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The Infiltration of Cobalt Silicides into Silicon Carbide Preforms

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Abstract

The wettability of SiC by cobalt silicide, Co saturated and Ti doped cobalt silicide was investigated by measuring the contact angles and calculating the surface tensions in order to access the possibility of using them to form CoSi/SiC composites by cobalt silicide infiltration. Spontaneous infiltration of SiC powder preforms was accomplished at 1600°C. The inftration process is analysed. The microhardness and fracture toughness of the infiltrated samples were measured and are reported. Published by Elsevier Science Limited.

Introduction

Metallic melt infiltration into porous SiC preforms could be an attractive and economic process capable of synthesizing fully dense, near-net-shape ceramic composites. Infiltration is driven by the capillary pressure resulting from good wetting of the ceramic material by the metal melt. An inherent difficulty encountered for the wide use of this technique is that many molten metals do not wet SiC. A common approach to overcome this problem is to physically force the melt in by applying pressure.[1] Because of practical reasons, the applied pressure is not very high (< 1 MPa) so that a poorly wetting metal cannot penetrate pores below a limiting size and residual porosity usually persists.[2] Poor wetting of aluminium metal to SiC preforms has been found and it was also found that an aluminium–silicon alloy was effective on promoting wetting and spontaneous infiltration of silicon carbide preforms in air.[3] Furthermore, it has been reported that coating the preform components with certain metals also helps to improve wetting, and pressureless infiltration may be realized.[4] Another problem with metal melt infiltration into SiC preforms is that most transition metals react with SiC to produce metal silicides and free carbon or metal carbides and free silicon[5,6] so that most conventional metals can not be used as infiltrants.

Many people have been trying to look for good infiltrants capable of infiltrating through porous ceramic preforms. Hilling[7] reported infiltration of molten CaF_2, $CaSiO_3$ and $SrSiO_3$ into particulate and whisker SiC. Gonzalez and Trumble[8] recently reported spontaneous infiltration of alumina by copper–oxygen alloys. Many intermetallic compounds have excellent high-temperature oxidation resistance and have a higher yield strength than their metal components. Possible infiltration of intermetallic compounds into recrystallized SiC has been investigated by Rawers and Wrzesinski[9]. According to their work, intermetallics, such as Ni_3Al, Fe_3Si and TiAl, can be chosen as candidate materials for infiltration of SiC preforms. For the infiltration of ceramics, the details of the infiltration process, the formation of defects during infiltration and the mechanical behaviour of infiltrated bodies have been less reported.

In a study of the chemical instability of SiC in the presence of transition metals, Pan and Baptista[5] have found that CoSi, an intermetallic, is thermodynamically the most favorable product of the reaction of SiC with cobalt. In this work, the wettability of stoichiometric CoSi and of CoSi saturated with excess Co, CoSi(Co) and containing excess Ti, CoSi(Ti) has been studied and spontaneous infiltration of SiC by the respective melts has been attempted. The progress of the infiltration is described. The microhardness and the indentation fracture toughness of the infiltrated samples were measured.

Experimental

The SiC powders used in the infiltration study are described in Table 1. SiC powders with average size bigger than 1 μm were pressed unidirectionally into

Table 1. SiC powders used in this study

Source	*Type*	*Average size (μm)*	*Size distribution*
H. C. Starck	UF-15	0·3	Narrow*
H. C. Starck	UF-05	0·5 and 0·8	Bimodal*
GMBH	NF-0/860	1	Narrow*
NORTON	F-1200	2·5–3·5	Wide bimodal
SIKA	F-1200	3·0	Narrow
SIKA	F-1000	4·5	Narrow
SIKA	F-800	6·5	Narrow

*Measured in our laboratory by using Zetasizer 4 (Malvern). Others from the sources.

disks of 20 mm diameter and 4–6 mm thickness and further pressed isostatically at 280 MPa. The finer SiC powders were shaped into preforms of 25 mm diameter and 4–6 mm thickness, by slip casting. The channel (pore) size distributions of the SiC disks were determined by the mercury intrusion method on a Pore Sizer 9320 (Micromeritics).

