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Microstructure and Properties of Metal Infiltrated RBSN Composites

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Abstract

Reaction-bonded silicon nitride (RBSN)–metal composites were fabricated using gas-pressure infiltration. Various RBSN types have been infiltrated with molten Al, an Al–Si–Mg alloy, a Ti–Al intermetallic, and Si, resulting in considerable increase in mechanical properties when compared to uninfiltrated RBSN. For example, strength was raised to 510 from 227 MPa when infiltrated with a Ti–39 wt% Al alloy and the toughness to >5 from 2·7 MPa$\sqrt{m}$ when pure Al was infiltrated. Si infiltration proved to be most effective in enhancing the wear resistance.

Reaktionsgebundenes Siliciumnitrid (RBSN) wurde unter Gasdruck mit reinem Aluminium, einer Al–Si–Mg-Legierung, einer Ti–Al-Legierung und mit Silicium infiltriert. In allen Fällen wurden die mechanischen Eigenschaften von RBSN z. T. erheblich verbessert. Beispielsweise konnte die Festigkeit von 227 auf 510 MPa durch eine 39 Gew% Al-haltige Ti-Legierung und die Bruchzähigkeit von 2·7 auf >5 MPa$\sqrt{m}$ durch reines Aluminium gesteigert werden. Silicium erwies sich zur Verbesserung des Verschleißwiderstandes am besten geeignet.

On a élaboré des composites Si_3N_4 (RBSN)–métal par infiltration sous pression de gaz. Différents types de RBSN ont été infiltrés par de l'aluminium fondu, un alliage Al–Si–Mg, un intermétallique Ti–Al et enfin par du silicium, conduisant à des matériaux ayant des propriétés mécaniques considérablement améliorées. L'infiltration par un alliage Ti–39 wt% Al permit par exemple de faire passer la résistance mécanique de 227 à 510 MPa tandis que la ténacité passait de 2·7 à plus de 5 MPa$\sqrt{m}$ pour une infiltration par de l'Al pur. L'infiltration par du silicium s'est avérée être la plus efficace pour améliorer la résistance à l'usure.

1 Introduction

Ductile metal reinforcements considerably increase the fracture toughness of ceramic materials. The dominant toughening mechanism in this case results from bridging of the extending crack by the plastically deforming metal behind the crack tip.[1–5] Several processing methods have been used to produce metal-reinforced ceramic composites.[4,6–9] One of the preferred techniques to fabricate ceramic–metal composites, where the inherent properties of the ceramic dominate the overall properties, is pressureless infiltration of a porous ceramic with a liquid metal which has to wet the ceramic phase. This is the case for most carbides, e.g. Si–SiC composites can easily be made by infiltration processing.[10] Problems usually arise with oxides and nitrides where either the wettability by the metal must be improved, e.g. by alloying, or pressure has to be applied during the infiltration.[11]

Reaction-bonded silicon nitride (RBSN) typically exhibits porosities of >15%, mainly as open porosity. It is hence desirable for some applications to fill the pores with a metal phase in order to improve mechanical and surface properties. Leimer & Gugel[12] and Schmidt[13] tried to infiltrate RBSN with a number of metal alloys. However, in spite of reasonable wettability by some alloys, infiltration could only be observed when reactions with the Si_3N_4 matrix took place. This was essentially the case for Si and Mg alloys with high Ca content. However, the mechanical properties of infiltrated and reacted RBSN composites were hardly im-

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proved when compared to the uninfiltrated RBSN matrix.

In this work, a gas-pressure technique was successfully applied to infiltrate various RBSN types with molten aluminum, an aluminum alloy, a titanium–aluminum intermetallic compound and silicon.

2 Experimental

RBSN ceramics with open porosities of ~18% (Annawerk, Rödental, FRG, pore size distribution given in Fig. 1), ~15% (Hoechst CeramTec, Selb, FRG) and ~25% (Iscar, Naharia, Israel) and average pore diameters of 0·16 μm, 0·1 μm and 0·25 μm, respectively, were infiltrated with Al (99·9%; VAW, Bonn, FRG), Al alloy (2·5 wt% Mg, 5 wt% Si, 1 wt% Zn; VAW), Ti–39 wt% Al intermetallic (Kobe Steel, Kobe, Japan) and Si (99·99%; H. C. Starck, Berlin, FRG).

