ou équivalentes à celles des matériaux Al-SiC ou Al-Al_2O_3.

Zusammenfassung

In dieser Arbeit werden erste Ergebnisse über Nitrieren von Aluminiumpulver und die Herstellung von Al-AlN-Verbundwerkstoffen nach dem Mahlen und Heiβpressen vorgestellt. Das Nitrieren ist offensichtlich ein komplexer Prozeβ und energisches Mahlen ist ein wichtiger Vorgang, wenn homogene Werkstoffe mit nanoskaligen AlN-Körnern erhalten werden sollen. TEM- und EDX-Nanoanalyse haben gezeigt, daβ die Al-Körner von AlN-Nanokristallen mit einigen Al_2O_3-Nadeln und AlON-Kristallen umgeben sind. Die Eigenschaen thermische Ausdehnung, thermische Leitfähigkeit, Härte, E-Modul, Bruchfestigkeit-Zähigkeit dieser Verbundwerkstoffe ändern sich mit dem AlN-Gehalt, wobei die Werte für 0% AlN durch Verunreinigungen geändert worden sind und nicht mehr den Werten des reinen Aluminiums entsprechen. Ein Vergleich der Verbundwerkstoffe, hergestellt mit dem Verbundpulver (Rennes) und gemischten Komponenten ist interessant. Im Allgemeinen zeigen die neuen Verbundwerkstoffe bessere Eigenschaen als Al-SiC oder Al-Al_2O_3 Verbundwerkstoffe mit gleichem Anteil an Verstärkung.

1 Introduction

Direct nitriding of aluminium by nitrogen at low temperatures offers the possibility of obtaining Al-AlN composite powders at a reasonable price.[1] The physico-chemical, mechanical and thermal properties of aluminium nitride suggest that it would be a suitable reinforcement material for aluminium. However, because Al does not wet AlN and because of AlN hydrolysis has resulted in little interest has been shown in this system. Imai *et al.*,[2,3] have shown that Al-AlN composites prepared by mixing powders possess superplastic properties which could be useful when forming. The aim of this study is to define optimum conditions of preparation of this new class of metal matrix composites (MMC) and to determine their main properties in order to correlate these properties with the microstructure and the method of production.

2 Production of the Al-AlN Composites

The fabrication, milling and consolidation of the Al-AlN powder will be presented in the following sections.

2.1 Preparation of composite Al-AlN powder

Nitriding of pure aluminium in gaseous nitrogen to form AlN powder is possible but the conversion is incomplete.[4-7] If certain salts,[1] such as $CaCO_3$, are employed, the reaction reaches completion. A differential thermal analysis shows that the reaction is vigorous (Fig. 1) at temperatures depending directly on the homogeneity of the mix Al + $CaCO_3$, the reaction between aluminium and nitrogen being very exothermal.[8] The role of calcium carbonate remains obscure: the formation of an aluminate which removes the protective oxide layer has been suggested.[9] At least the presence of calcium or magnesium[7] catalyses the nitriding reaction by forming an unstable intermediate compound such as Ca_3N_2.

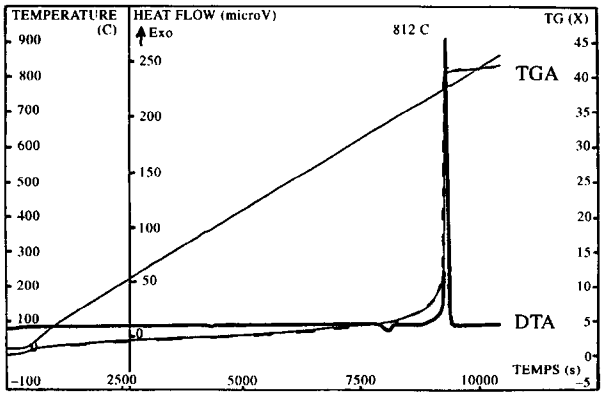

Fig. 1. DTA and TGA curves during nitriding of the aluminium powder.

The production of partially nitrided powder in sufficient quantity requires the use of a quasi-continuous process such as rotary furnace; the temperature of the furnace and the flow rate of the powder affects the fraction converted. A mixture of fine powders and aggregates was obtained. In any event it was not possible to manufacture powder with a predetermined nitrogen content. Powders with 8–30 vol.% of AlN have been prepared.All these products were crushed in a shuttle mill for 5 min and sieved at 200 μm.

2.2 Milling and co-milling of the powders

Two types of powder were milled in a planetary ball mill with steel balls (100 C6) in inert atmosphere. The first one corresponds to a 'composite' powder produced as described previously, the other to a mixture of commercially available powders (called 'mixed' powders): Al (350 TV from Pechiney; Al > 99·7; Fe < 0·2; Si < 0·12; Cu < 0·01; spherical grains 15 μm) and AlN (grade B from Starck, 3 μm). The milling time varied from 15 to 330 min. (Table 1)—the liquid phase sintering is forbidden—gives more information .

