JOURNAL OF MATERIALS SCIENCE 26 (1991) 1412–1420

High temperature reactions between SiC and platinum

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Solid state reactions between SiC and platinum have been studied at temperatures between 900 and 1100 °C. In the reaction zones, alternating layers of Pt_3Si and carbon, and Pt_2Si and carbon were formed at 900 and 1000 °C, respectively. Both the Pt_3Si and Pt_2Si phases were stable at respective temperatures. Annealings at 1100 °C, however, produced alternating layers of mixed Pt-silicides and carbon. The formation of platinum silicides gave rise to interfacial melting between SiC and platinum at all the temperature regimes. Laser Raman microprobe indicates that SiC decomposes into carbon and silicon at all the temperatures. The silicon reacts with platinum and forms platinum silicides, while the carbon forms clusters and stays unreacted. Based on the Raman results, the carbon exists in two different crystalline states depending upon its location from the SiC reaction interface. The reaction kinetics between SiC and platinum and the formation of periodic structure, respectively, are discussed based on the decomposition of the SiC and the phase separation of carbon from platinum silicides.

1. Introduction

Solid state reactions between metals and ceramics have long been an important subject. Recently, studies [1–4] of compatibility between metals and ceramics have attracted considerable attention due to the need for developing better ceramic reinforced metal matrix or intermetallic matrix composites for applications under extreme environments. Another important application of metal–ceramic interactions is in the joining between metals and ceramics. In composite materials, a subject of great interest is the solid state reaction between the reinforcements and matrices.

There is a technical dilemma with regard to the desired extent of interaction between the reinforcement and the matrix. A strong metallurgical bond between them through solid state reaction is essential in order to make composites with good mechanical strength. Nevertheless, extensive interaction causes degradation of the reinforcement, which in turn impairs the overall mechanical properties of the composites. Other important issues to be addressed are the thermal, physical and mechanical properties of the reaction zones.

Among the ceramic reinforcements being used in metal matrix composites, SiC is a popular one. As a result, understanding the chemical reactions between SiC and various types of metal substrates is important from an engineering point of view.

2. Experimental details

The metal–ceramic reaction was carried out by a diffusion bonding method. Rectangular pieces of β-SiC (hot-pressed) and platinum of 1 to 2 mm thick were used in this study. The SiC samples were polished with a diamond disc of 15 μm grit, and the platinum samples were polished with alumina slurries of 0.3 μm particle size. The samples were ultrasonically cleaned in acetone, water rinsed, and then dried by compressed air.

The diffusion couples were formed by pressing two pieces of the reactant coupons together in a pressure clamp. The couples were then annealed in a tube furnace flushed with a helium gas. The samples were annealed at 900, 1000 and 1100 °C for different times. Upon finishing the anneals, the samples were cooled in air or liquid nitrogen.

To examine reactions between platinum and SiC, cross-sectional views of reaction zones were prepared. Scanning electron microscopy (SEM), scanning Auger microscopy (SAM), laser Raman microprobe and X-ray diffraction were used to characterize the reactions and chemistry of the reaction products.

The Raman spectra were obtained at room temperature from polished surfaces. The samples were illuminated with an argon ion laser beam ($\lambda = 514.5$ nm) focused down by the objective lens (100 ×) of the microprobe. The laser power at the samples was 65 mW, and the probe diameter was about 1 μm.

3. Results

Extensive reactions between SiC and platinum were observed at all the temperatures studied. Fig. 1a, b and c show typical plane and side-views of the reaction zones. Local melting followed by solidification were noted at the interface. A unique fibrous microstructure, as shown in Fig. 2, was observed in re-solidified regions. The observation of interfacial melting indicates that either a reaction product with a low melting