CoSi, CoSi(Co) and CoSi(Ti) were prepared by melting the mixtures of Co (powder 99·9% purity, Merck), Si (powder 99·0% purity, H. C. Starck) and Ti (powder ball milled from sponge 99·5% purity, Merck) in the adequate proportions (equimolar mixture of Co and Si, 5 wt% extra of Co added to the equimolar mixture of Co and Si and 5wt% of Ti added to the equimolar mixture of Co and Si, respectively, at 1600°C for 100 min in a grafite furnace with argon flow. Homogenized ingots of CoSi, CoSi(Co) and CoSi(Ti) were analyzed by both wet chemical analysis and X-ray diffraction. The results are shown in Table 2. Extra Co and Ti were found to be dissolved in CoSi.

The equilibrium melting point of pure CoSi is 1450°C according to the phase diagram. The melting points as well as the wetting angles of our three cobalt silicides were determined by sessile drop experiments done also in the grafite furnace. The furnace was heated up quickly to 1300°C and then slowly at the rate of 5°C min^{-1}. During the heating period the shape of the ingot placed on the top of a sintered SiC plate was observed and the contact angles were measured through the furnace window. The infiltration experiments done in an argon atmosphere were performed in the same furnace using three methods. The three infiltration methods are schematically shown in Fig. 1. Methods 1 and 2 are called direct infiltration because the melt directly touched the samples, and method 3 is called indirect infiltration because the melt infiltrated in through a small SiC column supporting the sample to be infiltrated. In method 3, the melt supply to the sample was effectively limited. The heating program was the same for all the infiltrations, the samples being heated up to 500°C at 20°C min^{-1}, kept at this temperature for 30 min to get rid of the organic binders, then again heated until 1400°C at 20°C min^{-1} followed by another dwelling for 5 min.

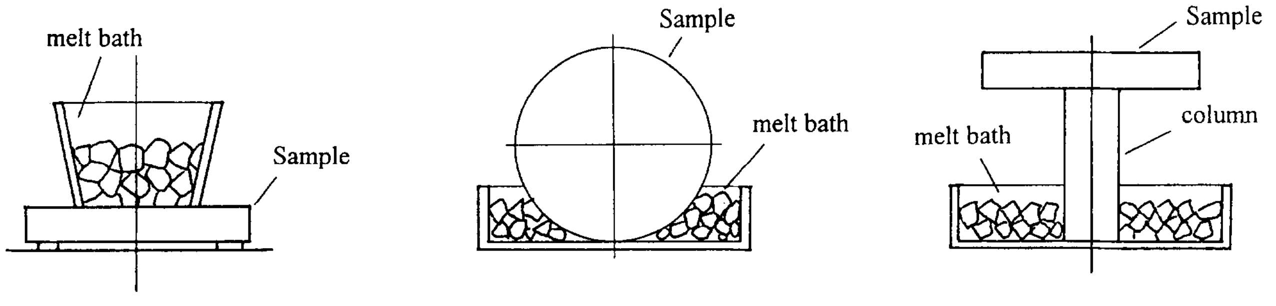
The samples were further heated at 5°C min^{-1} up to 1600°C with a soaking at this temperature for 2 h. During cooling, the electric power supply was off and the cooling water was on.