An addition of stearic acid is necessary to limit powder sticking to the wall of the jar and to the

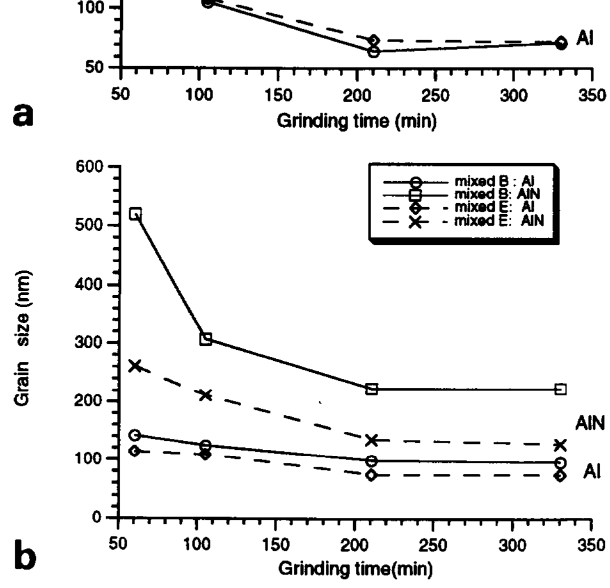

Fig. 2. Change in the mean size of the nanocrystals as a function of the grinding time for (a) 'composite' powder and (b) 'mixed' powder.

Table 1. The studied compositions

Names	*'Composite' powders Al-AlN*	*'Mixed' commercial powders Al + AlN*
A 'crushed'	Shuttle milled after nitridation	—
B	—	Al + 8 vol% AlN (15–330 min planetary ball milled)
C	Al-8 vol% AlN (shuttle milled + 15–330 min planetary ball milled)	—
D	Al-26vol% AlN (shuttle milled + 15–330 min planetary ball milled)	—
E	—	Al + 26 vol% AlN (15–330 min planetary ball milled)
F	Al + 18 vol% AlN (15–330 min planetary ball milled)	—

Table 2. Values of microhardness and standard deviation as a function of grinding time

Materials from 'composite' powders	*Grinding time (min)*	*Microhardness (HV_{200})*	*Standard deviation*
F = 18 vol.% AlN	0	113	67
	60	157	24
	105	150	19
	330	168	9

balls. At the beginning of milling, flakes are formed which subsequently agglomerate in the case of mixed powders. The composite powder crumbles resulting in an advantage for this type of powder.

The change in the size of the coherent areas is accompanied by broadening of the X-ray diffraction peaks (200) for Al and (100) for AlN. From that broadening, using the Warren-Averbach method[10] and the specific Dosophatex equipment (trade mark),[11] it is possible to calculate the size of the nanocrystals. After 210 min, continuation of milling appears ineffective for both powders (Fig. 2). The nitride content has no effect on the milling behaviour of the 'composite' powders, but auto milling of AlN takes place for 'mixed' powders with a ceramic content of 26 vol.%.

2.3 Forming the material

The densification of the material was carried out by sintering under load according to the cycle shown in Fig. 3. Sintering is carried out under vacuum (10^{-3} torr). The optimum pressure was found to be 120 MPa and was maintained during cooling (Fig. 3). Figure 4 shows the change in shrinkage as a function of the temperature for pure aluminium and a milled composite (D) for 15 or 105 min. A significant increase in deformation occurs between 525 and 615°C, the lower temperature corresponding to the powder was milled for the longer period. The homogeneity produced by milling can be quantified, for example, by the standard deviation in hardness measurements on sintered samples (Table 2).

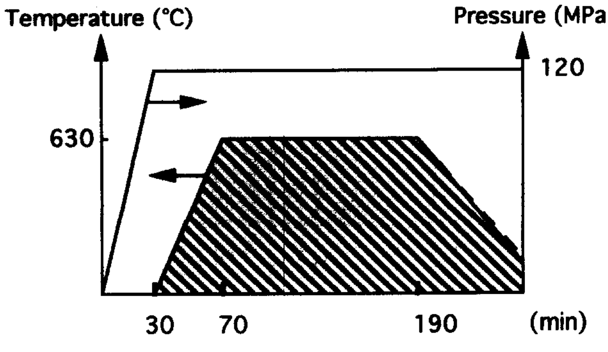

Fig. 3. Sintering cycle for Al-AlN composites.

The grain size of bulk materials versus grinding time is presented in Fig. 5. The AlN dispersion limits the grain growth of the aluminum matrix. For higher fraction of AlN, 'composite' materials have a smaller aluminum grain size than 'mixed' materials.

In Fig. 6 some micrographs are presented showing materials fabricated over time.The homogeneity increases with grinding time as shown previously by hardness measurements.

