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Elaboration and Characterization of a Metal Matrix Composite: Al/AlN

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Abstract

Metal matrix composites consisting of 56·5 vol% aluminum nitride in various aluminum matrices were manufactured. Through the selection of both reinforcement and matrix variables, the thermal properties of the composite were tailored to make it suitable for use in electronic packaging. AlN reinforcement consists of pressed and partially sintered AlN powder to obtain preforms with adjustable porosity. Al–Si aluminum alloys were used as matrices, with Si content ranging from 0 to 22 wt%. The composite exhibits very attractive properties, including a relatively high thermal conductivity (100 $Wm^{-1}K^{-1}$), a low coefficient of thermal expansion ($9{\cdot}10^{-6}$ K^{-1} for an Al–22·5 wt% Si matrix) as well as a good specific strength. Basic models used to predict the thermal and mechanical properties of the composite show a good agreement between theoretical and experimental data, except for thermal conductivity. For this last property, it is assumed that the matrix–reinforcement interface may have an important effect which is not taken into account in the theoretical model. Published by Elsevier Science Limited.

1 Introduction

Metal matrix composites (MMCs) have emerged as a class of material capable of advanced structural, thermal and wear applications.[1] The performance of MMCs is superior to conventional materials in terms of stiffness, creep and wear resistance, density reduction and thermal expansion control.[2,3] The low coefficient of thermal expansion (CTE) of ceramics used as reinforcement can be used to tailor the composite expansivity to match that of many materials. This may indeed be useful in electronic packaging applications, where the composite/substrate junction must remain without significant distortion under temperature changes.[4,5] The specific properties required for a material to be used in electronic packaging include high thermal conductivity for heat dissipation, low CTE for dimensional stability, along with low density and high stiffness.[6–8]

Among the different reinforcement geometries for MMCs (fibres, whiskers, particulate), the particulate form is very attractive as particles are easier to produce and process than long fibres, and they result in isotropic properties for the composite.[9,10] Several reinforcement materials are available (carbides, nitrides, oxides), SiC being the most used reinforcement in aluminum.[11]

The results presented here concern the elaboration of an Al/AlN composite. The choice of AlN is directed by its excellent thermal conductivity, good resistance to molten metal and oxidation at high temperature. Aluminum alloys were used as matrices, as they offer a high thermal conductivity (in the range 180–230 $Wm^{-1}K^{-1}$) with low density ($2{\cdot}7 g cm^{-3}$). Al alloys are also easier to process, compared with other high thermal conductivity metals such as copper.[12] The major drawback of pure aluminum is its high CTE ($23{\cdot}10^{-6}$ K^{-1}), but the use of Al–Si alloys can decrease the CTE to about $18{\cdot}10^{-6}K^{-1}$.

As the composite processed in this study is designed for use in electronic packaging, a very high volume fraction Vr of reinforcement (Vr = 56·5%) is necessary to attain a CTE close to that of substrate materials ($8{\cdot}10^{-6}$ K^{-1} for alumina). Therefore, the medium pressure infiltration technique is one of the most suitable technique to infiltrate the porous preform with molten Al.[13] This process involves preheating the preform within a mold, then molten aluminum is forced into this preform by application of an external

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pressure to overcome capillary and fluid drag forces.

This paper reports on the elaboration of the Al/AlN composites with partially sintered powder as preform and Al–Si alloys as matrix. Among the different experimental variables (preform porosity, infiltration parameters, matrix properties), the influence of Si content in the matrix on the final composite CTE has been studied. The aim is to control the thermal properties of the composite through the choice of appropriate matrix. The results of basic models prediction for the CTE are also presented.

2 Experimental Procedure

The most important features related to the elaboration and characterization of both preform and composites are now briefly presented.

The AlN preform were prepared from Pyrofine®ASD spray dried powder supplied by Elf–Atochem. AlN powder is produced by carbothermal nitridation of alumina in a continuous reactor. The reaction occurs in the range 1400–1700°C and is followed by an excess carbon burning out near 600°C. The physical properties of the powder include a mean diameter of about 1·5 μm, and a specific surface area of 4·0 $m^2\ g^{-1}$ with low standard deviation.

