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Borosilicate Glass-Ceramic Composites Reinforced by Ni₃Al Ribbons and Particles

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Abstract

Rapidly solidified ductile powders of Ni₃Al + 8 at% Cr + 0·1 at% B and pure Ni₃Al ribbons have been considered as strengthening dispersions for brittle borosilicate glass-ceramic matrices. Al₂O₃ and NiO were alternatively added to the matrix to modify the interface reactivities and it has been found that the latter could play a role to optimise the interfacial properties with ribbons. The peculiar geometry of the ribbons caused some difficulties in the preparation of the composite, while the intermetallic powders were easily incorporated in the glass matrix even though the presence of Cr in Ni₃Al particles gave a slight modification on the interface stability. The Ni₃Al particle/glass-ceramic composites showed densities close to their theoretical values and improved elastic moduli. © 1997 Elsevier Science Limited.

1 Introduction

In spite of their attractive characteristics (specific mechanical properties, thermal and chemical stability and low cost of the raw materials), intermetallics still have some difficulties for application in massive form; especially their brittleness and the poor workability limit their applications. However, as has already occurred for ceramics, their use as matrices or reinforcements for composites seems to be promising, particularly at medium and high temperatures. Ni₃Al is the best-known compound among intermetallics and its peculiarity — the increase of the yield stress on increasing the temperature — has been widely investigated.[1,2]

The rapid solidification (RS) of Ni₃Al induces some ductility in the material[2] and allows its forming in two interesting shapes to use as a secondary phase in composite materials: ribbons, prepared by melt-spinning technique and powders by gas atomisation processes. The specific geometry of the ribbons (large aspect ratio, i.e. width/thickness) in general can be successfully used to create a large bond surface between matrix and reinforcement, being also very effective in enhancing the mechanical properties of various matrices.[3–6] Particles are the most widely used shape as reinforcement and/or as a toughening phase in composites. The first use of powders of RS Ni₃Al, as far as we are aware, is in this work, and Refs 7–9. RS intermetallics can replace as secondary phase both ceramic materials (traditionally brittle and expensive) and pure metals (usually reactive, soft and with high density).

The use of RS Ni₃Al powders seems to be particularly favourable for glass and glass-ceramic matrix composites, rather than other matrices such as metallic and ceramic. The former are extremely reactive towards Ni₃Al, even those having low melting point, e.g. Al and Mg.[4,10] The latter involve high temperatures during their processing, and probably during their use, which can induce some detrimental effects on the microstructural properties of RS intermetallics; in one case Ni₃Al has shown reactivity also with a ceramic matrix up to complete reaction.[7]

This work is focused on the use of rapidly solidified Ni₃Al ribbons (r) and particles (p) as reinforcement for borosilicate glass-ceramic matrix composites. This kind of composite can be tailored in terms of glass composition, interfacial reactions and working temperature, while the addition of RS ductile Ni₃Al would improve fracture toughness, strength, hardness and fracture behaviour of the intrinsically brittle matrices.

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A glass-ceramic matrix offers several advantages:

— the composite preparation occurs in the glassy state, just above the softening temperature of the glass matrix, which means lower temperatures and pressureless sintering than with ceramic-matrix composites;

— the subsequent ceramisation of the matrix can be controlled to obtain the required crystallinity in the composite improving its thermomechanical properties;

— the glass matrix can be tailored to match the physical and chemical characteristics of the reinforcement, i.e. the coefficient of thermal expansion (CTE), Young's modulus and interface compatibility;

— the interfacial strength between matrix and reinforcement can be controlled by adding suitable oxides to the glass matrix.[11,12]

Common borosilicate glass matrices were selected for this work: Al_2O_3 and NiO were alternatively added to the matrix to study their effect on the interface between Ni_3Al particles or ribbons and matrices.