3 Results

Some results concerning chemical, microstructural characterization and physical properties will be

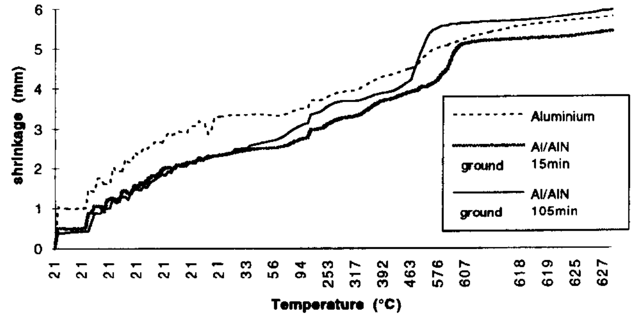

Fig. 4. Shrinkage curve for pure Al powder, and 'composite' Al-AlN powder after 15 and 105 min grinding time (the temperature scale is not linear, the beginning is the pressure effect (see Fig. 3)).

presented, all the characterizations of the new metal matrix composite are described in the thesis of Troadec.[8]

3.1 Chemical and microstructural characterization of materials

Nitrogen and oxygen were analysed using a Leco analyser in both the powder and chips of sintered material. The results show that the oxygen content of the powder does not depend on the degree of nitriding and that sintered 'composite' powders contain more oxygen than sintered 'mixed' powders and that milling has only a limited effect on oxidation.

The mean grain size was measured using X-ray diffraction line broadening. It was found that after 105 min milling, no further change in the grain size of the Al or AlN occurred. This was true for both the composite and mixed material and for all AlN contents.

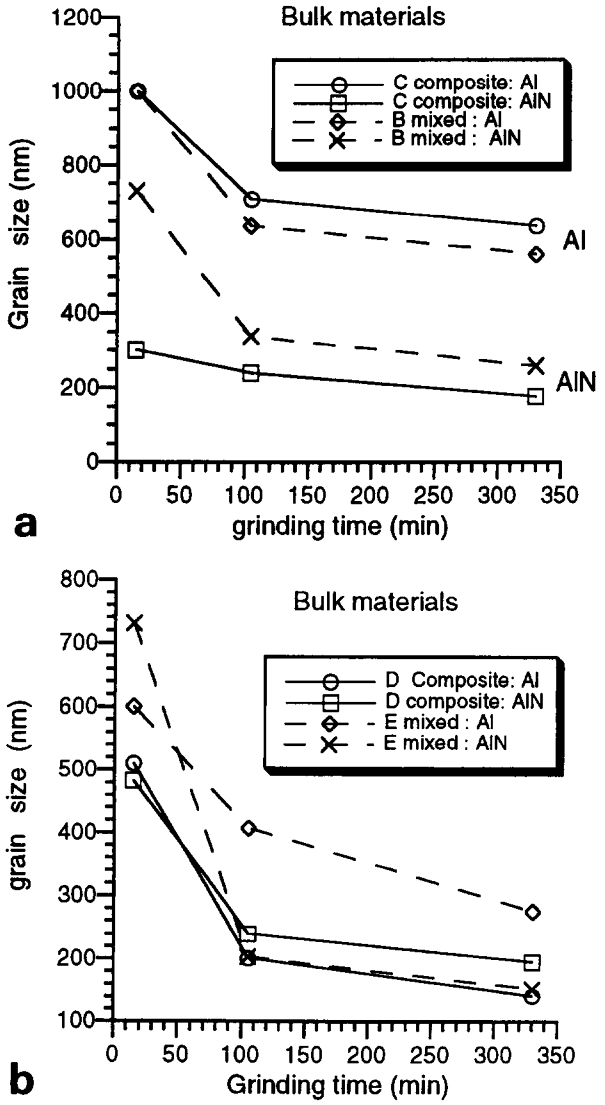

Fig. 5. Change in the mean grain size of the nanocrystals as a function of grinding time for bulk composites with (a) 8 vol.% and (b) 26 vol% AlN made from 'composite' (C,D) or 'mixed' powders (B,E).

For the TEM studies, Al-AlN powders, wetted by alcohol, were applied to carbon coated copper grids. Sintered samples obtained by hot-pressing of 'composite' powders were also prepared for TEM studies. Thin slices were cut with a diamond saw and polished to a thickness of 80 μm. Disc-shaped samples (3 mm in diameter) were mechanically ground and dimpled to 10 μm thickness before