To obtain preforms with sufficient mechanical strength for handling and infiltration, the powder is pressed and partially sintered. The pressure is applied to the powder with an hydraulic ram. Pressure from 30 to 100 MPa were applied to various samples in order to vary the porosity volume fraction. Then the preforms are debinded at 600°C for 2 h to eliminate organic phases. Finally, the partial sintering operation is achieved at three different temperatures (1400, 1500 and 1600°C) for 1 h in a nitrogen atmosphere ($P_{N2} = 5$ bar). These three temperatures were chosen to study the effect of partial sintering temperature on porosity. Preforms produced in this way have a cylindrical shape with 35 mm diameter and 10 mm thickness.

Four commercial Al–Si alloys were used as matrices. The Si content of these alloys is varying from 0 wt% for A9 (pure Al) to 22·5 wt% for AS22. Table 1 gives the main composition and properties of these alloys.[14]

The preform properties are obtained by different methods:

1. Flash method[15] to get the thermal diffusivity of the samples. Thermal conductivity (K) is calculated from the measured diffusivity (a) by the relation:[15] $K(\mathrm{Wm^{-1}K^{-1}}) = a(\mathrm{m^2\,s^{-1}})^* \rho(\mathrm{kg.\,m^{-3}})\ {}^*Cp(\mathrm{Jg^{-1}K^{-1}})$, where ρ and Cp, respectively, represent the density and specific heat of the material.
2. Four points bending and Grindo–Sonic measurements for the mechanical properties.
3. Immersion density measurements for porosity level evaluation.
4. Nitrogen porosimetry to study the pore volume, surface and shape.
5. Scanning electron microscopy (SEM) investigation of the preform structure. The medium pressure infiltration device has been described elsewhere.[13] In this study, three preforms are infiltrated in a single processing for each alloy matrix. Preforms are placed in a stainless steel cylindrical mold, and both mold and the alloy are preheated at 750°C. The molten aluminum alloy is then forced into the preform by pressurized nitrogen, the pressure being slowly increased from 0 to 9 MPa in 45 s. The resulting composite pieces are extracted from the mold by machining and characterized as following:

1. Composites are cut and polished for metallographic observations;
2. Square section bars (5×5×30 mm) are cut and grounded for CTE measurement. An Adamel Lomargy automatic dilatometer is used to plot the strain–temperature response of the sample. The CTE is taken as the slope of the strain versus temperature curve in the 20–150°C range.
3. The basic mechanical properties are evaluated with the help of a non-destructive technique which is the measure of the propagation velocity of ultrasonic pulses in the composite, from which the Young modulus and Poisson ratios are calculated.

Table 1. Main composition and properties of the matrix alloys

Alloy	*Composition (wt%)*	*Density ($g\ cm^{-3}$)*	*Thermal conductivity ($Wm^{-1}K^{-1}$)*	*CTE ($10^{-6}\ K^{-1}$)*	*Melting point (°C)*	*Young modulus (GPa)*	*Bulk modulus (GPa)*
A9	99·99% Al	2·7	237	23·6	660	70	73
AS7G03	7% Si–0·3% Mg	2·68	160	21·5	555	74	77
AS13	13% Si–1·3% Fe	2·65	165	20	580	76	79
AS22	22·5% Si–0·4% Fe	2·61	160	17·5	690	75	78

3 Results and Discussion

3.1 Preform properties

The pressure applied to densify the powder and the sintering temperature *Ts* have been varied to assess the porosity range that was attainable. The evolution of the preform porosity volume *Vp* as a function of densifying pressure is shown in Fig. 1, where the three sets of sintering conditions are depicted. At a given temperature, porosity level decreases with increasing pressure, except for the preform sintered at 1600°C and 100 MPa. In the same way, higher sintering temperature results in lower porosity level. For the lower and higher sintering temperatures, a nitrogen absorption–desorption method was employed to study the pore structure. When *Ts* varies from 1400 to 1600°C, the BET surface varies from 3·4 to 2·8 $m^2 g^{-1}$. This is consistent with the porosity level evolution previously observed.

Specific preforms were prepared for infiltration, with a densification pressure of 50 MPa and *Ts* equal to 1500°C. This processing route leads to reproducible results in terms of prefom structure and porosity. For the composite elaboration, the AlN preform have a porosity level $Vp = 43{\cdot}5$ vol%. An example of the structure of these preforms is shown on Fig. 2. This SEM picture shows that the partial sintering only creates small aggregates of powder, and that the pore size is about 1 μm.

