

Reaction Bonded Silicon Carbide Materials with Favorable Properties for Thermal Management Applications

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Abstract

Composites of silicon carbide (SiC) and silicon (Si) are fabricated by the reactive infiltration of molten Si into preforms of SiC particles and carbon. This product is often referred to as reaction bonded silicon carbide (RBSC). SiC materials are used in many applications due to their favorable properties including high hardness, high thermal conductivity, low thermal expansion and high stiffness. RBSC has the ability to closely match the coefficient of thermal expansion (CTE) of many low CTE components, such as Si-based semiconductor devices and optical devices. This study shows that by incorporating aluminum (Al) and/or titanium (Ti) into the composite, the thermal expansion becomes tailorable, allowing CTE match with Al_2O_3 and AlN based components. Moreover, these alloy additions provide increased thermal conductivity. Additions of Ti and/or Al to these composites can raise the thermal conductivity more than 10 %, while keeping most of the favorable properties of standard RBSC. Herein, the properties of Si:SiC, Al-Si:SiC and Ti-Si/SiC composites are compared, and possible thermal management applications are explored. Properties evaluated include density, Young's modulus, specific heat, thermal diffusivity, thermal conductivity, and thermal expansion.

(Si, SiC, RBSC, Thermal Conductivity, Thermal Expansion, Composite)

Introduction

Silicon Carbide (SiC) based ceramic composites have found wide ranging applications in industry from armor, high hardness and modulus, to wear and mechanical products, stiffness controlled, low stress applications. SiC also provides excellent properties for thermal management applications with high thermal conductivity and low coefficient of thermal expansion (CTE). Discussed herein will be the properties and applications specific to reaction bonded SiC (RBSC) systems.

RBSC ceramic composites are generally made through the infiltration of molten Silicon (Si) into particulate preforms of SiC and Carbon (C). The Si reacts with the C as it infiltrates to form SiC [1-3]. This generally leaves some residual Si. Other alloys can be added to the Si to manipulate properties such as the thermal conductivity and thermal expansion for various applications.

Unlike traditional metals like aluminum (Al) and steel, when Si freezes, it increases in volume. Thus, shrinkage porosity present in traditional cast Al and steel components is not prevalent in RBSC. As SiC is formed by reaction of molten Si and C, a volume increase occurs. By minimizing the reaction formed SiC, however, dimensional changes from the preform stage to the infiltrated component

can be tailorable below 0.5%. This allows for production of net shape components with minimal post processing. The additions of other metals to the molten Si (e.g. Titanium (Ti), Al, etc.) which counter the expansion of Si upon solidification during the infiltration process allows for the production of complex shapes, such as finned structures or components with internal cooling channels [4].

The combined properties of tailorable CTE, high thermal conductivity, high specific stiffness and complex shape capability make RBSC-based materials ideal for implementation into today's advanced thermal management applications. Such properties allow dissipation of heat from demanding sources, such as dense electronic circuitry, without sacrificing weight. Example uses include power module base plates, power amplifier heat sinks, microprocessor lids/heat spreaders, air- and liquid-cooled cold plates (e.g., for electrostatic chucks or linear motors), package bases, and optoelectronic packages.

The objective of this study was to examine the effects alloying additions have on the properties of RBSC.

Experimental Procedures

All of the samples tested and characterized with respect to the properties presented in this paper were made in a similar fashion. A slip was made by mixing SiC powders with a C based binder. The slip was cast into a mold, dried and carbonized. Strong, handlable green parts (4"x4" plates) were then brought into contact with a molten alloy in a vacuum. The plates are differentiated by the various alloys used. These alloys and metals include the following: Si, high purity Si (HPSi), Si-15Ti, Si-20Ti, Si-30Ti, and Si-30Al. The numbers refer to the weight percent metal added to the Si. The regular Si had a purity of approximately 98% Si and the high purity Si had a purity of 99.999%. The infiltrated plates were machined into various sample sizes and characterized for density, Young's modulus, microstructure, flexural strength, fracture toughness, thermal diffusivity, thermal expansion, and specific heat according to the various requirements of the specific tests. The thermal conductivity is also presented.

The physical and mechanical properties were determined by the methods described below. The density was measured using the water immersion technique described in ASTM B 311. The Young's modulus and Poisson's ratio were measured using the non-destructive pulse echo technique presented in ASTM E 494-05. The flexural strength and fracture toughness of these materials were found using the 4-point tests described in ASTM C 1161 and ASTM C 1421, respectively. Both of these measurements were performed on a Sintech universal testing frame with TestWorks materials testing software. Specimens were prepared for microstructural observation via the usual metallographic techniques: cutting, mounting, grinding, and polishing with successively finer and finer diamond pastes. The microstructures were examined on a Leica D 2500 M optical microscope utilizing Clemex Vision PE image analysis software.