2 Experimental Procedure

Ni_3Al ribbons were prepared by induction melting under argon atmosphere. After homogenisation, rapid solidification (melt-spinning technique) was then performed on an iron wheel rotating at a peripheral speed of 30 m/s in a helium-filled process chamber. Continuous and folding ribbons, about 1 mm wide and about 30 μm thick, with microhardness value of 5·20 GPa and Young's modulus of 170 GPa, were obtained; XRD showed the typical spectrum of $L1_2$ superlattice of the Ni_3Al ordered-solid-solution.

The compositions of the glasses (mol%) used in this work are shown in Table 1.

Table 2 reports the conditions of sintering, the relative densities and the Young's moduli of the sintered glasses used as matrices.

Glasses were prepared by melting the oxides in the above percentages at 1650°C; each glass was analysed by DTA (404 S Netzsch) and heating microscopy (Leitz mod. AII) to determine the characteristic temperatures, i.e. the glass transition temperature (Tg) and the softening temperature range, respectively. Then glasses were ball-milled, sieved and cold pressed in bar shape (50 × 5 × 5 mm^3) without, as reference materials, or with 1 vol% of Ni_3Al rapidly solidified flakes of ribbons randomly oriented or 3 vol% of Ni_3Al powder produced by gas atomisation. The powder had the following composition, chosen in order to enhance its toughening effect: 73·12 Ni, 18·82 Al, 8·06 Cr, 0·019 Mo, 0·10 B at% (particle size about 50 μm), kindly supplied by Wright and Knibloe, INEL Lab.[13]

The composites (labelled as SB/Ni_3Al_r; SB/Ni_3Al_p; SBN/Ni_3Al_r; SBN/Ni_3Al_p; SBA/Ni_3Al_r and SBA/Ni_3Al_p, r = ribbons, p = particles) were sintered under an Ar flow at temperatures and times reported in Table 3. The sintering temperature was chosen for glass matrices and composites according to the softening range observed by heating microscopy, in order to sinter in a pressureless viscous flow process.

Each sintered matrix and the parent composite were characterised by X-ray diffraction (XRD, Philips PW1710), optical and scanning electron microscopy (SEM, Philips PW1830) with compositional analysis (EDS-EDAX 9100 which can only reveal the elements with atomic number higher than 11). Indentations (Vickers, 100 N) were carried out at the interfaces to observe the crack propagation in the composite. The Young's modulus was measured by a non-destructive sonic method (Grindosonic MK5, Lemmens Elektronika), except for Ni_3Al ribbons measured in tension. The densities of the sintered matrices and composites were measured by picnometry according to the Archimedean principle; the theoretical densities were calculated by the rule of mixture.

Table 1. Compositions and characteristic temperatures of glasses (mol%)

Glass	SiO_2	B_2O_3	NiO	Al_2O_3	$T_g(°C)$	Softening range (°C)
SB	80	20	—	—	1100	950–1100
SBN	80	18	2	—	1083	950–1100
SBA	80	10	—	10	1100	1150–1200

Table 2. Temperature and time of sintering, relative density and Young's modulus (E) of sintered glass matrices

Sintered glass matrices	Sintering temperature (°C)	Sintering time (min)	Relative density (%)	E (GPa)
SB	1100	150	91	45
SBN	1140	150	95·5	42
SBA	1250	150	97·4	58

Table 3. Temperature and time of sintering, relative density, Young's modulus of the composites, morphology and compositon of interfaces

Composite	Sintering T(°C)	Sintering time (min)	Relative density(%)	Interfacial morphology	Interfacial composition	E (GPa)
SB/Ni₃Al$_r$	1150	90	90·9	5 μm reaction zone	Si, Ni	45
SBN/Ni₃Al$_r$	1200	90	95·5	Continuous, sharp	Si, Ni	42
SBA/Ni₃Al$_r$	1350	90	—	Discontinuous, reaction zones	Si, Al, Ni	58
SB/Ni₃Al$_p$	1150	90	97·5	Continous, slight reaction layer	Si, Al, Cr, Ni	49
SBN/Ni₃Al$_p$	1200	90	97·9	Continous, 5 μm reaction zone	Al, Ni, Cr, Si	50
SBA/Ni₃Al$_p$	1350	90	98·4	Continuous, slight reaction layer	Si, Ni, Al	67