The infiltration degree f, defined as the percentage of the original porous space filled by cobalt silicide, was determined by the following equation:

$$f = \frac{\rho_s - 3{\cdot}2\rho}{\rho_a(1-\rho)} \qquad (1)$$

Table 2. Chemical and phase compositions of the cobalt silicides used for the infiltration

Cobalt silicide	*Co (wt%)*	*Si (wt%)*	*Ti (wt%)*	*Phase*
CoSi	67·81 ± 2·60	32·20 ± 0·75		CoSi JCPDS#8-362
CoSi(Co)	70·75 ± 3·54	29·25 ± 1·67		CoSi JCPDS#8-362
CoSi(Ti)	67·93 ± 3·10	27·79 ± 1·65	4·31 ± 0·14	CoSi JCPDS#8-362



Method 1 Method 2 Method 3

Fig. 1. Schemes of methods 1, 2 and 3 used in the infiltration studies.

where ρ_s is the density (g cm^{-3}) of the infiltrated sample, ρ is the relative green density of the preform in percentage, ρ_a (g cm^{-3}) is the density of the pure solid infiltrate. ρ_s, ρ and ρ_a were measured by Archimedes' method in mercury; 3·2 g cm^{-3} is the theoretical density of SiC.

Fracture surfaces of partially and fully infiltrated samples were observed by scanning electron microscopy (SEM) (S-4100, Hitachi) with secondary electron radiation. Fully densified samples were polished with diamond paste of 15-, 6- and 1-μm on a standard metallographic wheel to achieve mirrorlike surfaces finish. Vickers hardness and indentation fracture toughness of infiltrated samples and of three pure ingots were measured by using a microhardness testing machine (Shimadzu MHT) at 500 g load for 15 min. A total of 15 indentations were made on each of five samples prepared under the same conditions and the value reported is the average of them. Microstructures of polished surfaces were also examined using an optical microscope.

Results and Discussion

Wettability and surface tension

During the sessile drop experiments, it was found that the three silicides, CoSi, CoSi(Co) and CoSi(Ti) started to melt at 1453,1440 and 1437°C and became complete liquid drops at 1460, 1458 and 1448, respectively. The wetting angles (θ) of CoSi, CoSi(Co) and CoSi(Ti) to the sintered SiC plates measured in the range 1450–1600°C are summarized in Table 3. All the three cobalt silicides steadily wet SiC, the wettability being slightly enhanced by the addition of either Co or Ti, especially by Ti. Complete infiltration of CoSi and CoSi(Co) into porous SiC took place at 1600°C. For CoSi(Ti), complete infiltration was accomplished at 1575°C.

Specific surface energies, γ_{lv}, of liquid CoSi, CoSi(Si) and CoSi(Ti) were approximately determined by a melt-climbing-up method described bellow. During infiltration by method 3 (Fig. 1), the melt infiltrated ($f \geq 98\%$) through the small column made of F800 standing at the center of the melt bath. The rest melt climbed up along the column surface and froze after cooling down as shown by the dark area in Fig. 2. We assume that the net weight of the melt-climbing-up was balanced by the liquid surface tension. Therefore, the following equation was used to calculate the liquid surface tension

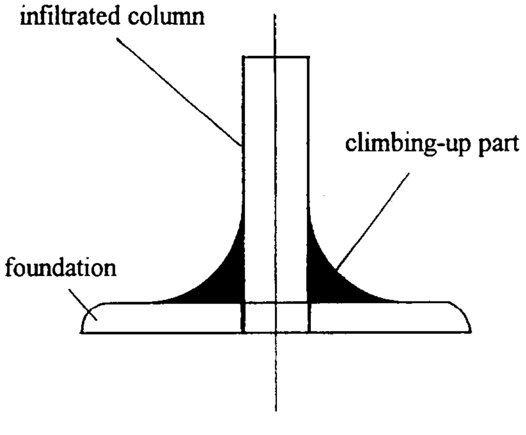


Fig. 2. Climbing-up part of infiltration melt along a column surface, shadowed.

$$\gamma_{lv} = \frac{W_t - W_c}{\pi \rho d \cos \theta} \qquad (2)$$

where d is the diameter of the column, W_t is the weight of the whole piece after the remaining foundation was completely removed by simple grinding and W_c is the weight of the infiltrated column which was calculated from its dimensions and infiltration degree. $W_t - W_c$ is the net weight of the climbed up part (dark area in Fig. 2); ρ is the green density of the small column. θ was always found to be 0 so that the calculated surface tension should be the value for the infiltration temperature (1600°C). This is true because the cooling rate (fast cooling water and no power supply) was high enough to freeze almost everything that occured at infiltration temperature. The calculated results are summarized in Table 4. Each value was an average of four samples.