X-ray diffraction (XRD) was also performed to determine the compositional make-up of the

samples. A Philips PW1800 diffractometer using copper radiation at 40KV/30mA was used for these measurements. Scans were performed from 10° to 70° with a step size of 0.02°. The *Powder Diffraction File* of the International Centre for Diffraction Data and the *Rietveld Refinement Method* were used to determine the quantitative phase data of the crystalline phases present [5,6].

The methods for measuring and calculating the thermal properties are described below. The CTE was measured using a dilatometer. The specific heat was measured by way of differential scanning calorimetry with a Perkin-Elmer DSC 7. ASTM E 1461-01 describes the laser flash technique that was used to measure the thermal diffusivity. The thermal conductivity was calculated using the following equation:

$$\lambda = \kappa * C_p * \rho \quad (1)$$

where λ is the thermal conductivity, κ is the thermal diffusivity, C_p is the measured specific heat, and ρ is the density.

Results and Discussion

The properties of constituent materials are compared in **Table 1**. The properties are as follows: density (ρ), Young's modulus (E), thermal conductivity (λ), coefficient of thermal expansion (α), and specific heat (C_p). Unless otherwise noted, the values tabulated below represent room temperature values.

The XRD analysis performed shows three different polytypes of SiC, those being 6H, 15R, and 4H. These polytypes match the polytypes found in the starting powders; therefore, polytype phase transformations are not taking place. In the titanium containing samples, a TiSi_2 phase was found.

Microstructures for the Si and Ti containing samples can be found in **Figures 1 to 4**, below.

Table 1: Constituent Material Properties

	Si [Ref.]		Ti [Ref.]		Al [Ref.]		TiSi_2		SiC [Ref.]	
ρ (g/cc)	2.33	[7]	4.51	[7]	2.7	[7]	4.07	[9]	3.21	[10]
E (GPa)	113	[7]	116	[7]	62	[7]	264	[9]	475	[10]
λ (W/m K)	84	[7]	16	[8]	222	[7]	--	--	490	[11]
α (ppm/K)	3.3'	*	7.6"	[8]	23.6"	[7]	8.5'''	[9]	2.3'''	*
C_p (J/kg K)	770	[7]	520	[7]	900	[7]	--	--	670	**

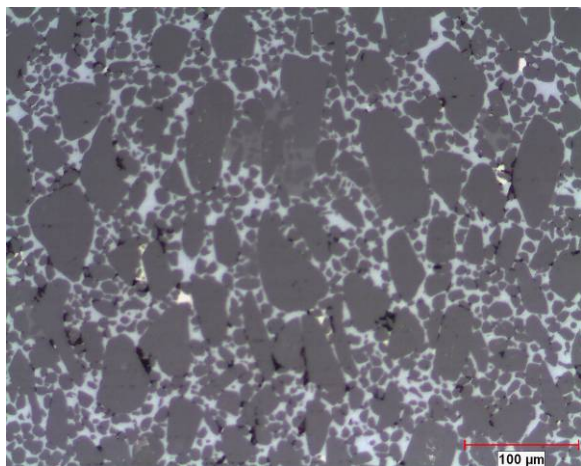
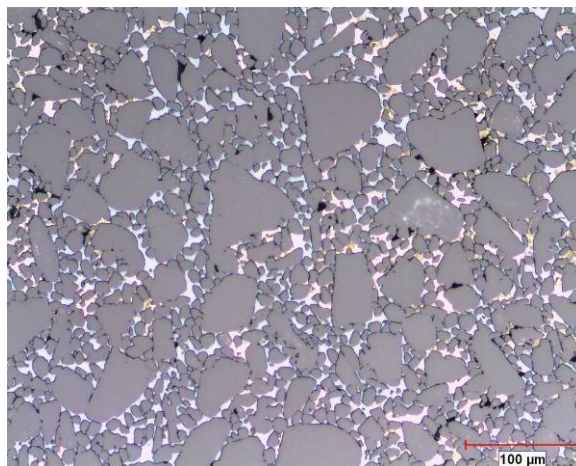
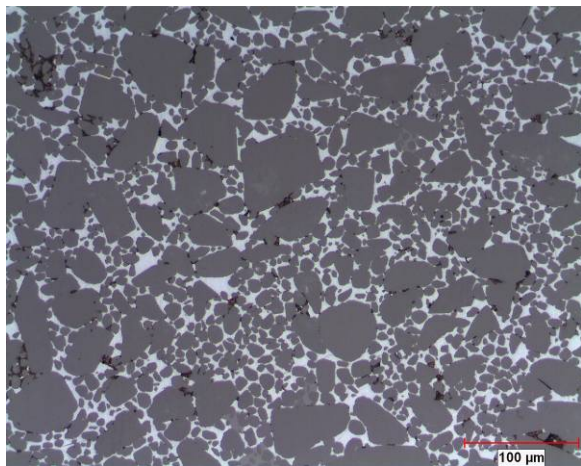
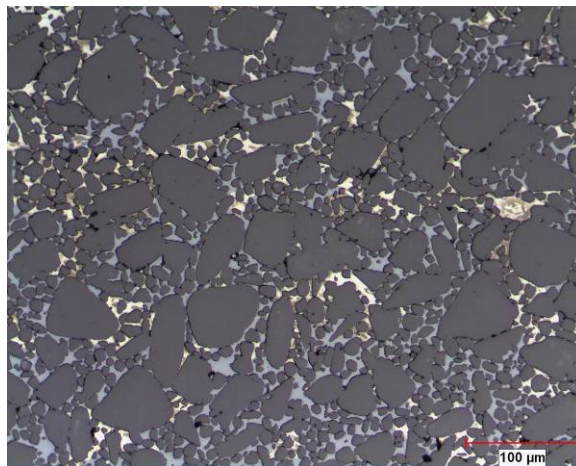
*Measured by M Cubed Technologies, Inc.