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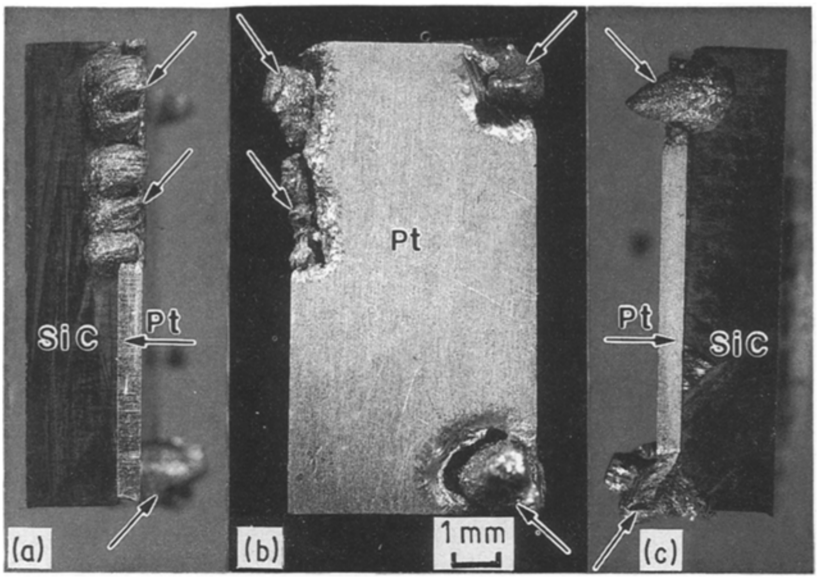

Figure 1 Optical micrographs showing the side-views (a and c) and plane-view (b) of the interactions between the SiC and platinum after 900 °C annealing for 5 h. The melted/solidified regions are indicated by arrows.

point is formed during the reaction (i.e. the melting point of the product is lower than the respective annealing temperatures), or the heat of mixing of $Pt_{(s)} + Si_{(s)}$ is so large that the total amount of heat at the reaction interface is greater than the heat of fusion of the reaction product.

To identify the structure and chemistry of the low melting point reaction product, the reaction zones were collected and analyzed by X-ray diffraction. Pt_3Si was identified from the samples annealed at 900 °C. Fig. 3 shows XRD of the Pt_3Si phase. The spectrum agrees well with that obtained from JCPD (Joint Committee on Powder Diffraction) standards. Development of structural texture due to solidification is indicated by a higher intensity of the (0 0 4) diffraction peak as compared to the ($\bar{2}$ 2 2) peak. An enhancement of intensity for the (0 0 2) peak is also noticed. For the samples annealed at 1000 °C, Pt_2Si was found to contribute to the interfacial melting. Annealing at 1100 °C, however, produces a mixture of platinum silicides (i.e. $Pt_3Si + Pt_{12}Si_5 + Pt_2Si + PtSi$).

Cross-sectional views of all the reaction zones show a typical teardrop as a result of a surface tension effect during the solidification of the interfacial melt. Two reaction interfaces, one on SiC side and the other on the platinum side, were generated. It is noted that the thickness of the Pt-side reaction zone is thicker than that of the SiC-side. This suggests that the reaction kinetics on the SiC side is slower than that on the platinum side. No parabolic relationship between the thickness of the SiC-side reaction zone and the annealing time was observed.

In the reaction zones, an intriguing reaction pattern featured by alternating layers of light and dark reaction products was observed. Fig. 4 shows a typical microstructure obtained from a reaction zone after annealing at 900 °C. The periodic layers grow either continuously or discontinuously. The spacing between the layers decreases as their location gets farther from the SiC reaction interface, which is located on the right of the micrographs. Energy dispersive spectrometry indicates that the light band consists of platinum and silicon, while the dark band is primarily carbon. Composition profiling across the periodic layers was conducted by scanning Auger analysis with an argon ion sputtering gun. Fig. 5 shows the Auger composition