Table 4 indicates that Co and Ti make their own contributions to the γ_{lv} of liquid CoSi changing the γ_{lv} values from 1348 to 1682 and 1767 mN m^{-1}, respectively. These values are very high when compared with the values for most molten metals and alloys, higher than pure liquid Si (865 mN m^{-1}), but lower than pure liquid Co(1873 mN m^{-1}).[10]

Table 3. Wetting angles of the three infiltrates to sintered SiC plates

Temperature (°C)	*1450*	*1480*	*1500*	*1520*	*1560*	*1575*	*1600*
CoSi	120°	80°	45°	30°	15°	≤5°	≈0° infiltrated
CoSi (Co)	100°	80°	60°	20°	10°	≤5°	≈0° infiltrated
CoSi (Ti)	90°	75°	30°	10°	≤5°	≈0° infiltrated	≈0° infiltrated

Table 4. Surface tensions of liquid cobalt silicides

Silicides	W_t *(g)*	W_c *(g)*	*d (mm)*	*γlv* $(mN\,m^{-1})$
CoSi	9·0461	6·7894	10	1348
CoSi(Co)	10·1713	7·3678	10	1682
CoSi(Ti)	8·7972	5·8526	10	1767

Infiltration process

The mercury intrusion data of the SiC preforms for the infiltration study are shown in Table 5. The mercury pressure is referred to peak values to fill 90% of total pore volume.

The SiC preforms listed in Table 5 were infiltrated at 1600°C for 2 h with CoSi, CoSi(Co) and CoSi(Ti) melts using the three infiltration methods. Results are collected in Table 6, in which the infiltration degree is an average over four samples made exactly in the same conditions.

CoSi(Ti) can infiltrate into all the preforms, but CoSi and CoSi(Co) can only infiltrate through the preforms the mean pore size of which are larger than 0·65 μm (F1200 Norton) and 0·2 μm (UF-05), respectively. This correlates with the best wettability of CoSi(Ti) (Tables 3 and 4). In samples that were not infiltrated by the liquid, a thin silicide skin, coating the whole sample, was always found. This was caused by the spreading of the melt over the surface at infiltration temperature. Complete coating will stop the infiltration because the gas inside the sealed sample cannot get out. Partial coating will also results in a high resistance to gas removal, slowing down the melt intrusion and as soon as the surface is completely sealed by the continuous coating the infiltration process will stop.

Method 3 always gave the highest infiltration degree and method 1 the lowest. Method 3 supplied the melt to the sample at a lower rate and probably the melt spread over the bottom surface of the sample was less than or just enough to infiltrate through even the finest particle preforms.

The infltration process has been modeled by Delannay *et al.*,[11] the capillary pressure, P, is given by Laplace–Young equation:

$$P = \frac{2\gamma_{lv} \cos \theta}{r} \tag{3}$$

and also modeled by Darcy's law[12]

$$h^2 = \frac{D\gamma_{lv} \cos \theta (1-\rho)^2}{15\eta\rho} t \tag{4}$$

where η is the melt viscosity, h the infiltration distance and t the infiltration time. The other parameters are the same as indicated before. They may be substituted with the conesponding values in Tables 4 and 5. The results show that the value of P for the three cobalt silicides in the seven SiC preforms are all over twice as much as the mercury pressures (Table 5) necessary for mercury intrusion into the pores of 90V%. The infiltration distance h after 2 h of CoSi (with the lowest γ_{lv}) in UF-15 (smallest D) is calculated to be about 31 mm by taking η as $2\,mN\,s\,m^{-2}$ (typical viscosity of molten metallic materials). But the real situation was that CoSi did not infiltrate into the preforms the particle size of which was smaller than 3 μm (Table 6). Even for CoSi(Ti) and coarse SiC preforms (ϕ20×4–5 mm), the complete infiltration always took about 2 h, much longer than the 20 min