3 Results

The sintering of these composites, in this case, requires higher temperatures than for the corresponding glasses, due to the presence of the reinforcement, whereas, in other cases, Ni₃Al has shown a sintering-aid effect.[9] A percentage higher than 1 vol% of Ni₃Al$_r$ did not give acceptable green densities; Ni₃Al$_p$ gave better results and 3 vol% was easily incorporated. All the sintered samples exceed 90% of the theoretical density, excluding SBA/Ni₃Al$_r$; the particle-reinforced composites show densities higher than 97%.

XRD on the sintered glasses revealed a broad peak typical of the amorphous state, with almost undetectable cristobalite peaks: the same results were found for the composites, where some Ni₃Al signals were revealed. All the samples are glass-ceramics with a small percentage of crystalline phase, according to the fact that no ceramisation treatments were performed.

Figures 1(a) and (b) show a polished surface of the SB/Ni₃Al$_r$ (a) and SB/Ni₃Al$_p$ (b) composites: a thin reaction zone (about 5 μm) surrounds the ribbons and only a slight reactive layer surrounds the particles.

The addition of the oxides, which Ni₃Al may form in a slightly oxidising environment, changes the morphology of the interfaces. The effect of adding NiO (SBN/Ni₃Al composites) is shown in Figs 2(a) and (b): the interfaces appear continuous and sharp with the ribbons (a), whereas a sort of reaction is observable with the particles (b). On the contrary, SBA/Ni₃Al$_r$ composite (addition of Al₂O₃ to the glass matrix) has discontinuous and poor interfaces, whereas SBA/Ni₃Al$_p$ composite has continuous interfaces with a layer of reactivity (Fig. 3).
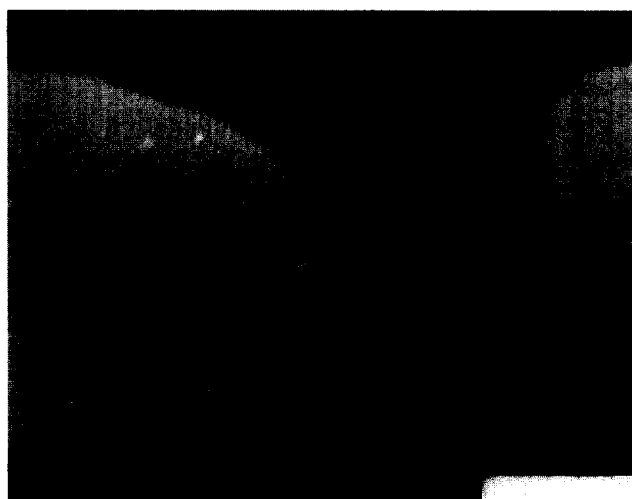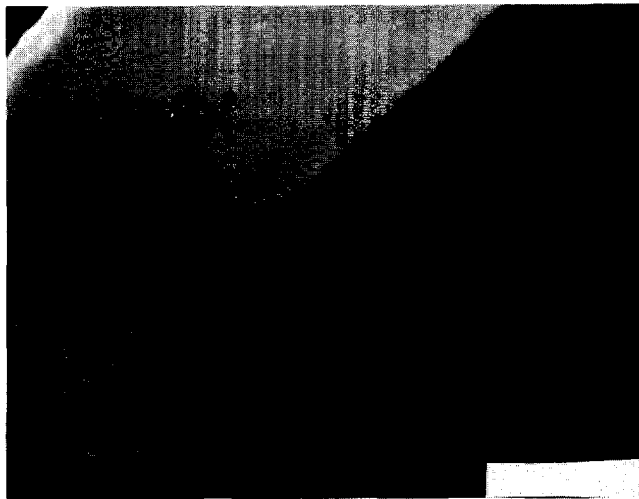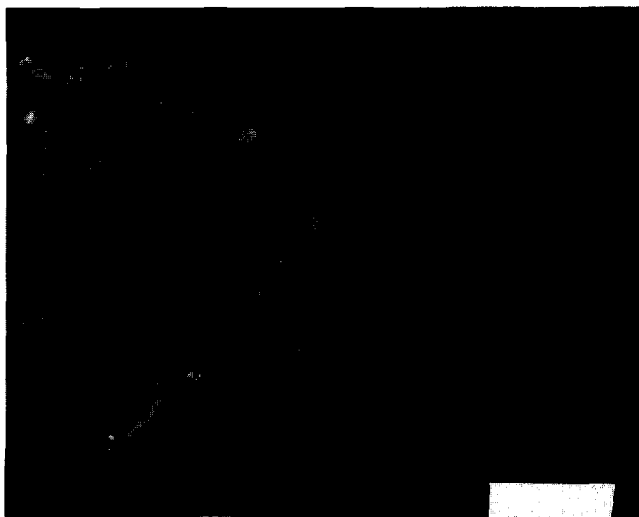