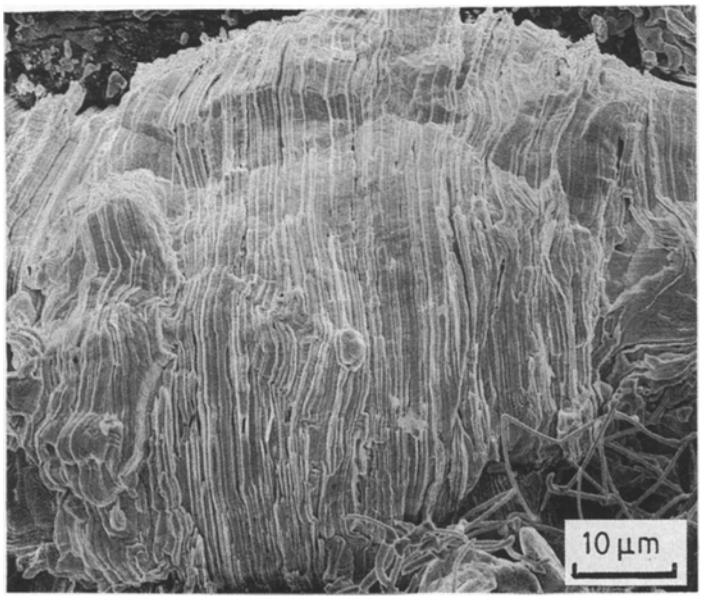

Figure 2 The typical fibrous microstructure observed in a melted/solidified region. The reaction annealing was conducted at 900 °C for 5 h.

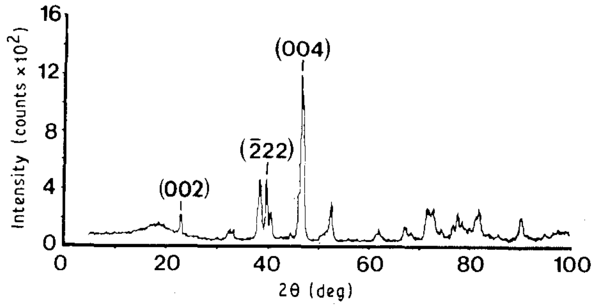

Figure 3 X-ray diffraction patterns obtained from the Pt_3Si reaction product, which was formed after annealing at 900 °C for 5 h.

profiles of platinum, silicon, carbon and oxygen across the reaction zone. Alternating layers enriched of platinum and silicon (the light bands), and carbon (the dark bands) are clearly seen.

Figs 6, 7 and 8 show a series of SEM micrographs of the reaction zones which were generated after annealings at 900, 1000 and 1100 °C, respectively. It is noticed that the microstructure of the reaction zone changes as a function of distance from the SiC reaction interface. In the areas close to the SiC, sparse and randomly distributed carbon precipitates were observed. The carbon precipitates start to form clustered periodic layers, and their spacings become increasingly smaller as their locations get farther from the SiC interface. In the areas close to the platinum, grain growth phenomenon was noted. The carbon was found to preferentially segregate into the grain boundaries of Pt-silicides. Furthermore, it is noted that the periodic dark bands grow thicker as annealing temperature increases. Granular microstructure starts to develop (see Fig. 8) in the dark bands from the samples annealed at 1100 °C. For samples which were quenched in liquid N_2, the reaction zones exhibit similar microstructural characters as compared to those that were air cooled, suggesting that the formation of periodic structure is independent of the cooling rate.

Fig. 9a and b show secondary electron image and its corresponding backscattered electron image, respectively, of the reaction zone from an as-reacted sample after annealing at 1000 °C for 5 h. In the areas immediately adjacent to the SiC component, the microstructure is similar to that of the as-received SiC. In addition, coagulated particles were formed (see Fig. 10) on the surface, indicating the occurrence of melting solidification. These particles have a fibrous microstructure which is similar to that were observed at the edge of re-solidified regions (Fig. 2), and they were identified to be Pt_2Si by EDS. As the location of the area moves away from the SiC interface, the formation of dendritic-shaped Pt_2Si as a result of melting/solidification was observed. A crack, originated from shrinkage during solidification, running parallel to the reaction interface, was observed and is indicated in Fig. 9a. As the area gets farther from the interface, finely-spaced periodic C/Pt_2Si structure were observed.

