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The role of silicon in wetting and pressureless infiltration of SiC_p preforms by aluminum alloys

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Silicon plays an important role in the production of Al/SiC metal matrix composites. As an alloying element in aluminum, silicon retards the kinetics of the chemical reactions that result in the formation of the unwanted intermetallics Al_4C_3 and Al_4SiC_4. As a thin coating on silicon carbide, silicon becomes an active participant in a thermally activated chemical reaction that enhances wetting of silicon carbide by aluminum alloys. Consequently, Al/SiC composites made with siliconized silicon carbide and silicon rich aluminum alloys show mechanical properties that are significantly different from those of similar composites produced with unsiliconized silicon carbide or with aluminum alloys that do not contain silicon. It is shown that a silicon coating on SiC significantly enhances wetting of SiC particles by aluminum alloys, reduces porosity, does not affect the modulus of elasticity, but decreases the modulus of rupture of Al/SiC metal matrix composites. © *2000 Kluwer Academic Publishers*

1. Introduction

Silicon carbide reinforced aluminum matrix composites have attracted considerable attention in recent years because of their potential to exhibit enhanced mechanical and physical properties in comparison to their individual components [1–3]. However, in order for these composites to achieve their full potential, the SiC/Al interface must be carefully tailored so that adhesion between the SiC and the aluminum alloy matrix is strong. Optimizing the Al/SiC interface requires balancing several factors. While a strong SiC/Al interface may be created by promoting metallurgical bonding between the SiC and the Al through interdiffusion and chemical reactions, extensive interactions may degrade the SiC and reduce the overall properties of the composite. Moreover, because useful aluminum alloys typically contain elements that have a high affinity for silicon and/or carbon, interfacial reactions may occur and result in reaction products with inferior properties. Most of the past effort dedicated to improving wetting of SiC by aluminum has centered on modifying the aluminum with surface-active alloying elements, and/or the SiC by surface coatings [4, 5]. For example, it has been shown that coating SiC particles with K_2ZrF_6 causes a substantial reduction in the magnitude of the threshold pressure required for infiltrating packed beds of the particles with liquid aluminum [6]. It has also been shown that coating SiC with Cu and with Ni improves the SiC/Al interface as reflected in improved mechanical properties [7]. In addition, the use of inert and/or reactive gases during the production of Al/SiC composites has been introduced as a means of controlling chemical reactions and interactions at the Al/SiC interface [5, 8].

In this paper, the effect of silicon additions to aluminum, and silicon coating on the surface of silicon carbide on the wetting characteristics and pressureless infiltration of SiC preforms with aluminum alloys are investigated.

2. Background

Wetting is a term that is commonly used to describe the distribution of liquid on solids. Factors that are important for determining the extent of wetting are easily understood by examining a liquid droplet that is in contact with a flat solid surface. In the idealized case where chemical reactions between the solid, liquid, and vapor phases are negligible, and where the liquid droplet is small enough so that the gravitational force can be ignored, the liquid droplet assumes an equilibrium configuration. This equilibrium configuration is dictated by surface free energy considerations in such a manner that the shape of the liquid droplet is uniquely characterized by θ, its contact angle with the solid substrate. The relationship between the contact angle θ and the surface free energies at the liquid-vapor γ_{lv}, solid-vapor γ_{sv}, and solid-liquid γ_{sl} interfaces is shown schematically in Fig. 1, and is represented mathematically by Young's equation, Equation 1 [9]