(a)   (b)

Fig. 1. SEM micrograph showing the interfaces of (a) SB/Ni₃Al$_r$ and (b) SB/Ni₃Al$_p$ composites.

(a)

(b)

Fig. 2. SEM micrograph showing the interfaces of (a) SBN/
Ni₃Al_r and (b) SBN/Ni₃Al_p composites.

Fig. 3. SEM micrograph showing the crack propagation in
SBA/Ni₃Al_p sample.

Chemical microanalysis of the interfaces was performed but, due to the instrumental limits in the determination of oxygen and boron and the interference between silicon and aluminium, only semiquantitative results can be reported such as a compositional hierarchy, starting from the most abundant element (Table 3).

Figure 3 shows the crack propagation at the interfacial zone in the SBA/Ni₃Al_p: the crack has deviated around the particles and debonds the interfaces. The same results were obtained with SB/Ni₃Al_p and SBN/Ni₃Al_p composites. In SBN/Ni₃Al_r as well as in SB/Ni₃Al_r, the crack is deviated by the ribbon and propagated along the interface matrix/ribbon, while in the SBA/Ni₃Al_r sample, the discontinuities at the interface act as a sink for the crack.

All the Ni₃Al particle-reinforced composites have a Young's modulus higher than that of the corresponding sintered matrix, as shown in Tables 3 and 2, respectively; the Young's modulus for
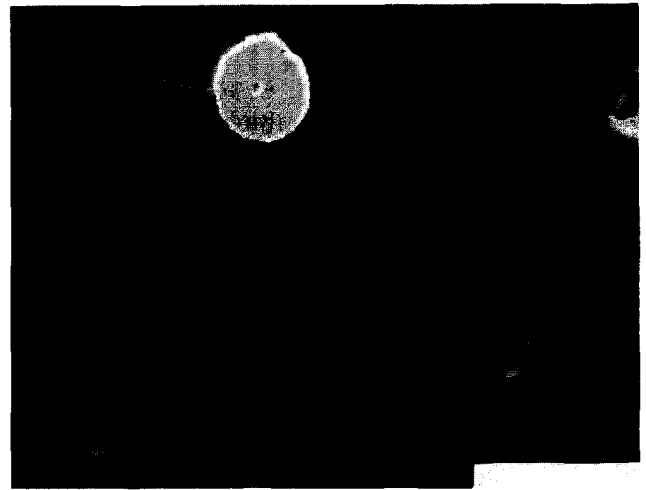
Ni₃Al ribbon-reinforced composites is the same of that of the matrices, due to the low percentage of ribbons contained in the composites.