A laser Raman microprobe was used to investigate the chemistry of the periodic carbon bands existing in the reaction zones. Fig. 11 shows a series of Raman spectra of the carbon bands from a sample annelaed at 1100 °C. It is found that the carbon layers exist in two different crystalline states, depending upon their location from the interface. The carbon generated in the areas close to SiC reaction interface existed primarily in a glassy state, which is characterized by the presence of a high intensity Raman peak at 1349 cm^{-1}. As the location of the carbon layer gets farther from the interface, graphitization of the glassy carbon was observed, which is characterized by a decrease of the intensity ratio (I_{1349}/I_{1591}) between the 1349 and 1591 cm^{-1} Raman peaks.

The microstructure of the carbon layer also varies depending upon its cystalline state. The glassy carbon layer shows a continuous microstructure, see Fig. 12a, with a uniform contrast within the layer. On the other hand, the graphitic carbon layer shows a discontinuous microstructure, see Fig. 12b, suggesting the occurrence of precipitation during its formation.

From Raman spectra, it is important to note that free carbon, but no silicon, was detected at SiC reaction interfaces, indicating a direct decomposition of the SiC. The dissociated silicon is believed to readily react with platinum and form Pt-silicides, rather than exist as a free specie in the reaction zone. We were unable to collect Raman spectra from Pt-silicide phases due to either high surface refractivity or poor Raman sensitivity.

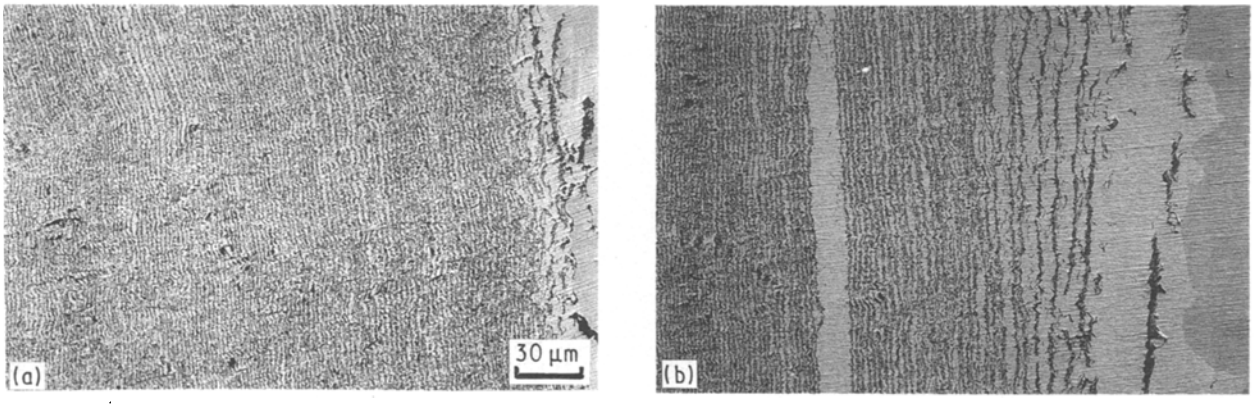

Figure 4 SEM micrographs showing the periodic structure in the reaction zones after annealing at 900 °C for 5 h. (a) Continuous and (b) discontinuous periodic structures were generated.

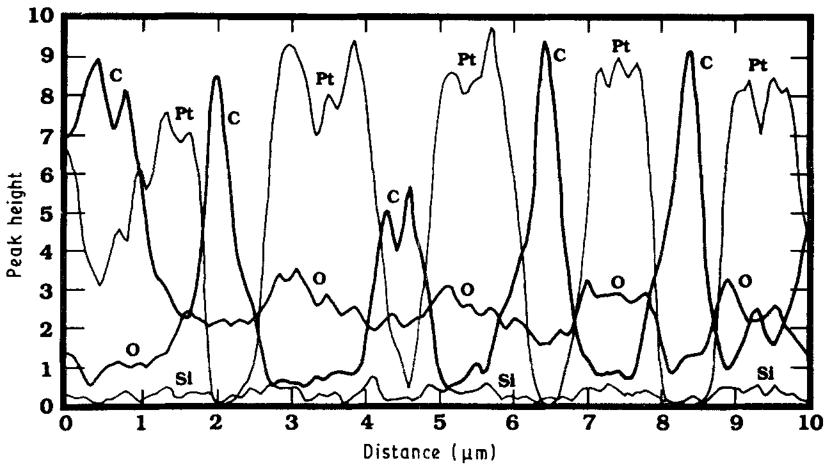

Figure 5 Scanning Auger profiles of platinum, silicon, carbon and oxygen across the periodic layers. The light bands were found to be enriched of platinum and silicon, while the dark bands contained carbon.