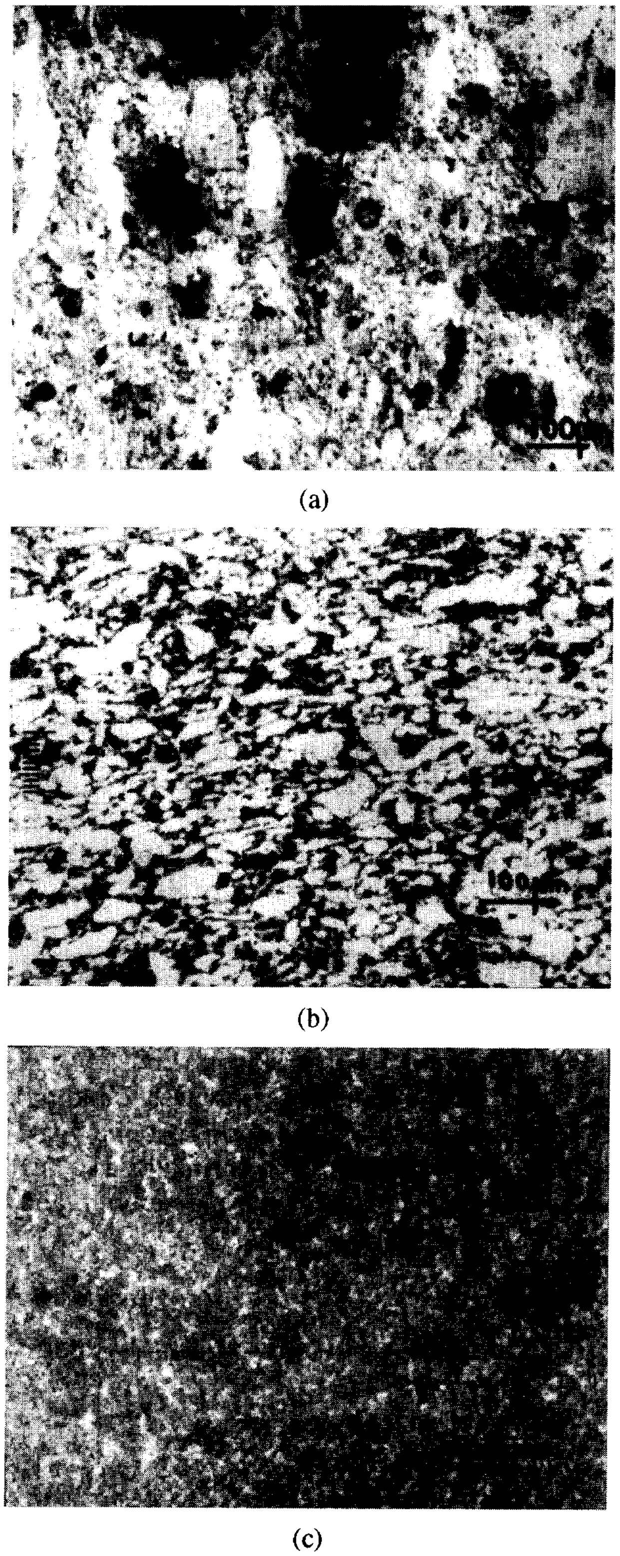

Fig. 6. Micrographs showing Al-AlN composites made from (a) crushed powder, (b) 'mixed' powder and (c) 'composite' powder after 120 min milling time.

thinning by ion-milling (Ar^+, 5 kV). During the ion-thinning process, continuous cooling of the sample was maintained by liquid nitrogen to avoid any degradation. The microstructures were observed using a Jeol 200CX electron microscope operating at 200 kV. A Topcon EM002B electron microscope equipped with a Kevex EDX microanalyser and operating at 200 kV (Cs = 0·4 mm) was used for HREM and microanalysis studies. For all sintered samples, only two main parameters were varied: the AlN content (8 and 26 vol.% AlN) and the grinding time (15, 105 and 330 min). TEM observations were first conducted on the powders and then on the sintered samples.

The as-produced partially nitrided aluminium powders contained aluminium oxide (Al_2O_3) and oxynitride (AlON) whiskers up to 5 μm long, such whiskers were previously observed by SEM in as-produced powders.[8] The grinding process (15 to 330 min) leads to agglomerates down to 500 nm, AlN crystals (100 nm) were observed within these agglomerates. However the aluminium phase was difficult to identify among the AlN grains.

Regardless of aluminium content and grinding time, every sample exhibits common features. The microstructure appears heterogeneous, consisting of both dense polycrystalline areas and porous zones. The microstructure of a sintered sample (26 vol.% AlN, 330 min) is shown in Fig. 7.

The dark areas are composed mainly of aluminium grains, whereas the bright areas contain nanometer-scale aluminium nitride grains and microporosity. The microporosity does not appear to be a consequence of the thinning procedure used. Throughout the sample, Al_2O_3 and AlON needles were found in dark as well as in bright zones. These needles were randomly dispersed within the aluminium grains (dense zones) or pockets (porous areas). The presence of these oxide or oxynitride phases is not surprising knowing the powder production process.During nitridation, milling and sintering oxidation cannot be prevented so aluminum oxide and oxynitride may be present in the samples. A detailed view of a porous zone is presented in Fig. 8. Alumina needles of 250 nm and aluminium nitride grains (up to 100 nm) can be seen.

The composition of both phases has been determined by nanoprobe analysis. An HREM micrograph of AlN grains is presented in Fig. 9.

An EDX spectrum of the layer surrounding the AlN grain (zone marked with an arrow in Fig. 9) reveals the presence of a small amount of calcium used as an additive ($CaCO_3$) during the nitridation of the aluminium powder and some impurities not yet identified.

3.1.1. *Role of aluminium nitride content*

Irrespective of the grinding time, the major influence of AlN content is limited exclusively to the distribution of AlN grains within the dense areas. AlN grains (100 nm) were observed in aluminium grains or aluminium grain boundaries only for the highest AlN content studied (i.e. 26 vol.%) as shown below.