Four points bending experiments were conducted on AlN bars (5×5×40 mm) processed with the same parameters as the infiltrated preforms. Loading curves exhibit a brittle behaviour with a maximum strain at rupture of 0·17%. The flexural strength and modulus are quite high, respectively 22 ± 3 MPa and 18 ± 1 GPa. Tests were performed on eight available specimens, and a Weibull analysis was therefore not possible. These mechanical properties are confirmed by Grindo–Sonic measurements. In this experiment, the proper frequency

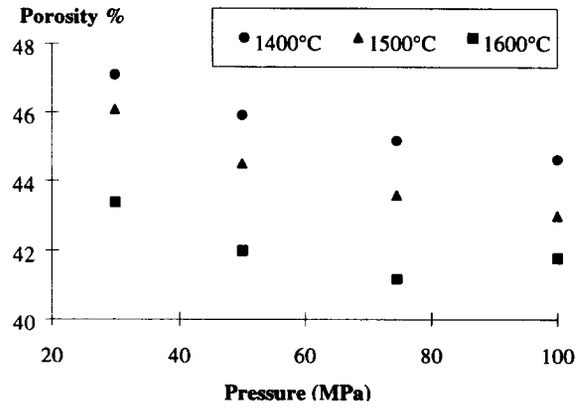

Fig. 1. Preform porosity volume fraction as a function of the densifying pressure. The three sintering temperatures are presented.

of the AlN test piece is measured, which is directly related to its Young modulus. A Young modulus of $21{\cdot}5 \pm 0{\cdot}9$ GPa for the AlN ceramic is obtained by this simple non destructive technique. This method appears of a great interest to characterize the preform material before elaboration, in order to ensure their mechanical resistance to infiltration pressure.

Finally, the thermal conductivity of the preforms was measured before and after the partial sintering operation.

The thermal conductivity of the preform goes from 1 $Wm^{-1} K^{-1}$ after pressing to 6 $Wm^{-1} K^{-1}$ after pressing and sintering. These values have to be compared with 170–200 $Wm^{-1} K^{-1}$ for a fully dense AlN ceramic (with sintering aid).

3.2 Composite properties

3.2.1 Microstructure

Density value was measured for all composite pieces, and it ranges from $2{\cdot}9 \pm 0{\cdot}01$ to $2{\cdot}97 \pm 0{\cdot}01$ g cm^{-3}, due to matrix density variations. With an aluminum volume fraction *Vm* of 56·5 vol%, this would indicate that our composites have attained 98% of their maximum theoretical density. A microstructural investigation gives some confirmation of this result. As shown in Fig. 3, the composite is fully infiltrated, and little porosities are only observed in few zones. These porosities seem to be due to some closed porosity of the AlN preform which can not be filled by the liquid aluminum. Thus, this residual porosity does not seem to indicate an infiltration problem but rather a preform defect that would need further investigations to be solved. Despite these small microstructural inhomogeneities, the mechanical and thermal properties of the composite are not altered.

3.2.2 Mechanical properties

Ultrasonic measurements were performed on the composite pieces. Longitudinal and transversal pulses are generated at the top surface of the specimen and the response spectrum is recorded. After the calculation of the ultrasonic speed in the material, the Young modulus and Poisson ratio are derived with the help of basic propagation equation. A mean Young modulus of 150 GPa with $\nu = 0{\cdot}28$ was obtained. It is to notice that this non-destructive analysis allows a simple control of the infiltration quality. In fact, multi-echo response spectrums are obtained as soon as the composite is cracked or partially infiltrated. This was verified with the AS13 matrix composites for which accidental cracks were produced during processing and with a set of pieces elaborated with only 4 MPa of nitrogen pressure.

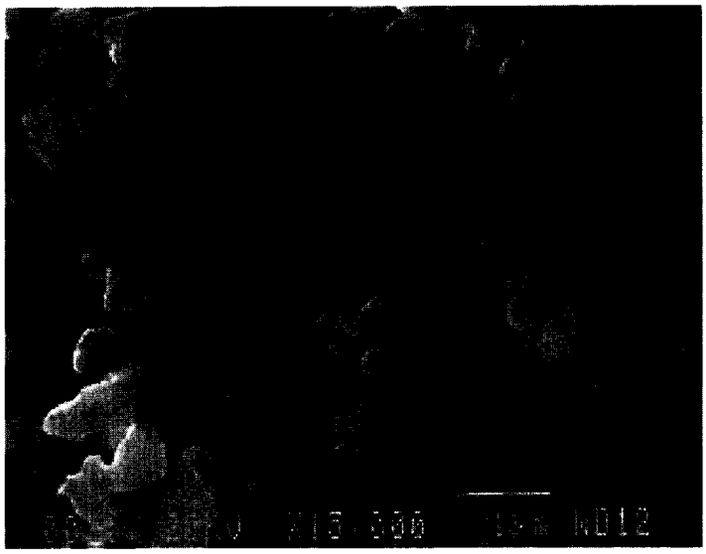

Fig. 2. SEM view of the preform structure.