A schematic diagram of the gas-pressure infiltration technique applied is shown in Fig. 2. RBSN bodies to be infiltrated were mechanically fixed at the bottom of an Al_2O_3 crucible and covered with a metal plate. Then, the system was heated in a gas-pressure furnace under vacuum to a temperature above the melting point of the metal (Al and Al alloy to between 775 and 900°, Ti–39 wt% Al and Si to 1575°). The application of an Ar gas pressure between 5 and 80 bar for 5 min forced the molten metal to infiltrate the RBSN samples. On cooling, application of pressure was continued until solidification of the melt occurred. An Al-infiltrated

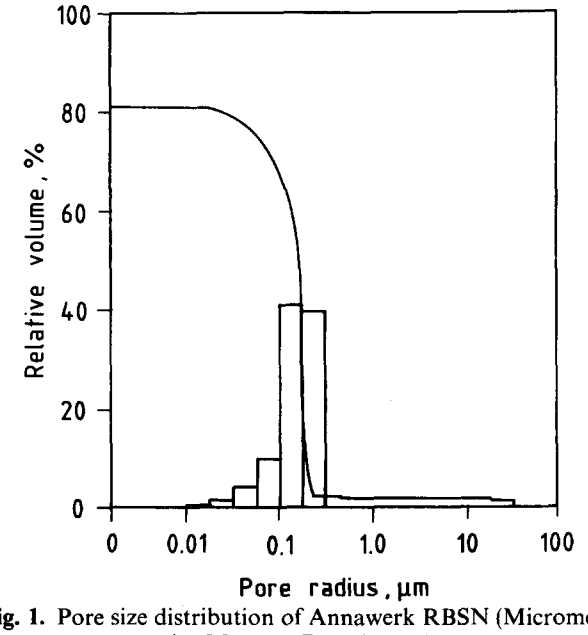

Fig. 1. Pore size distribution of Annawerk RBSN (Micromeritics Mercury Porosimeter).

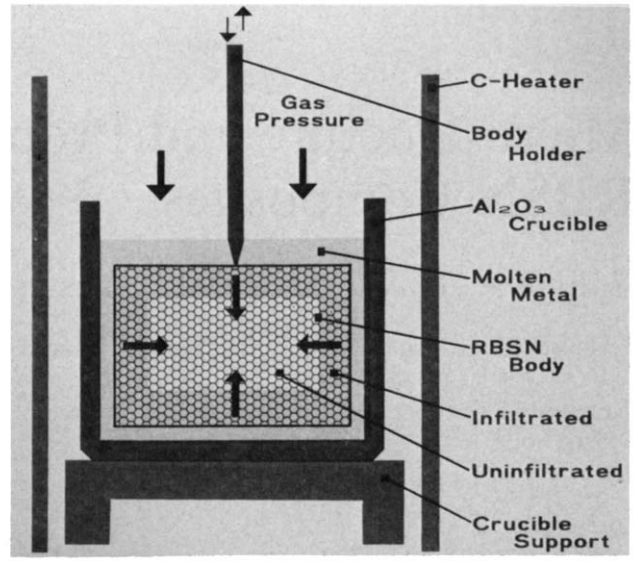

Fig. 2. Schematic diagram of gas-pressure infiltration of RBSN.

RBSN was annealed for 12 h in both air and N_2 at ambient pressure.

Bending strength of uninfiltrated and infiltrated bars (3 mm × 4 mm × 34 mm) was measured by four-point bending using spans of 30 and 10 mm. Fracture toughness was measured by the indentation strength in bending (ISB) technique.[14] The indented samples (load 100 N) were broken in three-point bending with a 16 mm span. The tensile surface of the samples was polished to a 1 μm finish. The crosshead speed was 10 μm min^{-1} in all cases. For comparison, the fracture toughness by the indentation crack length (ICL) technique[15] was also determined. The Vickers microhardness was measured for all samples using a load of 100 N. Wear properties of uninfiltrated and infiltrated samples (3 mm × 4 mm × 4·5 mm) were measured using a pin-on-disc technique with 180 mesh (70 μm) and 600 mesh (15 μm) SiC papers.[16] The composites were analyzed by XRD, SEM and optical microscopy.