3.1.2. *Influence of the grinding time*

For a grinding time of 330 min, the diameter of the porous zones in the sintered samples is about 2 μm. Large aluminium grains in the dense areas are ~1

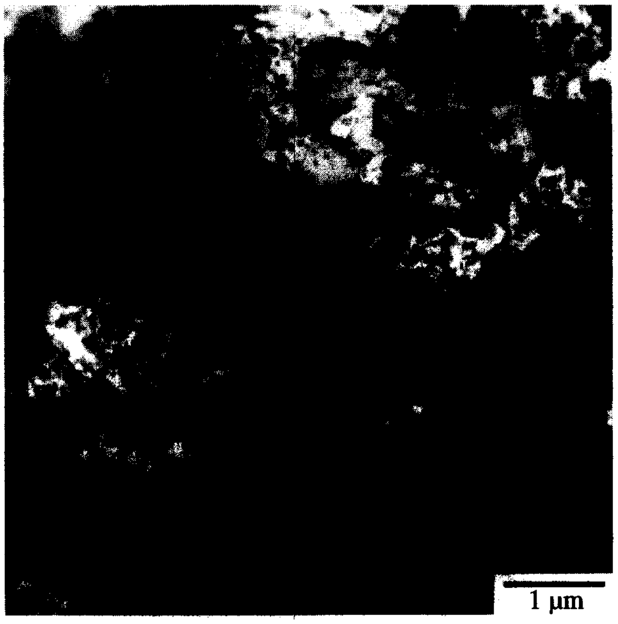

Fig. 7. Microstructure of a sintered sample (26 vol.% AlN, 330 min) showing dense (dark) and porous (bright) areas (TEM micrograph).

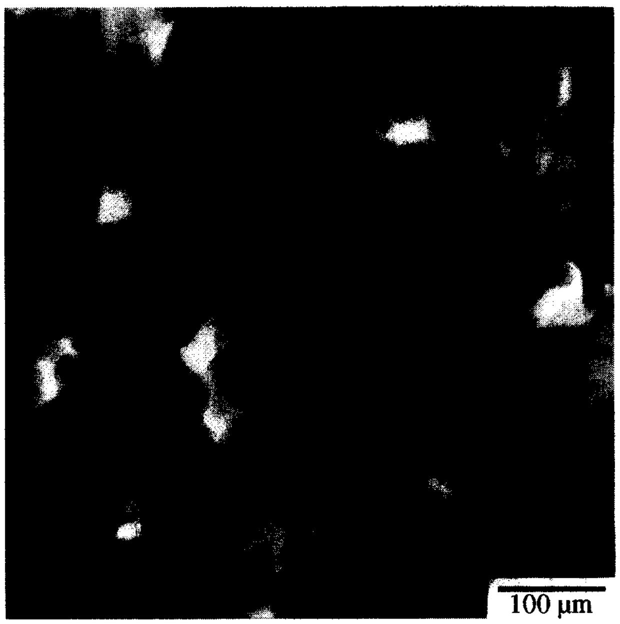

Fig. 8. Alumina needles and aluminium nitride grains within a porous zone (26 vol.% AlN, 330 min).

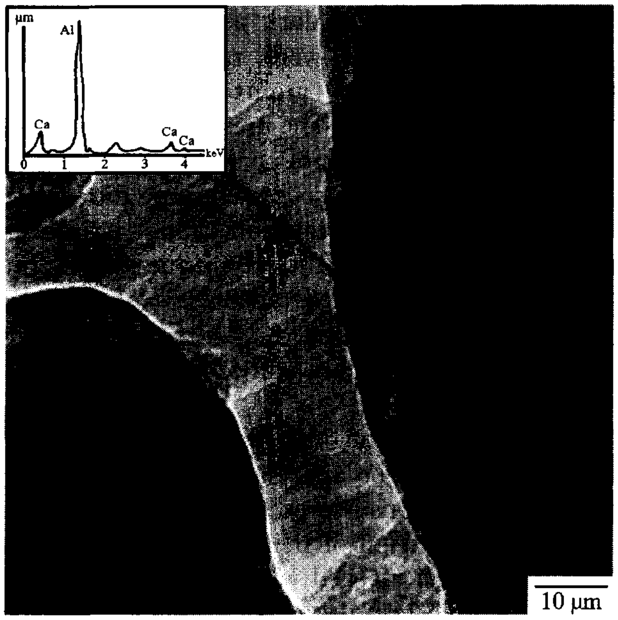

Fig. 9. HREM micrograph of AlN grains (26 vol.% AlN, 105 min) with EDX spectrum taken in the surrounding layer (arrowed on the picture of a AlN grain).

or 2 μm with Al_2O_3 or AlON needles up to 400 nm long. For the highest AlN content (i.e. 26 vol. %), a particular microstructure is obtained (Fig. 10). Large aluminium grains (marked (a) on the micrograph) enclose AlN grains (b) and alumina needles (c). Such grains located at the central part of dense areas are surrounded by a layer (~μm thick) of nanometric (~100 nm) AlN grains (d). The external part of this layer is in contact with the porous zone.