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \tag{1}$$

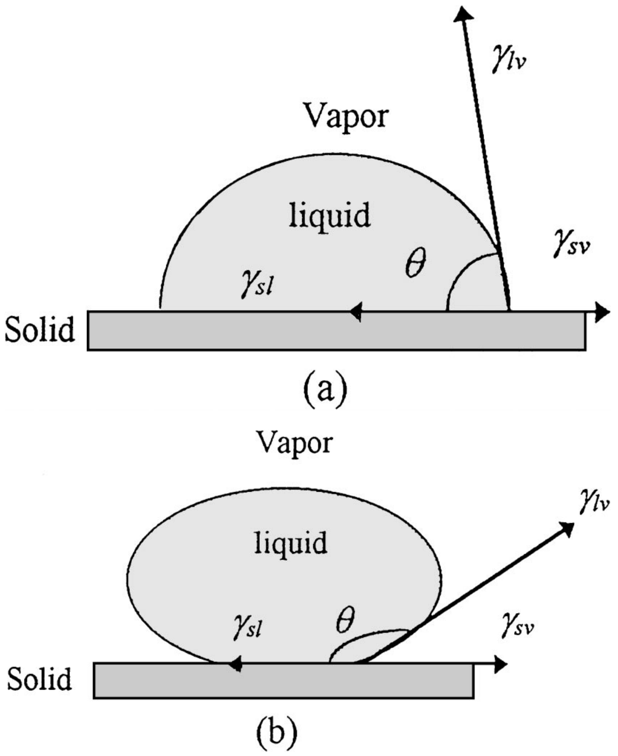

Figure 1 Schematic diagram showing a sessile drop during: (a) wetting and (b) non-wetting.

The boundary between wetting and non-wetting conditions is generally taken as $\theta = 90^\circ$. Wetting occurs when $\theta < 90^\circ$, while $\theta > 90^\circ$ represents a non-wetting condition. Measurement of wetting is usually based on the configuration of a steady state drop of liquid on a flat solid surface. This is referred to as a sessile drop. The extent of wetting is quantified by the magnitude of the contact angle, θ, and the liquid-vapor surface tension which is determined from the shape of the sessile drop using Equation 2 where g is the gravitational acceleration, ρ is the density of the liquid, d_m is the maximum drop diameter, and f is a geometric factor [10].

$$\gamma_{\text{lv}} = \frac{g\rho d_{\text{m}}^2}{4}\left[\frac{0.052}{f} - 0.1227 + 0.0481 f\right] \qquad (2)$$

It is important to realize that whether the contact angle, θ, is acute or obtuse, wetting of the solid by the liquid can be enhanced by a thermally activated chemical reaction at the solid/liquid interface. The contribution of the reaction to wetting may be represented mathematically by modifying Young's equation for a non-reacting, steady state sessile drop (Equation 1) to include the contribution of the free energy of the reaction, ΔF_{r} [11].

$$\gamma_{\text{sv}} - (\gamma_{\text{sl}} + \Delta F_{\text{r}}) = \gamma_{\text{lv}} \cos\theta \qquad (3)$$

However, it is also important to understand that reactions that enhance the liquid/solid interface are only the ones that contribute to the driving force for wetting without creating undesirable reaction products. Dissolution of a component of the solid into the liquid is an example of beneficial interface reactions [12]. In these reactions, the free energy of the reaction at the perimeter of the liquid contributes to the driving force for wetting. As the liquid drop expands, the advancing liquid front maintains contact with unreacted solid and thus the free energy of the reaction continues to contribute to the driving force for wetting.

3. Experiments

3.1. Sessile drop experiments

High purity, flat, 5 cm × 5 cm × 1.6 mm rectangular CVD silicon carbide substrates were used in all sessile drop experiments. When needed, a 0.28 mm thick electronic grade silicon wafer that represents 10% of the alloy's weight was placed on top of the SiC substrate. Prior to each test, cubic pellets weighing 6 ± 0.1 grams were cut from an aluminum alloy ingot and thoroughly polished with 400 grit SiC paper. The pellets and the SiC substrates were ultrasonically cleaned in acetone before use. Tests were performed in a horizontal tube furnace with a 6.5 cm diameter alumina tube that was closed at both ends with end-cap fittings. A K type thermocouple was inserted in one end of the tube, while at the other end an optical window allowed video recording and photography. Both end fittings were sealed with O-rings and are capable of maintaining a vacuum of at least 3.5×10^{-2} atm. The system was run at a very slight overpressure to ambient, and the test specimens were heated at a rate of 15°C/min until a soak temperature of 1235°C was reached. Once the soak temperature was attained, the specimens were held isothermally for 75 minutes. During this isothermal period, the specimens were photographed every 10 minutes to provide a record of the change in contact angle. Contact angles were measured from enlargements of these photographs. Surface tensions were determined using Equation 2 and geometrical parameters measured on photographs of the static interface obtained during the isothermal period. In addition to measuring the contact angle and calculating the surface tension, the Al/SiC interface was carefully examined using scanning electron microscopy (SEM) and energy disperssive x-rays (EDX). Two types of specimens were prepared for optical and SEM examination: cross sections, and "interface" specimens. The "interface" specimens were prepared by carefully removing the aluminum droplet from the silicon carbide substrate by gradual mechanical polishing with 400-grit silicon carbide paper. The alloys that were used in the sessile drop measurements are shown in Table I.