3 Results and Discussion

3.1 Infiltration of RBSN with molten metals

Nearly complete infiltration of all RBSN types with Al and Al alloy was obtained at pressures ≥40 bar applied for 5 min at 900°C. The threshold pressure P which is necessary to move the molten metal along the pores depends on the surface tension of molten metal γ, the wetting angle Θ and pore diameter d:[17]

$$P = -\frac{4\gamma \cos \Theta}{d} \quad (1)$$

For example, for the infiltration of pure Al ($\gamma = 1$ J

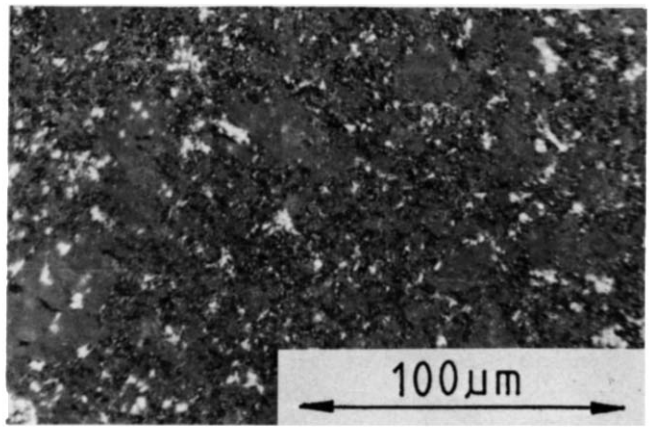

Fig. 3. Microstructure of Al alloy-infiltrated RBSN (Annawerk).

m^{-2})[18] into RBSN (Annawerk, $d \simeq 0{\cdot}16\,\mu m$) at 900°C ($\Theta = 110°$)[19] a threshold pressure at 85 bar would be necessary. The difference between the values of applied and calculated pressure is partially due to a chemical reaction between the molten Al and the RBSN[19] according to:

$$Al + \tfrac{1}{4}Si_3N_4 = AlN + \tfrac{3}{4}Si$$
$$\Delta G_R(1200\,K) = -21{\cdot}97\,kcal \qquad (2)$$

The reaction results in a change of the interfacial free energy and thus the wetting angle. Hence, chemical reaction between Al and RBSN enhances the infiltration. Long-time exposure of RBSN in molten Al, however, can result in a considerable change of the phase composition and in formation of Si_3N_4/AlN or AlN-based composites. In the case of RBSN with micropores $< 0{\cdot}1\,\mu m$, reaction products can prevent further infiltration of the molten Al when the reaction rate is higher than the rate of pressure increasing to the infiltration level. This was true for an experimental fine-porosity ($< 0{\cdot}05\,\mu m$) RBSN supplied by NGK Insulators, Nagoya.

3.2 Microstructure

The microstructure of Al-alloy infiltrated RBSN (Annawerk) is shown in Fig. 3. Similar microstructures were observed for all RBSN–metal composites.

XRD analyses of all uninfiltrated RBSN samples showed the presence of α- and β-Si_3N_4. For Al-infiltrated RBSN (Annawerk), the additional phases that could be detected next to Si_3N_4 and Al were AlN and Si. Traces of AlN, Si and Mg_2Si were detectable in RBSN–Al alloy composites. Traces of TiN and Ti_5Si_3 could be observed in RBSN–Ti–39 wt% Al composites next to Si_3N_4, TiAl and Ti_3Al. XRD analysis of the RBSN–Si composites only showed the presence of α-, β-Si_3N_4 and Si.

RBSN (Annawerk)–Al samples annealed in air and N_2 at 1200°C did not show any sweating out of Al. Rather Al_2O_3 or AlN, respectively, formed to seal off the surface channels.