For a grinding time of 105 min, the diameter of the porous zones increases to 4 μm. For 26 vol.% AlN content, AlN grains are observed inside aluminium grains and at the aluminium grain boundaries in the dense zone, but the AlN layer described above is no longer observed.

After only a 15 min grinding time, the microstructure of the sintered specimens is much different. The porous areas are rarely observed. When the foil plane contains the compressive sintering stress direction, AlN grains (100 nm) become aligned in successive parallel bands (2 μm wide) alternative with aluminium areas (Fig. 11). This particular layered microstructure has already been observed in SEM on the aluminium partially nitrided powder.

3.1.3. Comparison between samples made from 'composite' and 'mixed' powders

For the same grinding time and AlN content, samples prepared from 'mixed' powders are more heterogeneous. Porous zones are larger and no alumina needles were detected.

3.2 Physical and mechanical properties of Al-AlN composites

3.2.1. Coefficient of thermal expansion

The materials studied consist in reality of three phases: aluminium (matrix), aluminium nitride (reinforcement) and aluminium oxide. The experimental results are comparable with those predicted by the rule of mixtures of Turner[12] and Levin,[13] when they are extended to three phases (Al, AlN, Al_2O_3), (Fig. 12). The change of the coefficient of thermal expansion with the AlN content agrees with the prediction of the model by Levin for sintered

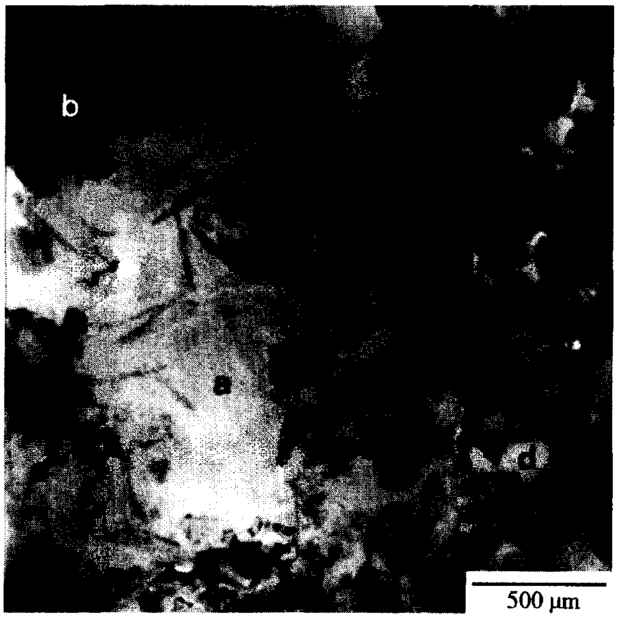

Fig. 10. Microstructure of 26 vol.% AlN composite milled for 330 min (the compressive stress direction is normal to the foil plane).

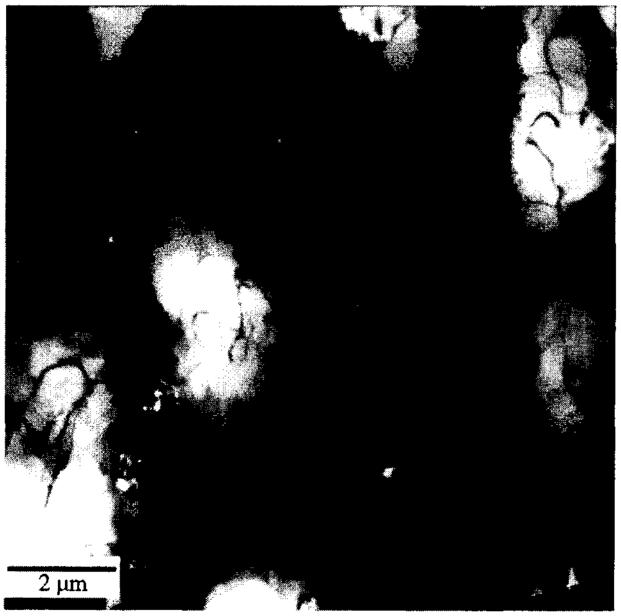

Fig. 11. Layered microstructure observed after a 15 min grinding time (26 vol.% AlN).