4 Discussion

In order to explain the interfacial reactivities and morphologies reported in Table 3, some data must be considered:

— As concerns Ni₃Al in slightly oxidising conditions, the diffusion of Al to the oxide–metal interface is less than that required to satisfy the growth rate of the Al₂O₃ scale. In this condition the formation of NiO and traces of NiAl₂O₄ has been observed.[14 16]

— The hot oxidation of a Ni–Al–Cr alloys with a chemical composition very similar to that of the powder used in this work was investigated within 1000 and 1200°C by Smialek et al.;[17] in a transient stage of the oxidation a surface layer of a spinel was observed and the formation of oriented α-(Al,Cr)₂O₃ and γ-Al₂O₃, which is more permeable than α-Al₂O₃, was also noted.

Ni₃Al in slightly oxidising conditions, such as in a borosilicate glass at its softening point, undergoes an oxidation:[11,12] NiO is the main reaction product. Its formation in these conditions is kinetically favoured over Al₂O₃ despite the ΔG formation of Al₂O₃ (ΔG_f NiO $= -108$; ΔG_f Al₂O₃ $= -1147$ KJ mol⁻¹ at 1500 K). Moreover, NiO (and also Al₂O₃) is soluble in a borosilicate glass: this means that the SB matrix could dissolve the oxides formed. EDS analyses of the interface between SB glass and Ni₃Al_r (pure Ni₃Al) have revealed a Si- and Ni-rich phase and no Al has been found in this zone, according to the facts

detailed above. These data can explain the interfacial reaction zone in the SB/Ni$_3$Al$_r$ composite, in terms of an acid-basic reaction between SiO$_2$ and NiO, with the formation, in equilibrium condition, of 2NiO·SiO$_2$ (nickel olivine).[18]

The addition of NiO to the SB matrix modifies the interfacial equilibrium; the solubility and the reactivity of nickel oxides in the matrix is unfavoured if the matrix already contains NiO. The Ni$_3$Al ribbon surface is still oxidised by the glass, but the reaction is limited because the matrix does not dissolve more nickel oxide if it already contains it. In other words, SiO$_2$ of the matrix makes NiO move from the ribbons in SB/Ni$_3$Al$_r$ and react with it, while this phenomenon is inhibited in SBN/Ni$_3$Al$_r$ by the presence of NiO in the matrix. From a morphological point of view, this means the formation of a sharp and continuous interface between Ni$_3$Al$_r$ and SBN matrix (Fig. 2(a)).

The addition of Al$_2$O$_3$ does not produce the same effects: the absence of the Al at the interface in SB/Ni$_3$Al$_r$ means that Al$_2$O$_3$ is not likely to be involved in the interfacial equilibrium; moreover the Al$_2$O$_3$ added can react with the layer of NiO formed on Ni$_3$Al$_r$ and the formation of NiO·Al$_2$O$_3$ (nickel spinel) can be expected in equilibrium conditions. As a consequence, in SBA/Ni$_3$Al$_r$ composite the interfaces are reactive and discontinuous.

A certain difference can be observed at the interface of glass/Ni$_3$Al$_p$ due to the different composition of the particles (8 at% Cr) as compared with the ribbons.

EDS analysis carried out on SB/Ni$_3$Al$_p$ interfaces, as above reported, reveals the presence of Si, Al, Cr and only traces of Ni.

Cr$_2$O$_3$, unlike NiO, is a more unreactive layer due to its more negative value of ΔG_r (-731 KJ mol^{-1} at 1500 K), moreover the SiO$_2$ of the glass matrix, having an acid character, reacts with NiO (basic character) formed on the surface of the ribbons (SB/Ni$_3$Al$_r$) while it does not react with Cr$_2$O$_3$ (acid character) grown on Ni$_3$Al particles (SB/Ni$_3$Al$_p$). These facts can explain the formation of only a slight reaction layer shown in Fig. 1(b), attributable to the formation of an (Al,Cr)$_2$O$_3$ type solid solution.