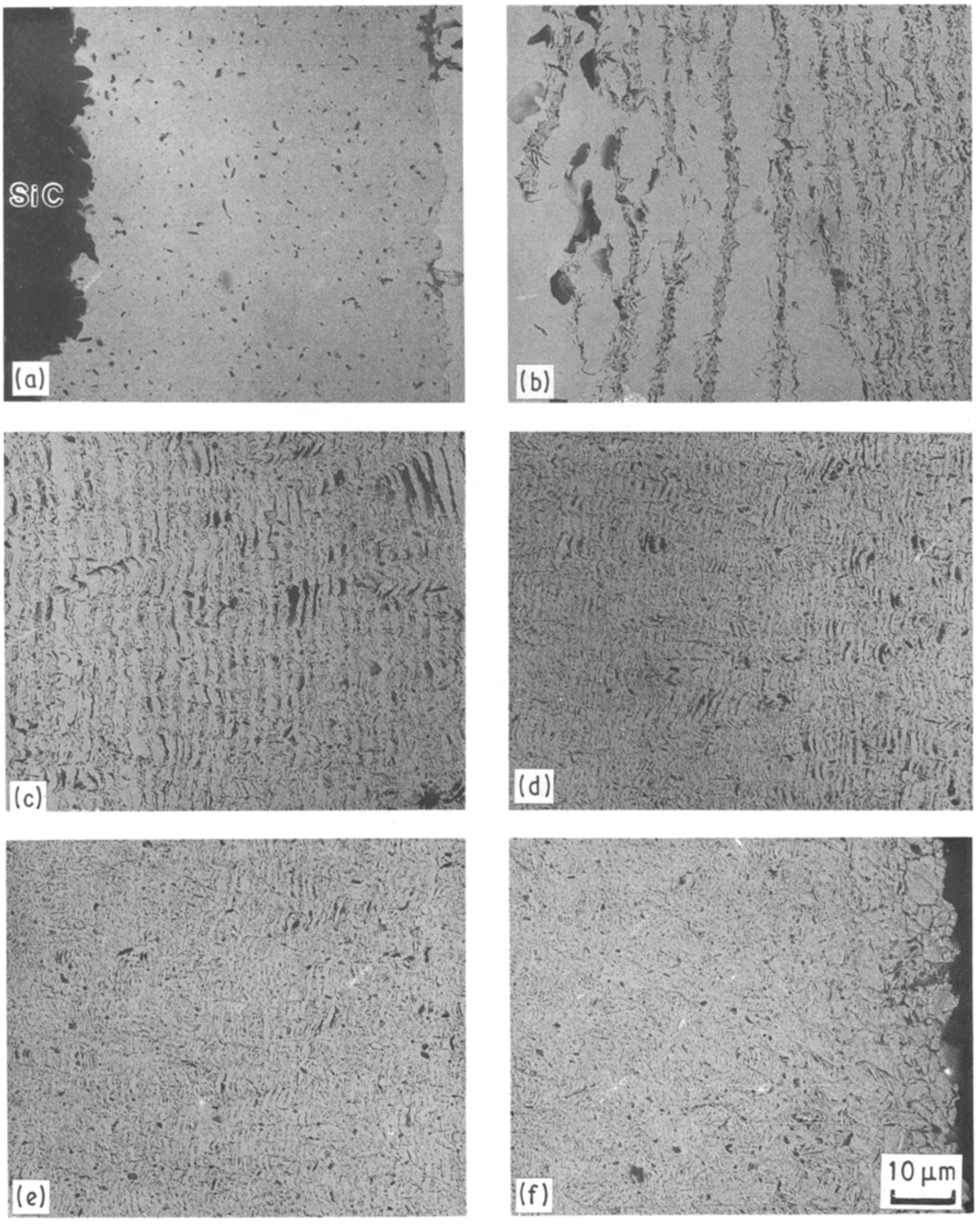

Figure 6 SEM micrographs showing the change of microstructure, in the reaction zone, as a function of distance from the SiC reaction interface. The sample was annealed at 900 °C for 5 h.