TABLE I Chemistry of alloys used in the sessile drop experiments

	Si	Mg	Fe	Cu	Zn	Ti	Ni	Other	Al
Alloy #1	0.08	<0.01	0.2	<0.01	<0.01	<0.01	0.01	<0.01	Balance
Alloy #2	14.4	<0.01	0.16	0.01	0.02	0.01	0.01	<0.01	Balance

TABLE II Chemistry of the alloy used in the infiltration experiments

	Si	Mg	Fe	Cu	Zn	Ti	Ni	Other	Al
Alloy #3	13.5	9.0	0.2	<0.01	<0.01	<0.01	0.01	<0.01	Balance

3.2. Infiltration experiments

Industrial grade silicon carbide powder with two differing particle sizes was used to manufacture 20-mm diameter cylindrical preformes with varying heights. A predetermined weight of the SiC powder was thoroughly mixed with 10% starch and 5% wax emulsion. The mix was placed in a steel die and pressed to produce preforms with a predetermined density. A preform, together with about 35 g of aluminum alloy cubes that were ultrasonically cleaned in acetone, was placed in a boron nitride coated ceramic container. Infiltration of these preforms with the aluminum alloys was performed in the same horizontal tube furnace that was used for the sessile drop experiments. The system was run at a very slight over-pressure to ambient and the specimens were heated under ultra high purity argon atmosphere at a rate of 15°C/min up to a soak temperature of 1235°C. Before reaching the soak temperature, the gas was switched to nitrogen and the system was held isothermally under nitrogen for a predetermined time. The nitrogen atmosphere was maintained as the specimens cooled down to room temperature. The infiltrated cylinders were then sectioned longitudinally to produce slabs for microscopic analysis and mechanical property testing. Archimedes' principle was used to calculate the density of the composites. The modulus of elasticity was determined using the ultrasonic technique described in ASTM standard E494-95, and the modulus of rupture was determined using the four-point bend test described in ASTM standard C1161-94. The test bars used to determine the modulus of rupture were "A size" and the tests were conducted on a universal-testing machine* at a rate of 0.2 mm/min. The alloy that was used in the infiltration experiments is essentially the one developed by Pech-Canul *et al.* [13] for enhanced wetting of SiC. This alloy was developed based on information gained from an optimization experiment. The Taguchi method for design of experiments was used and analysis of variance was performed on the data to predict the optimum alloy chemistry. The alloy's chemistry is shown in Table II. In addition to a relatively high silicon content (13.5%), the alloy contains a high level of Mg (9.0%). It has been shown [13, 14] that Mg reduces the surface tension and the contact angle between Al and SiC, and thus its presence in the alloy is essential in pressureless infiltrating SiC_p preforms with aluminum alloys.

4. Results and dicussion

4.1. The role of silicon as an alloying element in aluminum

Silicon is an important alloying element in aluminum alloys that are designed for infiltrating SiC preforms. Silicon additions to aluminum alloys positively affect the alloy's fluidity and reduce its melting temperature. More importantly, silicon influences the potential for chemical reactions between the aluminum alloy and silicon carbide. Aluminum/silicon carbide composites are non-equilibrium systems; consequently, chemical potential gradients exist at the Al/SiC interface. These gradients are a driving force for interfacial reactions that may occur during fabrication of the composites at high temperature. Although some interfacial reactions are beneficial to wetting, others are detrimental. At temperatures above the melting point of Al, and under atmospheric pressure, SiC becomes thermodynamically unstable and an invariant reaction occurs at 923 ± 3K and leads to the formation of aluminum carbide (Al_4C_3) according to Equation 4 [15, 16]. This is one of the most detrimental reactions that may occur during the fabrication of Al/SiC composites.

$$4Al + 3SiC \leftrightarrow Al_4C_3 + 3Si \qquad (4)$$

Not only does this reaction cause the dissolution of the SiC reinforcing particles and result in weakening of the composite, but also Al_4C_3 is unstable and will react slowly with atmospheric moisture to form aluminum hydroxide [15, 17]. This reaction is shown in Equation 5.