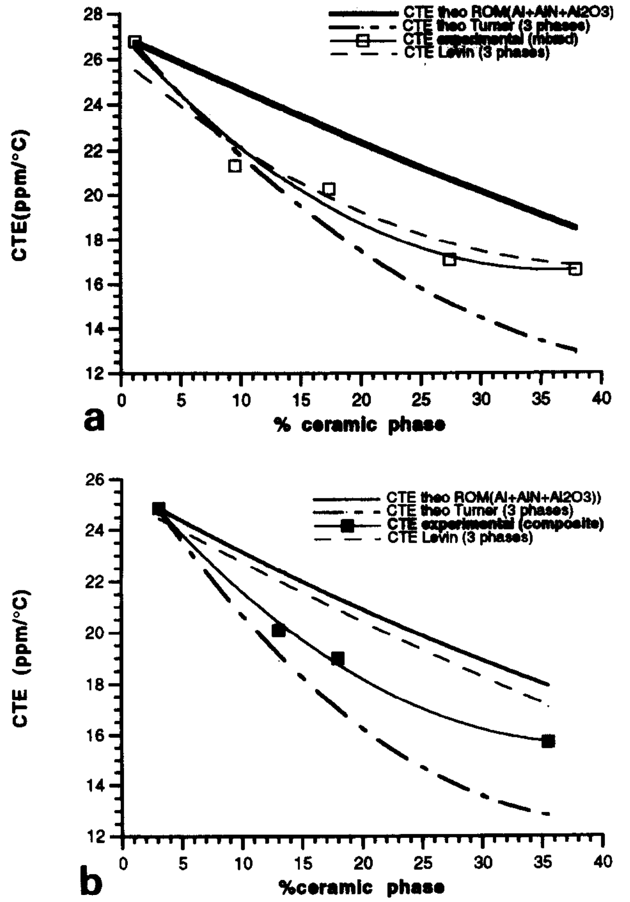

Fig. 12. Change in the coefficient of thermal expansion, CTE, as a function of AlN vol.%, for materials made from (a) 'mixed' and (b) 'composite' powders (experimental square).

'mixed' composites, but there was no agreement for sintered 'composite' materials.

3.2.2. Thermal and electrical conductivity

A marked drop in the thermal conductivity with increase in AlN content has been shown.[8] The presence of oxygen (oxide and oxynitride) is detrimental and the experimental values differ considerably from the prediction of the model of Rayleigh.[14] This discrepancy could be due to the very fine grain structure, as has been proposed by Geiger for Al-SiC.[15] But in order to verify it it is necessary to know the conductivity of the grain boundaries. The presence of AlN (and Al_2O_3) also causes a marked drop in the electrical conductivity of the Al-AlN composites.

3.2.3. Hardness

Hardness tests carried out at a load of 50 N for 10 s show a linear increase in hardness with AlN content. The milling time has no influence after 15 min for 'mixed' material, but is important for composite powder material even at times longer than 105 min when the grain size remains constant (Fig. 13).

3.2.4. Young's modulus

The Young's modulus E increases with the AlN content, for both types of material ('mixed' or 'composite'). The milling time however is an important parameter for the 'composite' materials (8 vol. % AlN) and insignificant for the 'mixed' material. Based on the assumption of a three-phase material such as discussed earlier, the modulus of compressibility K measured was compared with the predictions of the models by Voigt (ROM) and Hashin-Shtrikman.[16] The 'mixed' material lay within the limits of the two values whereas the 'composite' material lay close to the lower limit, probably because of the microporosity present. These materials can be considered therefore to be isotropic from a micromechanical point of view.

3.2.5. Resistance to hydrolysis

Using polished specimens immersed in water with an initial pH 6·1, the resistance to hydrolysis was measured by weighing for a period of 35 days. Figure 14 shows the results.

An incubation period of 4 days was observed after which all specimens lost their metallic sheen.

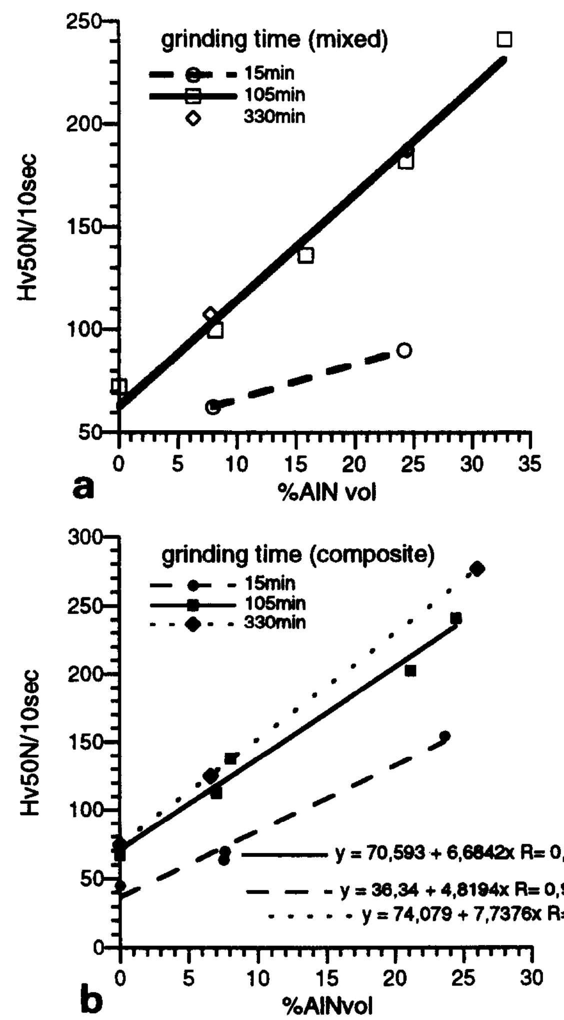

Fig. 13. Change in the hardness, H_v^{50}, as a function of AlN vol.%, for materials made from (a) 'mixed' and (b) 'composite' powders, for different grinding times.