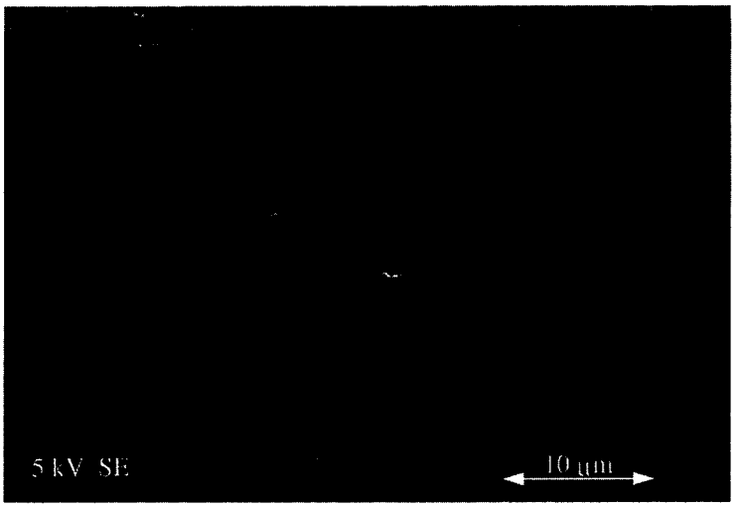

Fig. 3. SEM view of the polished surface of the A9/AlN composite.

3.2.3 Thermal properties

The thermal properties of the samples are now presented to understand the effect of the different Al–Si matrices.

The coefficient of thermal expansion (α_c) and thermal conductivity K_c of the composites are given in Table 2. The beneficial effect of Al–Si alloys clearly appears as a nearly 18% decrease in the CTE is observed when the matrix varies from pure Al to Al–22·5 wt% Si.

The CTE for the aluminum alloy of higher silicon content is very close to that of alumina ($8{\cdot}10^{-6}\,K^{-1}$), which is a commonly used material for electronic substrates.[16] The thermal conductivity remains of the order of $100\,Wm^{-1}\,K^{-1}$ and its variation with the silicon content of the alloy is surprisingly low. This property is very sensitive to infiltration defects: it can be effectively seen that the thermal conductivity of the AS13 composite is greatly affected by the accidental cracks produced during processing.

When compared to conventional alloys used for their low CTE[17] (for example Kovar® which is a Fe–29Ni–17Co alloy), our composite shows specific properties of a great interest. Table 3 compares the characteristics of the two materials.

Here is demonstrated the great advantage of MMCs when high specific properties are required. As can be seen, the specific modulus E/ρ of Al/AlN composite is 3 times that of Kovar®.

3.3 Use of basic models for the prediction of composite properties

Several mathematical models have been formulated to describe the effect of reinforcement parameters.[18–21] Properties of AlN used in these models are given in Table 4.[18] Of primary interest for electronic packaging are the CTE α_c, the thermal

Table 2. Coefficient of thermal expansion and thermal conductivity of the various composites

Matrix alloy	*Composite CTE* ($10^{-6}K^{-1}$)	*Composite thermal conductivity* ($Wm^{-1}K^{-1}$)
A9	10·8	110
AS7G03	9·9	100
AS13	9·5	80
AS22	8·9	95

conductivity K_c, and the Young modulus of the composite E_c. The E_c can be calculated, following the mathematical model developed by Hashin and Shtrickman:[22]

$$E_c = E_m.\frac{E_m.V_m + E_r.(V_r + 1)}{E_r.V_m + E_m.(V_r + 1)}$$

where V is a volume fraction, and the subscripts m and r refer respectively to the matrix and reinforcement. For our composite with the different matrices, values between 150 and 160 GPa are obtained, which are very close to the values derived from ultrasonic measurements.