$$Al_4C_3 + 12H_2O \rightarrow 3CH_4 + 4Al(OH)_3 \qquad (5)$$

Fig. 2 shows an x-ray diffraction pattern of the Al/SiC interface from a sessile drop experiment performed with the low Si alloy, i.e., Alloy #1 in Table I. Fig. 2 shows that Al_4C_3 readily forms in this system. Fig. 3 is an optical photomicrograph showing the dissolution of SiC in the aluminum alloy at the interface and the resultant Al_4C_3 particles. Fig. 4 shows an x-ray diffraction pattern of the Al/SiC interface from a sessile drop experiment performed with the high Si alloy, i.e, Alloy #2

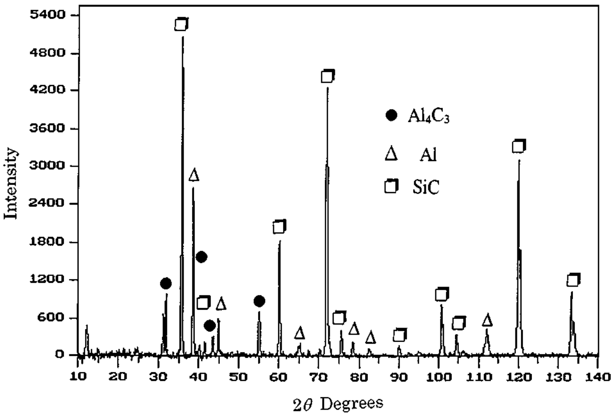

Figure 2 X-ray diffraction pattern of the Al/SiC interface showing the presence of Al_4C_3.

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*Instron model 4201 with a 50 kg load cell.

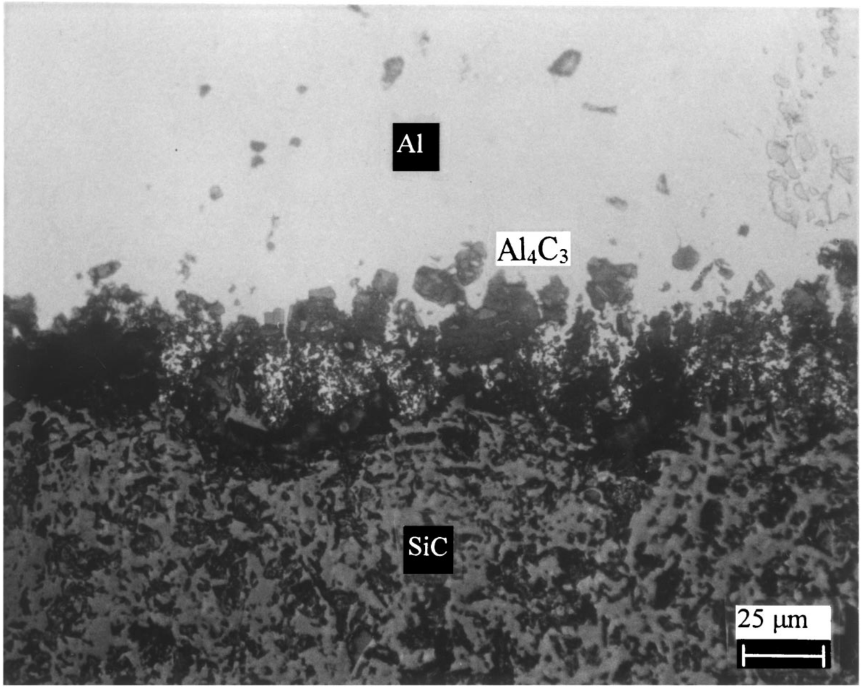

Figure 3 Optical photomicrograph showing the dissolution of SiC in the Al alloy and the formation of Al_4C_3 at the interface.