3.3 Mechanical properties

The mechanical properties of infiltrated RBSN–metal composites are compiled in Table 1. In all cases, the properties of infiltrated RBSN are considerably improved. Al and Al alloy especially enhance the fracture toughness, while Ti–39 wt% Al intermetallic improves bending strength and hardness of RBSN from 227 to 510 MPa and from 5·1 to 15·3 GPa, respectively.

The less porous RBSN (Hoechst CeramTec) exhibits an even greater hardness increase when infiltrated with the Al alloy. The opposite effect is shown by the high-porosity RBSN (Iscar).

Fig. 4 shows the influence of infiltration pressure on mechanical properties of RBSN (Annawerk)–Al alloy composites. From gas pressures >10 bar, bending strength, fracture toughness and Vickers hardness increase with pressure. This is due to

Table 1. Mechanical properties of metal-infiltrated RBSN

	Material	*Bending strength (mPa)*	*Fracture toughness ($mPa\sqrt{m}$)*		*Hardness HV 10 (100N)*
			ISB	*ICL*	
RBSN (Annawerk)	Not infiltrated	227 ± 15	2·70 ± 0·15	—	510
	Al alloy	450 ± 18	4·52 ± 0·11	5·23 ± 0·15	1 170
	Al (99·9%)	478 ± 15	5·00 ± 0·20	5·58 ± 0·14	1 100
	Si (99·99%)	427 ± 20	3·90 ± 0·20	4·74 ± 0·11	1 530
	Ti–39 wt% Al	510 ± 20	n.m.	4·90 ± 0·50	1 524
RBSN (Hoechst)	Not infiltrated	n.m.	n.m.	—	550
	Al alloy	n.m.	n.m.	5·00 ± 0·08	1 340
RBSN (Iscar)	Not infiltrated	n.m.	n.m.	—	216
	Al alloy	n.m.	n.m.	4·15 ± 0·10	900
	Si (99·99%)	n.m.	n.m.	3·60 ± 0·20	960

n.m. = not measured.

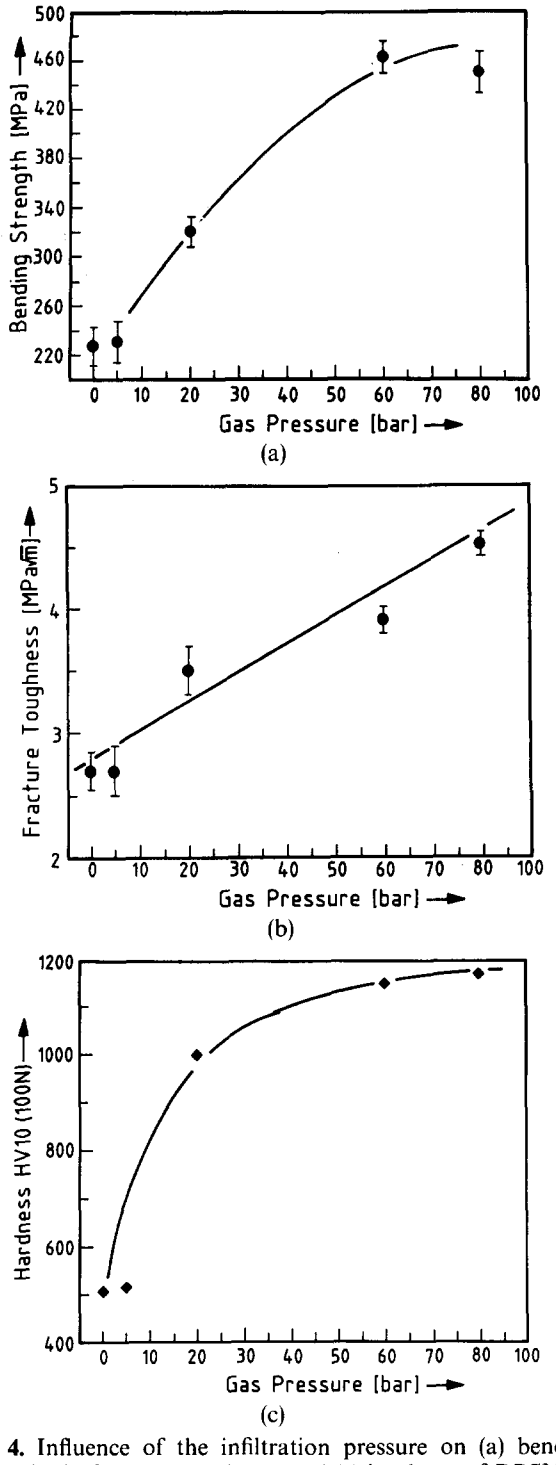

Fig. 4. Influence of the infiltration pressure on (a) bending strength, (b) fracture toughness and (c) hardness of RBSN–Al alloy composites.