Referring to the 5 μm of reaction layer depicted in Fig. 2(b), the presence of NiO in the glass matrix enhances, as already mentioned, the reactivity at the interface due to the formation of a NiO·(Al,Cr)$_2$O$_3$ type spinel, and this is consistent with the finding of a larger amount of Ni in SBN/Ni$_3$Al$_p$ than in SB/Ni$_3$Al$_p$ interfaces.

EDS analysis in SBA/Ni$_3$Al$_p$ has revealed the absence of Cr, with a high segregation of Al; probably the presence of Al in the matrix enhances the formation of Al$_2$O$_3$ inhibiting Cr$_2$O$_3$, and

the formation of a mixture constituted by SiO$_2$ + 2NiO·SiO$_2$ + NiO·Al$_2$O$_3$ in equilibrium conditions, can be inferred.[18]

The discontinuities present at the interfaces of SBA/Ni$_3$Al$_r$, as compared with SB/Ni$_3$Al$_r$, SBN/Ni$_3$Al$_r$ and particle-reinforced composites, can be explained in terms of sintering temperature and stress accommodation, respectively. In fact SBA/Ni$_3$Al$_r$ was processed at 1350°C, i.e. 200°C higher than the processing temperature of the SB/Ni$_3$Al$_r$ and 150°C higher than that of SBN/Ni$_3$Al$_r$; in these conditions, the difference in CTE (3–4 × 10^{-6} K^{-1} for SB glass, 12 × 10^{-6} K^{-1} for Ni$_3$Al) between matrix and reinforcement becomes more important and more effective in the formation of voids at the interface glass/ribbon than glass/particle due to a better accommodation of thermal stresses in an spherical-shaped inclusion than in a needle-shaped.

In order to investigate, from a mechanical point of view, the interfacial behaviour some Vickers indentations were produced to observe crack propagation near the interfaces. The continuous and sharp interface between SBN and Ni$_3$Al$_r$ acts as an energy consumption factor by deviating the crack propagation from perpendicular to parallel with respect to the ribbon length, while in SBA/Ni$_3$Al$_p$, in addition to the crack deviation effect of the particles, the most important toughening mechanism is the debonding of the continuous interfaces between matrix and reinforcement, as shown in Fig. 3. An analogous mechanism occurs in SB/Ni$_3$Al$_p$ and SBN/Ni$_3$Al$_p$.

The measurement of the Young's modulus for each particle-reinforced composite in comparison with the respective matrices allows other considerations about the interfaces (Tables 2 and 3). First of all, each composite has higher modulus than the unreinforced matrix. This is the case of a brittle matrix with a reinforcement having higher modulus, according to the rule of mixtures. The good agreement with the rule of mixtures is possible only if the interfaces are continuous, otherwise, the particles act as pores and the Young's modulus of the composite is lower than that of the unreinforced matrix. In our case, the morphology and density results were confirmed by the elasticity values of the composites. For the ribbon-reinforced composites, the small percentage of Ni$_3$Al$_r$ did not give rise to significant variations in the moduli as compared with the pure matrices.

5 Conclusions

A new class of glass-ceramic composite materials has been prepared by a pressureless sintering

method: Ni_3Al ribbons and particles have been alternatively added to the glass matrices as reinforcing dispersions and the resulting composites showed densities close to theoretical and improved elastic properties.

The starting glass matrix was modified to match the properties of the intermetallic and to optimise the interfacial properties. The presence of Cr in the intermetallic particles gave a slight modification on the interfacial stability, without interfering with the preparation of the composites. On the other hand, the specific geometry of the ribbons caused some difficulties in the preparation of the composites by pressureless sintering. In any case, the use of Ni_3Al as reinforcement for the preparation of glass-ceramic matrix composites for medium- and high-temperature applications was demonstrated.

A few qualitative considerations about the toughening effect of the RS Ni_3Al on the glass matrices can be drawn: in the presence of continuous interfaces, ribbons deviate cracks parallel to their interfaces before the cracks reach them; while with particles, cracks enter the interfaces and debond them close to the particles.