Figure 4 shows the evolution of the A9/AlN composite CTE with Vr, as predicted by several models. The rule of mixture (ROM) is the simplest model, but most sophisticated ones are also presented. In the ROM, the composite CTE is simply the addition of the matrix and reinforcement weighted by their volume fractions:

$$\alpha_c = \alpha_m.V_m + \alpha_r.V_r.$$

Turner's model[23] proposed in 1946 considers the effect of isostatic stresses on adjacent phases, and the predicted values are lower than the ROM approximation:

$$\alpha_c = \frac{\alpha_m.V_m.K_m + \alpha_r.V_r.k_r}{V_m.k_m + V_r.k_r}$$

where k is the bulk modulus of the phase.

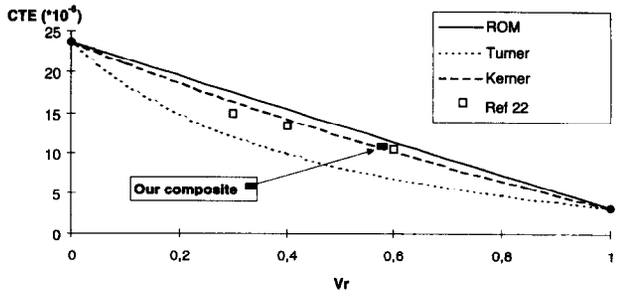

Fig. 4. Evolution of A9/AlN coefficient of thermal expansion as a function of AlN volume fraction.

The Kerner's model[24] takes into account the shear strain at the matrix–reinforcement interface:

$$\alpha_c = \alpha_m - V_r.(\alpha_m - \alpha_r).$$
$$\frac{k_m.(3k_r+4G_m)^2+(k_r - k_m).(16G_m^2+12G_m.k_r)}{(3k_r+4G_m)[4V_r.G_m.(k_r - k_m)+3k_r.k_m+4G_m.K_m]}$$

where G is the shear modulus. As can be seen, this model predicts values of CTE very close to measured experimental data. For example, a value of 8·6 10^{-6} K^{-1} for the 'Al–22·5 wt% Si' is obtained, to compare with an experimental value of 8·9 10^{-6} K^{-1}. The CTE of the composite is also strongly dependent on the volume fraction of reinforcement, and that high Vr (> 50%) is required for close CTE between the composite and the electronic substrate.

For the prediction of the thermal conductivity, an estimation is possible from the model proposed by Lord Rayleigh:[25]

$$K = K_m.\frac{1 + 2V_r.\frac{1-K_m/K_r}{2K_m/K_r+1}}{1 - V_r.\frac{1-K_m/K_r}{K_m/K_r+1}}$$

where K is the thermal conductivity.

In our case, this model predicts a conductivity of 160 $Wm^{-1}K^{-1}$ for A9/AlN composite, which is higher than that obtained experimentally (110 $Wm^{-1}K^{-1}$). This difference could be due to

Table 3. Comparison between Kovar® and AS22/AlN composite properties at room temperature

Material	*Density* ρ ($g\,cm^{-3}$)	*Thermal conductivity K* ($Wm^{-1}K^{-1}$)	*CTE* α ($10^{-6}K^{-1}$)	*Young modulus E* (*GPa*)	E/ρ ($Gpa/g\,cm^{-3}$)
AS22/AlN	2·9	95	8·9	150	52
Kovar	8·36	17	5·4	138	17

Table 4. Properties of the AlN reinforcement

Material	*Density* ($g\,cm^{-3}$)	*Thermal conductivity* ($Wm^{-1}K^{-1}$)	*CTE* ($10^{-6}K^{-1}$)	*Young modulus* (*GPa*)	*Bulk modulus* (*GPa*)
AlN	3·26	125	3·3	345	228

the fact that interfacial effects are not taken into account in this model.

4 Conclusion

The AlN reinforced aluminum composite studied in this work shows very attractive thermal properties, with a minimum CTE very close to that of alumina (CTE = 8·9 10^{-6} K^{-1} with the 22·5 wt% Si aluminum matrix). The composite also shows a high thermal conductivity (110 $Wm^{-1}K^{-1}$) required for heat dissipation of electronic substrates, and this property remains unaffected by the Si content of the matrix. The mechanical response of the samples, although not extensively studied, show promising opportunities for this composite. Concerning the processing route, two major objectives have been achieved: the preform porosity control and the ability of low pressure infiltration to elaborate composites with a very high volume fraction of reinforcing ceramic.

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