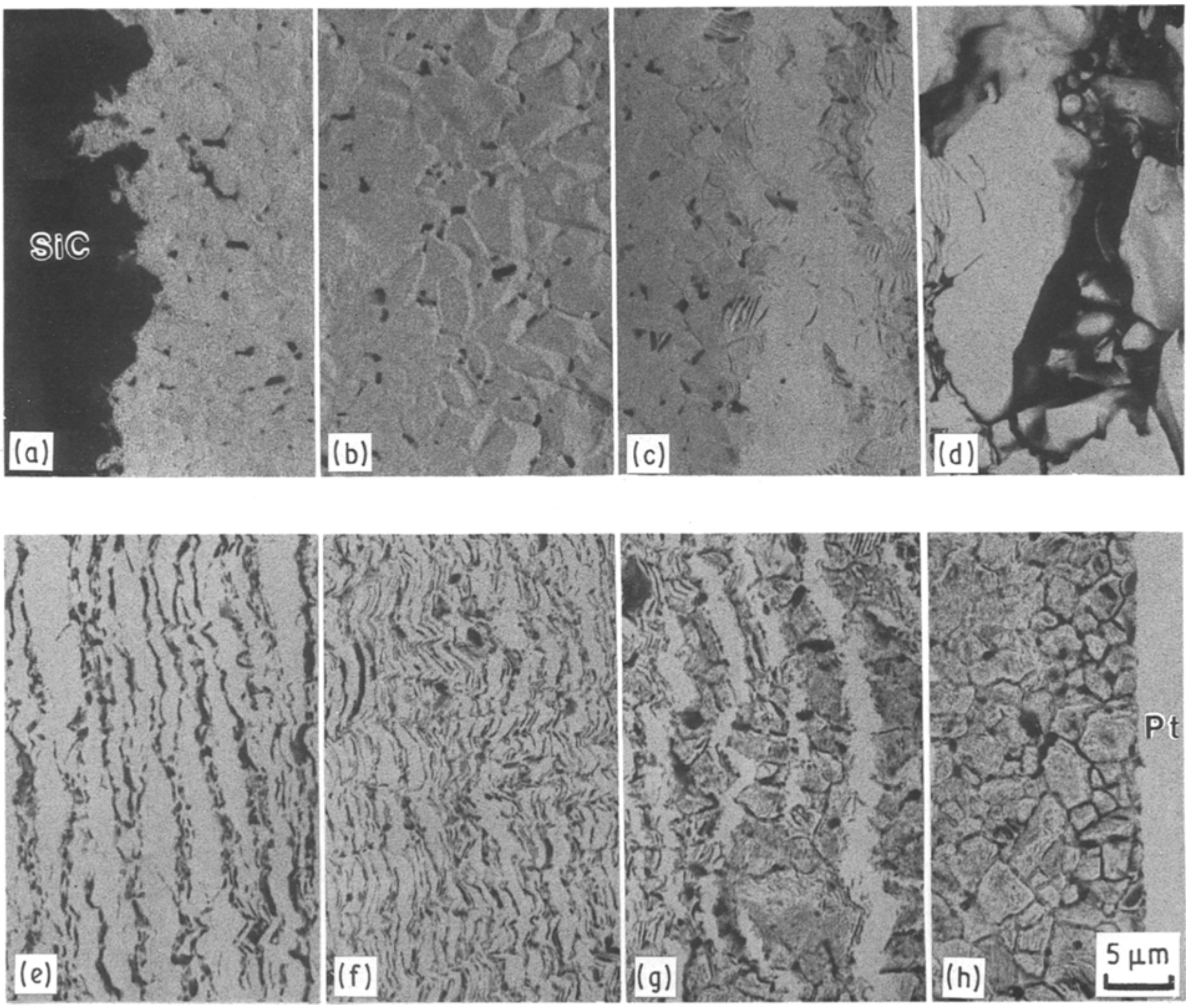

Figure 7 SEM micrographs showing the change of microstructure, in the reaction zone, as a function of distance from the SiC reaction interface. The sample was annealed at 1000 °C for 5 h.