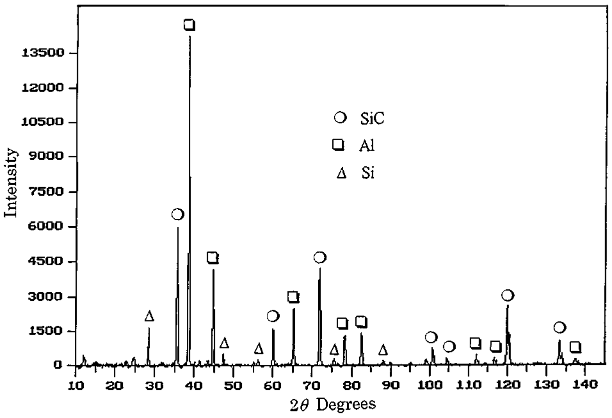

Figure 4 X-ray diffraction pattern of the Al/SiC interface showing the absence of Al_4C_3.

in Table I. In contrast to Fig. 2, Al_4C_3 was not detected at the Al/SiC interface when the high silicon content alloy is used. Clearly, high levels of silicon in the alloy reduce the tendency of the system to form Al_4C_3 at the interface. Another potential reaction product in the SiC/Al system is the ternary carbide Al_4SiC_4 that may form according to the chemical reaction shown in Equation 6 [18]

$$4Al + 4SiC \leftrightarrow Al_4SiC_4 + 3Si \qquad (6)$$

The deterimental effects of both reaction products, Al_4SiC_4 and Al_4C_3, are compounded by an alteration in the chemical composition of the alloy. This change in chemical composition is brought about by an increase in the Si content of the alloy in areas adjacent to the Al/SiC interface. If the Si content in these areas increases beyond the Al-Si eutectic composition (12.6 wt% Si), excessive precipitation of primary silicon particles may occur. See Fig. 5. Since Si particles are relatively brittle, they tend to degrade some mechanical properties of Al/SiC composite [19].

4.2. The role of silicon as a coating on silicon carbide

Pech-Canul *et al.* [13] have shown that silicon metal present at the surface of silicon carbide has a very significant positive effect on wetting of silicon carbide by aluminum alloys. This is reflected in a dramatic decrease in the contact angle between SiC substrates and Al alloys. The positive effect of silicon on wetting of SiC by Al alloys may be best understood by referring to the Al-Si binary phase diagram shown in Fig. 6 [2]. When a drop of liquid alloy with the composition indicated by point C on the diagram is placed on a pure silicon substrate (point A), wetting occurs readily as the substrate becomes a participant in a reaction that changes its surface composition toward equilibrium (point B). Similarly, the liquid becomes a participant in a reaction that changes its composition towards point B.

Sessile drop experiments performed under the conditions shown in Table III resulted in an equilibrium contact angle of 31 ± 2° and a measured surface tension of 375 ± 13 mN/m. In the absence of the silicon wafer on the surface of the SiC substrate, but otherwise similar conditions, the equilibrium contact angle was 74° and the measured surface tension was 397 mN/m.

Pech-Canul *et al.* have also shown that the presence of silicon on the surface of the SiC substrate does not

TABLE III Conditions for sessile drop experiments

Alloy chemistry	Al-13.5%Si-9%Mg
Substrate condition	SiC with a thin silicon wafer on top
Temperature	1235°C
Atmosphere	100% nitrogen