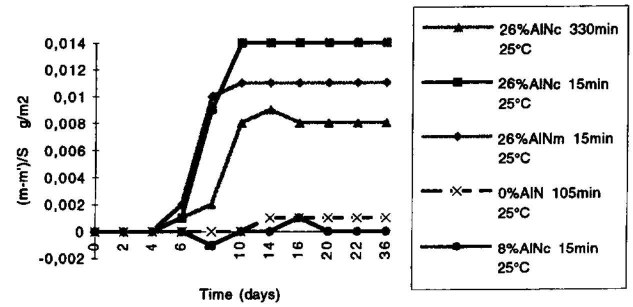

Fig. 14. Change in the loss of weight in aqueous media for Al-AlN composites made from © 1997 Elsevier Science Limited. 'composite' and (m) 'mixed' powders, at 25°C (it is not a time scale: it is a series of different experiments).

The rate of corrosion between the 4th and 10th day is the same for all specimens containing 26 vol% AlN, but it can be observed that in the most homogeneous specimen and for which the nitride is most finely dispersed (ground 330 min), the corrosion remains at a lower level. Finally in the case of 8 vol.% AlN there was absolutely no change in weight.

The finer the dispersion, the lower is the probability of finding in the surface of a component a large agglomerate of nitride likely to react with water.

4 Discussion

When a new class of materials is developed, many problems must be solved with respect to processing to achieve the desired microstructure and properties.

Nitriding of aluminium powders is a highly exothermal reaction, which is self-propagating (SHS). In fact the exact mechanism is not fully understood: this is due to the fact that pure aluminium is very reactive and reacts with oxygen to produce a thin film of alumina on the aluminium grains. Hence in order to sinter or melt such powders, the alumina film must be removed. This has been achieved by adding $CaCO_3$. It can be supposed that a reaction between alumina and calcium carbonate takes place to form an aluminate of calcium. Then one can imagine the reduction of the calcium oxide by aluminium due to the high local temperature during nitriding, leading to calcium which can be an intermediate step in nitriding via the calcium nitride, Ca_3N_2.[4,8] Up to now, the exact role of the anion is not known as results obtained with $CaCO_3$ and with CaF_2 are different.[8]

In order to produce good physical (thermal, electrical) or mechanical properties, the powder must be milled energetically to decrease the mean grain size and to disperse the AlN as homogeneously as possible. But the oxygen content must be drastically controlled and an optimum must be found at the grain size level.

Comparison of the physico-chemical properties of the two types of Al-AlN composites showed that thermal expansion, thermal conductivity and electrical conductivity decrease with increasing aluminium nitride content, whereas mechanical properties such as hardness, Young's modulus, fracture strength,[8] increase with increasing AlN content, but in a different manner for the two types of composites. Moreover for these properties, the values corresponding to 0 vol.% AlN are always higher or lower than the values observed for pure aluminium. This is due both to the presence of impurities, Al_2O_3 and AlON, a characteristic of the process, and to the decrease in the mean grain size. Classical models for composites, based on a pure or complex rule of mixtures, can be utilized, but the experimental results for the two types of material cannot be explained by the same model.

It appears that some aspects of the mechanical behaviour of Al-AlN materials fabricated from 'composite' powders can be likened to nanocomposites. The variation with mean grain size and reinforcement content is different from those obtained with composites made from 'mixed' powders. For example, composites made from 'composite' powders exhibit a higher strength than composites made from 'mixed' powders, and in addition are less ductile for equivalent[8] AlN contents. Moreover a superplastic behaviour may be expected, as shown by Imai *et al.*[2,3]

Compared with other MMC based on aluminium alloys (for example: Al 7090-SiC, Al 6090 T6-SiC, Al 2080 T4-SiC, Al 2124-SiC, Al 2119 T4-TiC, Al 2219 T6-TiC, Al 6061 T6-Al_2O_3,[17–22] Troadec[8] has shown that Al-AlN composites made either from 'composite' or 'mixed' powders exhibit a higher yield stress and fracture strength. It is thus reasonable to assume that by nitriding of high strength aluminium alloys, high performance Al-AlN composites could be achieved.

5 Conclusion

This preliminary study on a new class of metal matrix composites, Al-AlN, has shown the importance of the degree of dispersion of the ceramic phase (AlN) in the matrix (Al) in determining a number of properties of the composite Al-AlN. An electron microscope study has shown there is considerable inhomogeneity on this scale with, in particular, porous zones, which is one of the aspects needing improvement.

Apart from this, the composites show some remarkable properties when compared with those of the non-reinforced matrix: modulus elasticity, hardness, fractural strength, thermal expansion coefficient, resistance to hydrolysis. The less convincing results were thermal conductivity where a control of the oxygen content and a compromise on the particle size of AlN are necessary.

Compared to Al-SiC or Al-Al_2O_3 materials, Al-AlN composites appear to be an interesting class of metal matrix composites, with improved properties if high strength aluminium alloys can be used for nitriding.

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