4. Discussion

Based on a binary phase diagram of Pt–Si [5], Pt_3Si has a melting point ranging from 830 to 870 °C, depending upon its alloy stoichiometry. Although the enthalpy of the formation of Pt_3Si phase is unavailable, the presence of Pt_3Si still well explains the interfacial melting occurring between the platinum and SiC at 900 °C. On the other hand, Pt_2Si melts congruently at 1100 °C. Nevertheless, its melting point decreases drastically (from 1100 to 980 °C) as the composition deviating from the alloy stoichiometry. To explain the melting of Pt_2Si at 1000 °C, there are two possibilities. The first one is that the formation enthalpy of Pt_2Si at 1000 °C is sufficiently large than its heat of fusion. Recently, the standard enthalpy of formation and the heat of fusion of Pt_2Si were reported [6] to be -185 and $+56\ \mathrm{kJ\,mol^{-1}}$, respectively. Since no specific heat data (C_p), as a function of temperatures, of Pt_2Si phase is available, an estimation of the temperature rise due to the formation of Pt_2Si at 1000 °C is difficult. The other one is attributable to the compositional inhomogeneity of the Pt_2Si during its formation through atomic interdiffusion. A concentration gradient is expected to exist in the reaction zone during a solid state reaction.

In the microelectronics industry, platinum silicide (PtSi) is frequently used as a Schottky or Ohmic contact for interconnection. The platinum silicide is usually formed by solid state reactions [7–9] between a deposited platinum thin film and a polycrystalline silicon layer followed by low temperature annealing (300 to 500 °C) in a protective ambient. It is reported that the first phase formed is usually Pt_2Si which is then converted into a stable PtSi phase. The formation of Pt_3Si, Pt_2Si and PtSi mixtures has been reported in as-deposited [10], and electron irradiated [11] Pt–Si thin films. The Pt_3Si phase disappeared, however, after thermal annealings between 450 and 600 °C in an inert ambient. To our knowledge, Pt_3Si compound has never been formed exclusively by a solid state reaction nor has it been stabilized for any length of time at temperatures as high as 900 °C.

Considering an overall reaction between platinum and SiC at 900 °C,

$$SiC_{(s)} + 3Pt_{(s)} \rightarrow Pt_3Si_{(l)} + C_{(s)}$$

the reaction kinetics can be limited by either the decomposition of SiC or the interdiffusion of silicon and platinum. The effect of carbon diffusion on the reaction kinetics is expected to be small due to its