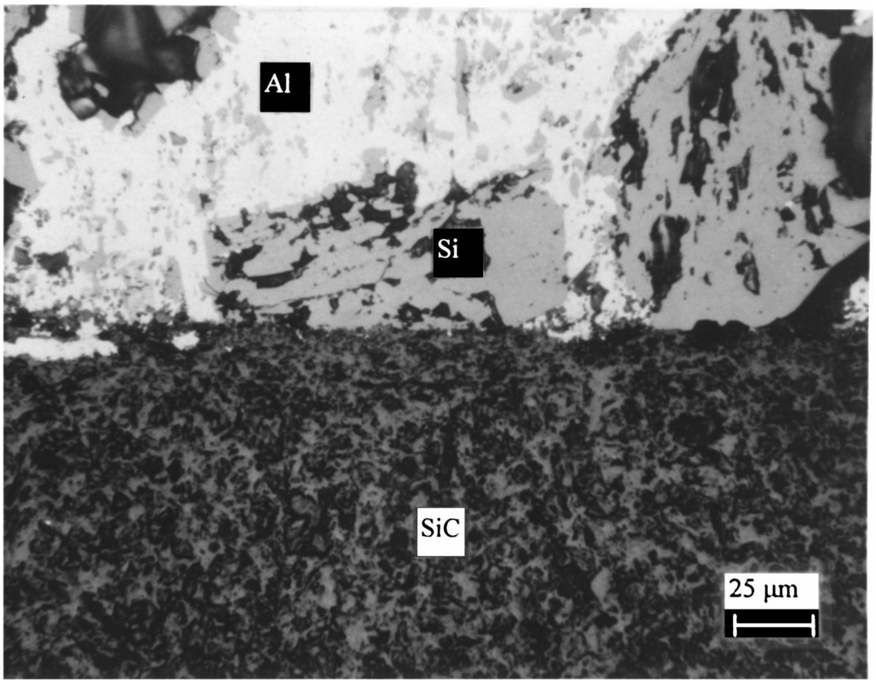

Figure 5 Optical photomicrograph showing Si particles from the silicon wafer dissolved in the aluminum droplet.

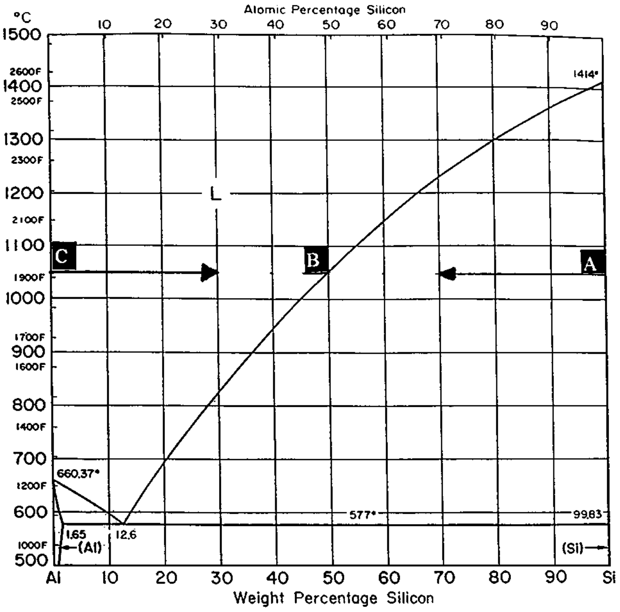

Figure 6 Aluminum-silicon equilibrium diagram [2].

TABLE IV Conditions for making composites for mechanical property tests

No.	Infil. time (min)	Particle size (mm)	Preform height (mm)	Aluminum (%)	SiC surface condition
1	45	65	32	50	Uncoated
2	45	25	44	50	Uncoated
3	60	65	44	60	Uncoated
4	60	25	32	60	Uncoated
5	45	65	44	60	Coated
6	45	25	32	60	Coated
7	60	65	32	50	Coated
8	60	25	44	50	Coated

TABLE V Average measured properties of Al/SiC_p composites

Composite type	Average P (%)	Average E (GPa)	Average MOR (MPa)
Uncoated (Nos. 1–4)	5.9	196	231
Coated (Nos. 5–8)	2.9	198	188

P is porosity, E is modulus of elasticity and MOR is modulus of rupture.

seem to have an effect on the magnitude of the surface tension between SiC and Al. However, it has a positive effect on the driving force for wetting [13].

In order to investigate the effect of silicon coating on pressureless infiltration of silicon carbide powders with aluminum alloys, silicon carbide powder was coated with a thin layer of pure silicon metal.† Preforms were made from this powder and their infiltration characteristics were compared to those of uncoated powders. Table IV shows the conditions under which the various composites were produced. These conditions were chosen based on a Taguchi design of experiments in order to optimize the mechanical properties of the composite materials. Table V shows a summary of the composite's average mechanical properties. For better visualization, the information in Table V is shown graphically in Fig. 7.

Table V shows that the presence of silicon on the silicon carbide particles' surface helps minimize the average retained porosity in the composites. This is understandable in light of the positive effect that silicon has on wetting and spreading of aluminum alloys on silicon carbide. During pressureless infiltration, the presence of Si on the SiC particles wicks the aluminum alloy up the multitude of capillary channels that exist between SiC particles, thus aiding infiltration and reducing retained porosity. Table V also shows that the presence

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† Courtesy of Materials and Electrochemical Research Corporation, Tucson, Arizona.