increased filling of the pores. Application of pressures ≥ 40 bar resulted in a twofold improvement in mechanical properties of the composites when compared to the uninfiltrated material.

The toughness increase of RBSN–Al, RSBN–Al alloy or RSBN–Ti–39 wt % Al composites is clearly related to crack bridging by the ductile phase, as demonstrated in Fig. 5(a). The dominant contribution to the fracture toughness is the plastic deformation of the ligaments as demonstrated in

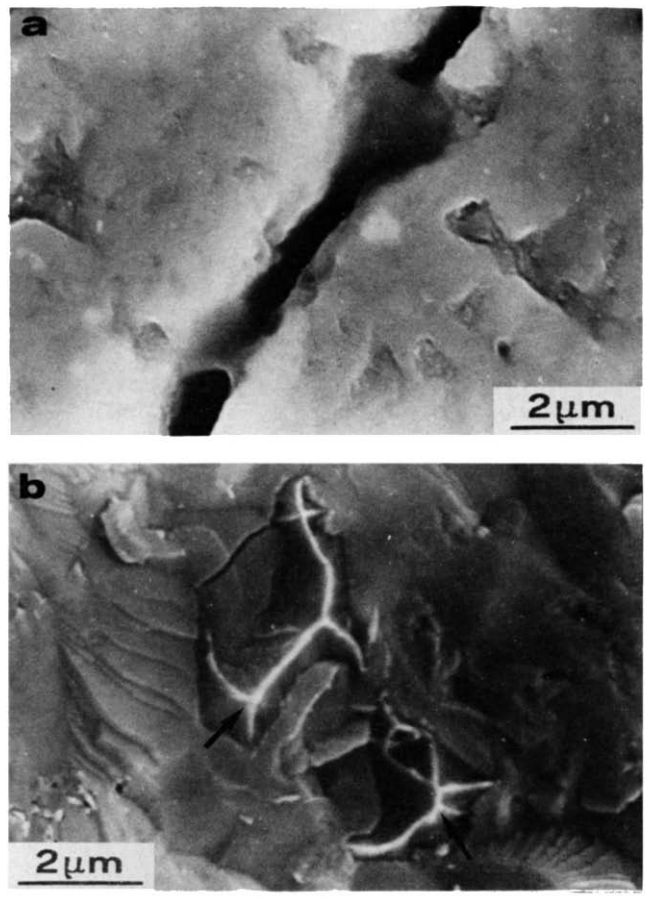

Fig. 5. (a) Bridging Al ligaments and (b) fracture surface of such ligaments in RBSN (Annawerk)–Al composite. Al has plastically deformed to sharp edges (arrows).

Fig. 5(b). The Al phase has necked down to sharp edges (see arrows in Fig. 5(b)).

The enhanced properties of RBSN–Si partially be explained by the microstress concept.[20,21] Compressive residual microstresses are generated in the weak Si phase resulting mainly from the relative volume increase of Si on solidification. Wear resistance to SiC (180 mesh) paper abrasion increased up to a factor of 7 when Si was infiltrated into Annawerk RBSN.[16]

4 Conclusions

Gas pressures >40 bar are necessary to fully infiltrate RBSN with Al, Al alloys and Si. Strength, toughness, hardness and wear resistance are considerably improved when compared to the matrix material. Crack bridging is the dominant toughening mechanism for the Al- and Al alloy-containing RBSN, while residual microstresses are thought to be the major contributing mechanism in RBSN–Si composites. It is assumed that surface sealing of infiltrated RBSN by air or N_2 annealing will further improve the wear resistance.

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