**Calculated from condensed phase thermochemistry data for SiC and Si found at <http://webbok.nist.gov>

' 27-127°C; " 20-100°C; ''' 20°C

Table 2: Compositions (weight %) of various composites and starting powders as determined by XRD.

Material Type	SiC			Si	TiSi ₂
	6H	15R	4H		
Coarse SiC Powder	98.8	1.2	0	0	0
Fine SiC Powder	93.3	3.3	3.4	0	0
Si:SiC	84.1	3.1	1.2	11.6	0
HPSi:SiC	84.9	3.3	1.9	9.9	0
Si-15Ti:SiC	80.6	3.5	3.5	6.9	4.2
Si-20Ti:SiC	87.1	3.3	1.1	2.8	5.3
Si-30Ti:SiC	79.8	3.5	3.3	3.1	8.0
Si-30Al:SiC	--	--	--	--	--

**Figure 1: A Si:SiC microstructure is shown above.****Figure 3: A Si-15Ti:SiC microstructure is shown above.****Figure 2: A HPSi:SiC microstructure is shown above.****Figure 4: A Si-30Ti:SiC microstructure is shown above.**

As one would expect, the purity of the Si did not affect the microstructures as each of these is relatively similar. This matches with the similarity in the XRD samples shown above and the density data provided in **Table 3**.

The microstructures of Ti containing RBSC are again very similar. Because of the inherent inaccuracies in discerning the differences in the gray scale gradients during quantitative image analysis, it was not possible to accurately quantify Ti containing phases.

However, as seen in **Table 3** below, the composite density increases as Ti content increased from 0 to 15 to 30 wt. %. The Ti phase present has a higher density than Si leading to a higher composite density, therefore confirming the higher Ti content.

The densities, Young's moduli, and Poisson's ratios of these composites are presented in **Table 3**.

Table 3: Density, Poisson's Ratio, and Young's Modulus

Sample	Density (g/cc)	Poisson's Ratio	Young's Modulus (GPa)
Si:SiC	3.024	0.20	360
HPSi:SiC	3.026	0.19	363
Si-15Ti:SiC	3.111	0.19	371
Si-20Ti:SiC	3.153	0.19	383
Si-30Ti:SiC	3.178	0.19	375
Si-30Al:SiC	3.015	0.22	336

The Si purity did not significantly affect density or elastic properties of the RBSC ceramic. The addition of Al to the system resulted in a decrease in Young's modulus. This is expected based on the lower Young's modulus of Al relative to Si (**Table 1**). It would be anticipated that the Al-containing sample would have slightly higher density than the standard RBSC materials due to the higher density of Al relative to Si. However, slightly lower density is observed. The reason for this is believed to be slight solidification porosity in the Al-containing sample. That is, Si expands upon solidification. Thus, standard RBSC ceramics tend to be fully dense. Al, on the other hand, shrinks upon solidification. This shrinkage can lead to porosity. As expected, the addition of Ti to the system resulted in increases in density and Young's modulus. The higher Young's modulus is due to the fact that TiSi_2 has a higher Young's modulus than Si, as shown in **Table 1**. The drop in Young's modulus as Ti increased from 20 to 30 wt. % in the alloy could be explained by solidification porosity, per above discussion relative to Al (i.e., at high Ti contents, its shrinkage upon solidification can become greater than the counteracting expansion of Si).