Table 5. Mercury intrusion data of SiC preforms

No.	*SiC*	*Mean particle size D (μm)*	*Green density ρ (%)*	*Mean pore size 2r (μm)*	*Mercury pressure (MPa)*
1	Sika F800	6·5	51·51	2·0	1·323
2	Sika F1000	4·6	52·00	1·28	1·999
3	Sika F1200	3·0	51·13	0·65	3·993
4	Norton F1200	2·5–3·5	56·06	0·06–0·225	10·611
5	H.C.S. UF-05	2·0	57·73	0·20	13·265
6	GMBH NF 0/860	1	55·99	0·143	18·475
7	H.C.S. UF-15	0·5	55·72	0·06	42·809

Table 6. Infiltration degrees (%) of SiC preforms by CoSi, CoSi(Co) and CoSi(Ti) using infiltration methods 1, 2 and 3

SiC preform	*Sika F800*			*Sika F1000*			*Sika 1200*			*Norton F1200*			*H.C.S. UF-0·5*			*GMBH NF 0/860*			*H.C.S. UF-15*		
Method	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
CoSi	96	98	99	95	95	98	70	82	82	90	95	97	—	—	—	—	—	—	—	—	—
CoSi(Co)	95	95	99	96	93	97	72	86	85	92	94	97	85	89	93	—	—	81	—	—	—
CoSi(Ti)	94	95	99	89	93	98	75	87	88	84	89	97	81	87	97	78	83	96	70	78	90

calculated by using eqn (4). These results may suggest that the infiltration controling factor is the gas pressure built-up during melt intrusion when the capillary pressure is very high.

Morphology study

Figure 3(A)–(C) are pictures taken under the optical microscope showing typical morphologies of polished surfaces with indentations of F800, NFO/860 and UF-15 samples infiltrated with CoSi(Ti). They were basically dense and a few pull outs can be seen. The SiC particles were fairly distributed within the matrix, even in the sample of UF-15 [Fig. 3(C)].

Figure 4(A)–(C) are SEM pictures of typical morphologies of fracture surfaces of similar samples. Bare SiC particles were never found and the broken surfaces were all along the matrices,