Acknowledgements

References

1. Westbrook, J. H., Temperature dependence of the hardness of secondary phases common in turbine bucket alloys. *Trans. TMS-AIME*, 1957, **209**, 898–904.
2. Koch, C. C., A review of rapid solidification studies of intermetallic compounds. *Mat. Res. Soc. Symp. Proc.*, 1985, **39**, 397–409.
3. Halpin, J. C. and Thomas, R. L., Ribbon reinforcement for composite. *J. Compos. Mater.*, 1968, **2**, 488.
4. Varin, R. A., Metelnick, M. and Wronski, Z., Design and structural stability of metal matrix composites containing intermetallic ribbons. In *Proc. Int. Conf. on Evolution of Advanced Materials*, Milano, Italy, 1989. pp. 411–418.
5. Vaidya, R. U. and Subramanian, K. N., Metallic glass ribbon-reinforced glass-ceramic matrix composites. *J. Mater. Sci.*, 1990, **25**, 3291–3296.
6. Appendino, P., Badini, C., Ferraris, M. and Marino, F., Interface reactions of Ni_3Al ribbons/Al-MMC in ground preparation as preliminary test for microgravity experiments. In *Proc. VIIIth Eur. Symp. Mater. and Fluid Sci. in Microgravity*, Brussels, Belgium, 1992. pp. 845–847.
7. Zhang, B. R., Gialanella, S. and Marino, F., Chemical aspects of reaction-bonded sintering of Si_3N_4-intermetallic composite. *Advances in Science and Technology 7: Advanced Structural Fiber Composites*, ed. P. Vincenzini. Techna Srl, Faenza, Italy, 1995. pp. 429–436.
8. Marino, F., Zhang, B. R. and Fornari, B., Processing and microstructural development of reaction-bonded sintering of a Si_3N_4-intermetallic composite. *J. Mater. Sci.*, 1996, **31**, 2247–2255.
9. Zhang, B. R. and Marino, F., Influence of 1 vol% Ni_3Al addition on sintering and mechanical properties of reaction-bonded Si_3N_4. *J. Eur. Ceram. Soc.*, 1995, **15**, 1065–1070.
10. Varin, R. A., Metelnick, M. and Wronski, Z., Structure of as-cast aluminum matrix composite containing Ni_3Al-type intermetallic ribbons. *Met. Trans. A*, 1989, **20A**, 1153–1161.
11. Ferraris, M., Badini, C. and Couzinet, B., Interfacial equilibria in Ti-particles/glass ceramic composite. *Composites*, 1994, **25**, 494–498.
12. Donald, I. W., Preparation, properties and chemistry of glass- and glass-ceramic-to-metal seals and coating. *J. Mater. Sci.*, 1993, **28**, 2841–2486.
13. Wright, R. N. and Knibloe, J. R., The influence of alloying on the microstructure and mechanical properties of P/M Ni_3Al. *Acta Metall. Mater.*, 1990, **38**, 1993–2001.
14. Pettit, F. S., Oxidation mechanisms for nickel-aluminum alloys at temperatures between 900° and 1300°C. *Trans. TMS-AIME*, 1967, **239**, 1296.
15. Cathcart, J. V., The oxidation of nickel-aluminum and iron-aluminum alloys. *MRS Symp. Proc.*, ed. C. Koch, C. T. Liu and S. Stoloff, 1985, **39**, 445–459.
16. Takeyama, M. and Liu, C. T., Surface oxidation and ductility loss in boron-doped Ni_3Al at 760°C. *Scripta Metall.*, 1989, **23**, 727–731.
17. Smialek, J. L. and Gibala, R., Structure of transient oxides formed on NiCrAl alloys. *Met. Trans. A*, 1983, **14A**, 2143.
18. Levin, E. M., Robbins, C. R. and McMurdie, H. F., *Phase Diagrams for Ceramics 1969, Supplement*. American Ceramics Society Inc., Columbus, Ohio, USA, 1969.