The flexural strength and fracture toughness values for each of the systems are plotted in **Figures 5 and 6**. The Si:SiC, HPSi:SiC, and Si-30Al:SiC flexural strength are statistically similar in the neighborhood of 240 to 260 MPa. The Ti containing systems all gave strengths around 200 MPa, much lower than the Si and Al systems.

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The composites containing either just Si or Si and Ti have fracture toughness values right around $4.0 \text{ MPa m}^{1/2}$. The sample with Al has a fracture toughness of $5.5 \text{ MPa m}^{1/2}$, which is due to the increased ductility the Al addition provides to the system.

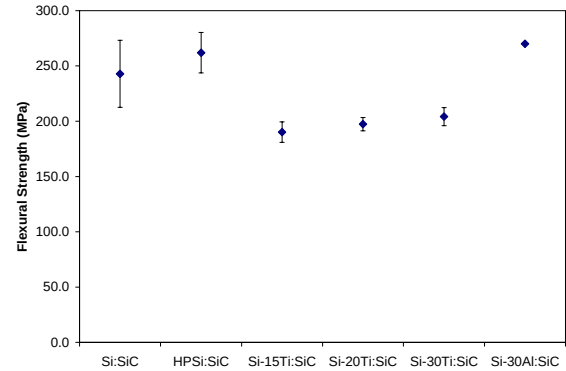


Figure 5: Flexural Strength

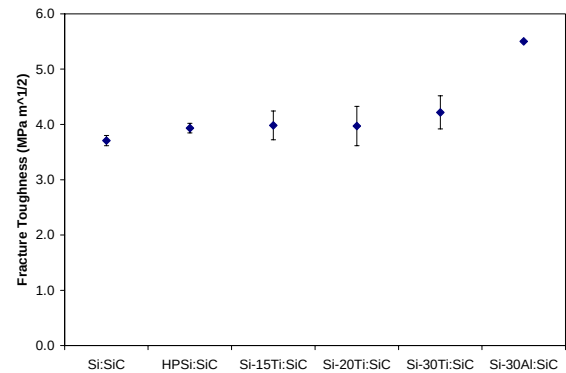


Figure 6: Fracture Toughness

CTE and thermal conductivity data for each of the samples are tabulated below (**Table 4**). The data represent room temperature to 100°C temperature range for comparison purposes.

Table 4: Coefficient of Thermal Expansion Data

	CTE ppm/K
Si:SiC (25° to 100°C)	3.2
HPSi:SiC (25° to 100°C)	3.0
Si-15Ti:SiC (25° to 100°C)	3.4
Si-20Ti:SiC (25° to 100°C)	3.5
Si-30Ti:SiC (25° to 100°C)	3.4
Si-30Al:SiC (25° to 100°C)	4.1

Additions of alloying elements to the Si base are all expected to increase thermal expansion values of the resultant composites. This tailorability allows

matching of other materials. For instance, the addition of Al to the RBSC system allows a good match to AlN which has a CTE of 4.4 ppm/K and Al₂O₃ which has a CTE of 6.5 ppm/K [12]. The trend in CTE's with Ti additions is expected to be increasing; however, due to the minor amounts added and the relatively low CTE of Ti when compared to Al, any trends found can be attributed to noise in the data.

The thermal conductivity data is presented in **Table 5** for several different temperatures from 25°C to 200°C.

Table 5: Thermal Conductivity Data (W/m K)

	25°C	100°C	150°C	200°C
Si:SiC	190	157	133	113
HPSi:SiC	209	171	142	119
Si-15Ti:SiC	203	161	131	107
Si-20Ti:SiC	187	154	129	110
Si-30Ti:SiC	191	157	132	111
Si-30Al:SiC	216	180	153	130

At room temperature it is clear that the HPSi and the Al provide the greatest increase in thermal conductivity. HPSi can have a thermal conductivity as high as 156 W/m K [13]; whereas, the regular Si is closer to 84 W/m K. Also, the thermal conductivity of Al is much higher than Si as well.

Small amounts of Ti seem to increase the thermal conductivity as well. There are two reasons why this is possible. The first is that the Ti is stripping the SiO₂ layer on the SiC [14] allowing for better contact between the phases for thermal conduction. The second reason arises from shrinkage porosity forming upon solidification. The combination of these two events explains the increase in the thermal conductivity with small additions of Ti but not larger additions. Another potential reason the thermal conductivity increases is the formation of the TiSi₂ intermetallic.

Conclusions

Reaction bonded silicon carbide systems were produced with Si, high-purity Si, Si-Ti alloys, and Si-Al alloys. The titanium is present as TiSi₂, as discovered by XRD experimentation. The presence of TiSi₂ or Al in the microstructure provides several useful properties in the ultimate part: the first being the ability to make complex shapes with finned or internal geometries, the second being an increase in thermal conductivity, and the third being tailorable thermal expansion to match other materials.

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