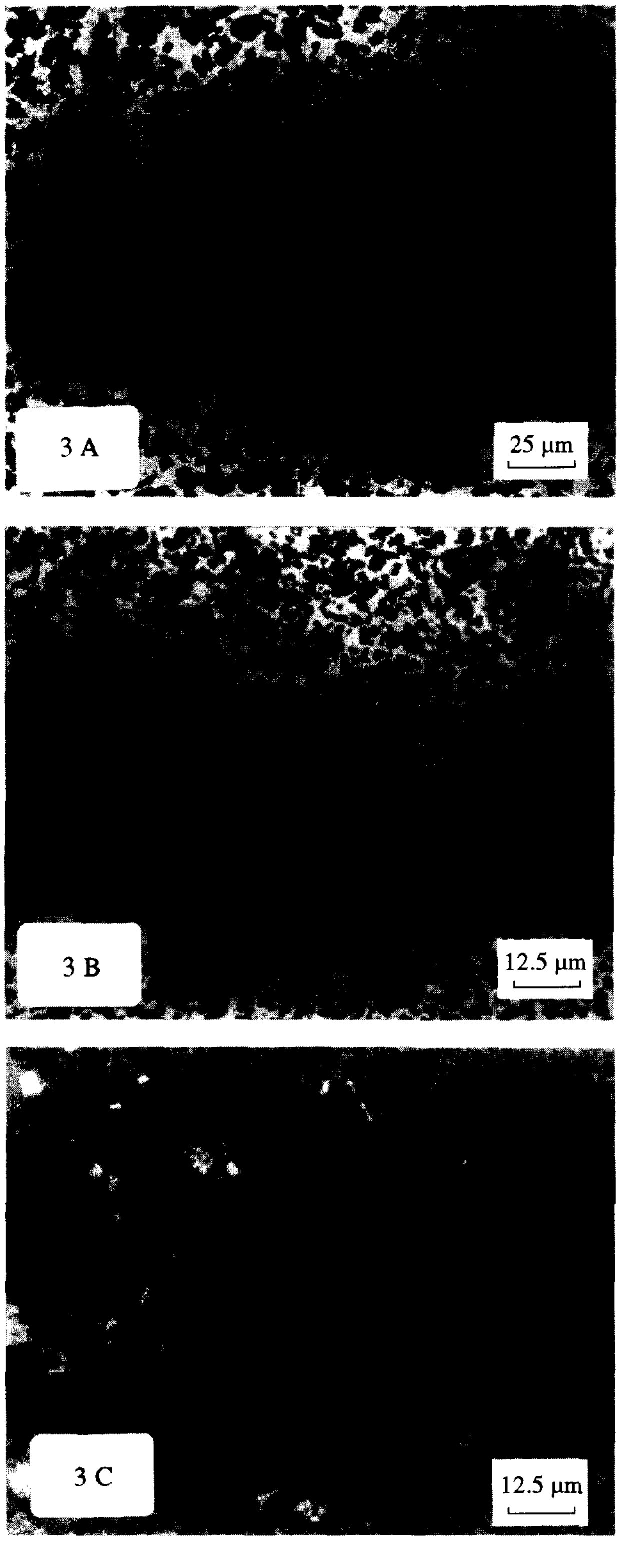


Fig. 3. Polished and indented surfaces of infiltrated samples under optical microscope: (A) infiltrated F800; (B) infiltrated NF 0/860; (C) infiltrated UF-15.