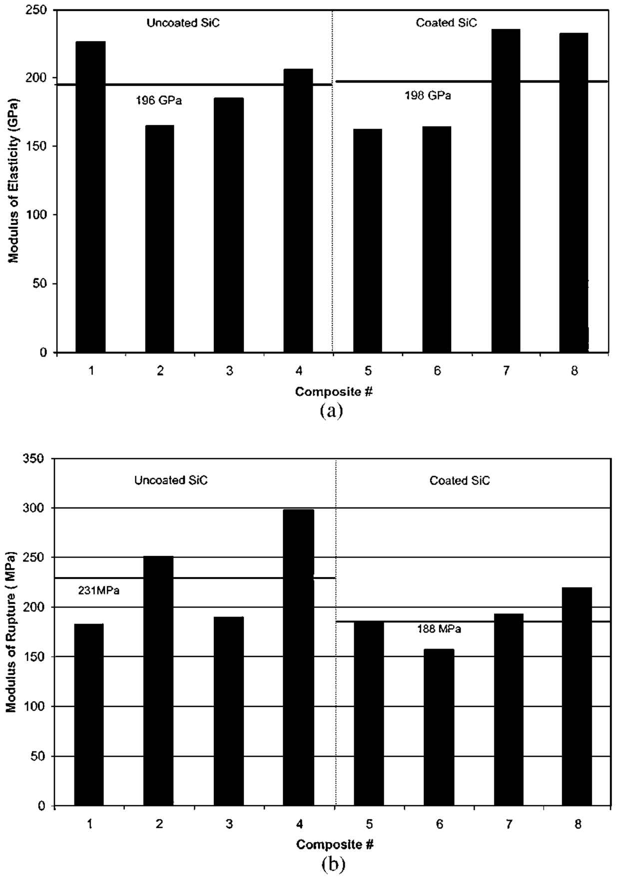

Figure 7 Mechanical properties of composites shown in Table IV. (a) Modulus of rupture. (b) Modulus of elasticity.

of silicon on the surface of the SiC particles does not affect the magnitude of the modulus of elasticity of the composites, but it significantly decreases the magnitude of the modulus of rupture. The modulus of elasticity of the composite is sensitive not only to the SiC and aluminum components of the composite, but also to the percent-retained porosity. Because the presence of silicon on the surface of the SiC minimizes retained porosity, it should enhance the modulus of elasticity. Moreover, with the presence of excess silicon at the SiC/Al interface, silicon particles tend to precipitate out of the alloy at the interface. However, close examination of Fig. 5 shows that the silicon particles are highly porous. The negative effect of this porosity in the silicon particles cancels the positive effect of reduced retained porosity. The net effect is an insignificant increase in the modulus of elasticity of the composite. Moreover, silicon particles are relatively weak and brittle [19], and thus they tend to degrade the strength of the Al/SiC interface. This loss of interface strength manifests itself in a degradation of the modulus of rupture.

5. Summary

Silicon plays an important role in the production of Al/SiC metal matrix composites. As an alloying element in aluminum, silicon retards the kinetics of the chemical reactions that result in the formation of the unwanted intermetallics Al_4C_3 and Al_4SiC_4. Both Al_4C_3 and Al_4SiC_4 are unstable, and if formed in an MMC, would react with atmospheric moisture and degrade the mechanical and physical properties of the composite. As a thin coating on silicon carbide, silicon becomes an active participant in a thermally activated chemical reaction that enhances wetting of silicon carbide by aluminum alloys. The free energy associated with the dissolution of the silicon coating into the aluminum alloy contributes to the driving force for wetting of the siliconized silicon carbide by the aluminum alloy.

Al/SiC composites made with siliconized silicon carbide and silicon rich aluminum alloys show mechanical properties that are significantly different from those of similar composites that are made with unsiliconized silicon carbide or with aluminum alloys that do not contain silicon. Specifically, Al/SiC composites made with siliconized SiC powders exhibit a lower average modulus of rupture than their counterparts made with unsiliconized SiC powders.

The overall silicon content of the system is critical to the successful production of Al/SiC composites. While a high overall silicon content is desirable to enhance wetting and eliminate unwanted chemical reactions between the aluminum alloy and the SiC reinforcement, excessive silicon in the system can cause precipitation of Si crystals at the Al/SiC interface. Since these Si crystals are relatively brittle, they tend to degrade the mechanical properties of the composite material, especially, the composite's modulus of rupture.

Acknowledgements

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