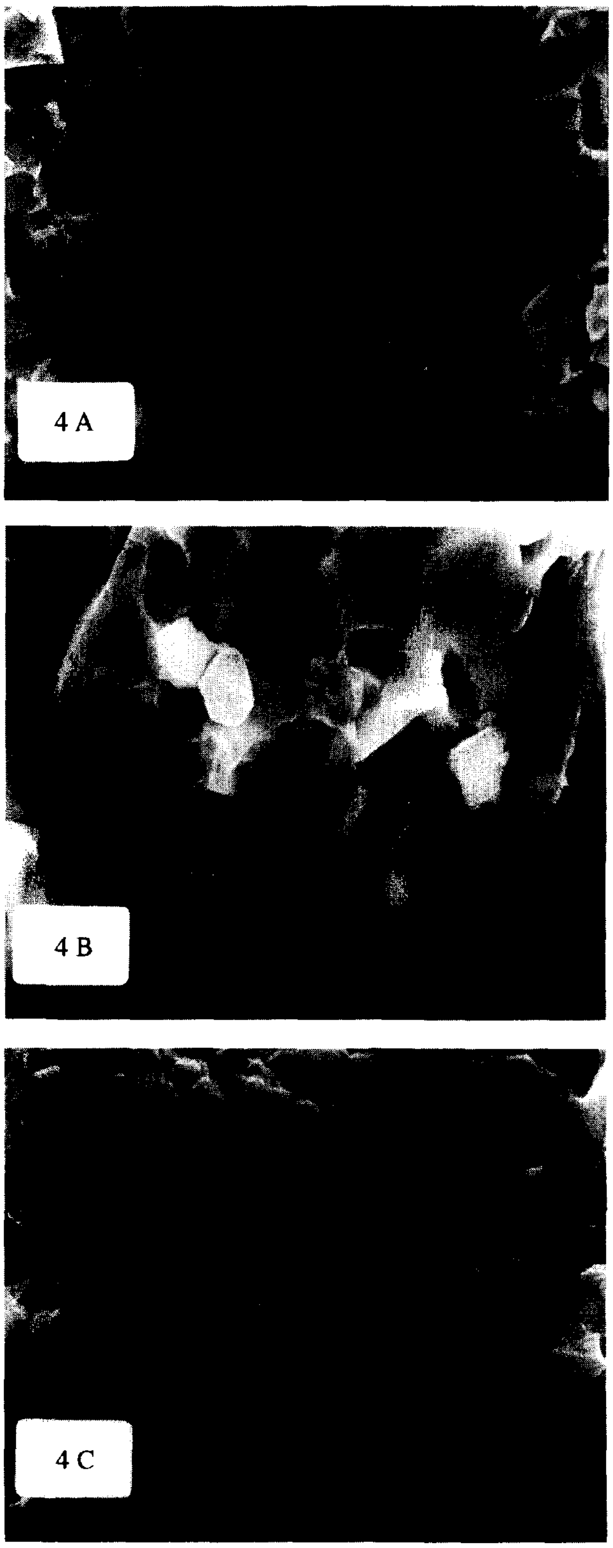


Fig. 4. Fracture surfaces of infiltrated samples observed under SEM: (A) infiltrated F800; (B) infiltrated NF 0/860; (C) infiltrated UF-15.

Fig. 5. Infiltration front of UF-15 partially infiltrated by CoSi(Ti).

indicating that the bonding between the two components was stronger than the matrix itself. Infiltration fronts were also studied under SEM and one is shown in Fig. 5. It can be seen that the SiC particles in the infiltration front were wrapped by melt and those wrapped particles joined one another. This suggests that infiltration proceeded first by melt wrapping of SiC particles, and then by melt filling the interstices between wrapped particles. A distinct infiltration front, such as reported by Aghajanian *et al.*[13] and Einset[14] was never found in this study.

X-ray diffraction analysis indicated that the infiltrated composites contained only SiC and cobalt silicides, no obvious chemical reactions between SiC and the melts were detected.

Indentation microhardness and fracture toughness

Typical indentations made on the microhardness testing machine were shown in Fig. 3. The microhardness and indentation fracture toughness of the CoSi(Ti) samples infiltrated by method 3 are presented in Table 7, in which the microhardness and the fracture toughness of the CoSi(Ti) ingot are also listed for comparison. The indentation fracture toughness was calculated by using the curve-fitting equation proposed by Landford.[15] The Young's modulus was estimated as 400 Gpa through a current study on the mechanical behaviour.

The microhardnesses of all infiltrated samples are higher than that of the pure CoSi(Ti) ingot, which means that the SiC particles effectively reinforced the CoSi(Ti) matrix. The reinforcement is more effective for the finer SiC particles. One exception was the samples of Sika F1200. They could not be polished and appeared to have poor bonding. The reason for this behaviour was not investigated but it may be due to unfavorable surface conditions of the powders.

Indentation fracture toughness, also shown in Table 7, increased as the particle sizes of the preforms were smaller. UF-15, the finest SiC powder was an exception, probably due to the lower infiltration degree. Toughening of CoSi(Ti) by SiC particles occurs only in some samples. Pure CoSi(Ti) had a fracture toughness of 4·12 MPa m$^{1/2}$, higher than F800 and F1000. It should be noticed that the microhardness and the fracture toughness reported in this paper were the properties of as-infiltrated samples. It is to be expected that mechanical properties can be improved by a careful control of the solidification process. Solidification control may include variations in the cooling program and heat treatments post-infiltration.

Conclusion

CoSi, CoSi(Co) and CoSi(Ti) melts can steadily wet SiC with almost zero contacting angles and high surface tensions. They are excellent infiltrates capable of spontaneously infiltrating into various SiC preforms. The infiltration process seems to start by melt spreading and coating of the sample surface followed by inward sinking. The spreading of the melt over the sample surface has to be inhibited in order to avoid an early coating of the samples which will prevent the gas inside the samples from getting out. Indirect infiltration overcomes this problem and is an effective way to obtain well infiltrated samples. The study on microhardness and indentation fracture toughness shows that the infiltrated composites have values comparable with some other structural materials.

Table 7. Microhardness and indentation fracture toughness of infiltrated SiC/CoSi(Ti)

SiC→	*F800*	*F1000*	*F1200*	*N.F1200*	*UF-05*	*0/860*	*UF-15*	*CoSi(Ti)*
Particle size (μm)	6·5	4·6	3·0	2·5/3·5	2·0	1·0	0·5	
Channel size (μm)	2·00	1·28	0·65	0·06/0·23	0·20	0·14	0·06	
Green density (%)	51·51	52·00	51·13	56·06	57·73	55·99	55·72	
Infiltration degree (%)	99·12	97·95	88·06	97·40	95·83	96·27	85·46	
H_v (kg mm^{-2})	1422	1960	—	2209	1895	2317	3300	1089
K_{Ic} (MPa m$^{1/2}$)	3·56	3·67	—	4·43	4·94	5·48	4·79	4·12

References

1. Lange, F. F., Velamakni, B. V. and Evans, A. G., Method for processing metal-reinforced ceramic composites. *J. Am. Ceram. Soc.*, 1990, **73**, 388–393.
2. Mortensen, A. and Cornei, J. A., On the infiltration of metal matrix composites. *Metall. Trans.*, 1987, **18A**, 1160–1163.
3. Xi, X. M. and Yang, X. F., Spontaneous infiltration of aluminium–silicon alloy into silicon carbide preforms in air. *J. Am. Ceram. Soc.*, 1996, **79**, 102–108.
4. Chen, Y. and Chung, D. D., Aluminium-matrix silicon carbide whisker composites fabricated by pressureless infiltration. *J. Mater. Sci.*, 1996, **31**, 407–412.
5. Pan, Y. and Baptista, J. L., Chemical instability of silicon carbide in the presence of transition metals. *J. Am. Ceram. Soc.*, 1996, **79**(8), 2017–2026.
6. Negita, K., Effective sintering aids for silicon carbide ceramics: reactivities of silicon carbide with various additives. *J. Am. Ceram. Soc.*, 1986, **69**, C308–C310.
7. Hillig, W. B., Melt infiltration approach to ceramic matrix composites. *J. Am. Ceram. Soc.*, 1990, **71**, C96–C99.
8. Gonzalez, E. J. and Trumble, K. P., Spontaneous infiltration of alumina by copper–oxygen alloys. *J. Am. Ceram. Soc.*, 1996, **79**, 114–120.
9. Rawers, J. C. and Wrzesinski, W. R., Melt infiltration of selected intermetallics into SiC. *J. Mater. Sci. Lett.*, 1990, **9**, 503–505.
10. Smithells C. J. and Brandes E. A., *Metal Reference Book*, 5th ed. Butterworths, London, 1976, pp. 944–947.
11. Delannay, F., Froyen, L. and Deruyttere, A., Review: the wetting of solids by molten metals and its relation to the preparation of metal–matrix composites. *J. Mater. Sci.*, 1987, **22**, 1–16.
12. Tu, W. C. and Lange, F. F., Liquid precursor infltration processing of powder compacts: I, Kinetic studies and microstructure development. *J. Am. Ceram. Soc.*, 1995, **78**, 3277–3282.
13. Aghajanian, M. K., Rocazella, M. A., Burke, J. T. and Keck, S. D., The fabrication of metal matrix composites by a pressureless infiltration technique. *J. Mater. Sci.*, 1991, **26**, 447–454.
14. Einset, E. O., Capillary infiltration rate into porous media with application to silcomp processing. *J. Am. Ceram. Soc.*, 1996, **79**, 333–338.
15. Lankford, J., Indentation microfracture in the Palmqvist crack regime: implications for fracture toughness evaluation by the indentation method. *J. Mater. Sci. Lett.*, 1982, **1**, 493–496.