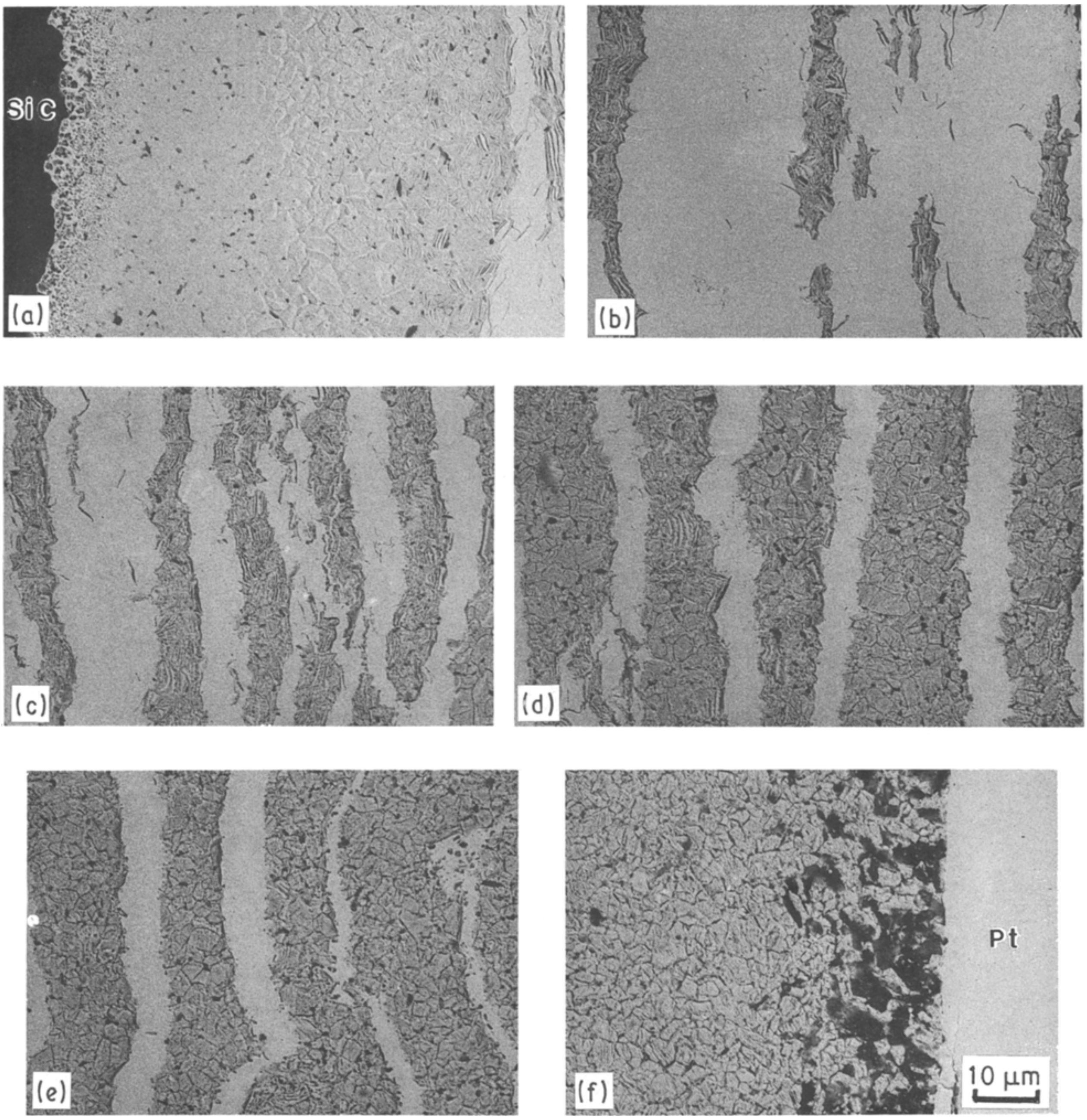

Figure 8 SEM micrographs showing the change of microstructure, in the reaction zone, as a function of distance from the SiC reaction interface. The sample was annealed at 1100 °C for 4 h.

chemical inertness and small atomic size. Based upon the fact that the thickness of the SiC-side reaction zone is smaller than that of the Pt-side, it is suggested that the Pt–SiC reaction kinetics is controlled by the decomposition of SiC.

Thermodynamically, the Gibbs free energy (ΔG) of SiC decomposition [12],

$$SiC_{(s)} \rightarrow Si_{(s)} + C_{(s)}$$

is highly positive even at high temperatures ($\Delta G = 12.0$, 11.9 and 11.8 kcal mol^{-1} at 900, 1000 and 1100 °C, respectively). It is not reasonable to expect that SiC alone would decompose in an inert environment at temperatures between 900 and 1100 °C. Furthermore, carbon has a low solid solubility in platinum, and it does not form stable platinum carbide(s). Considering these facts, it is believed that the Gibbs free energy for the platinum silicide formation is highly negative, which serves as a thermodynamic driving force for the SiC–Pt interfacial reactions.

The present experimental results describe a complex kinetic problem involving chemical reaction, melting, and precipitation. To comprehend the details of the chemical reactions between platinum and SiC, and the formation of periodic structure, information such as thermochemistry and interdiffusion kinetics in Pt–SiC system, decomposition characteristics of SiC, and dissolution (or rejection) rates of carbon atoms is vitally important.

Formation of periodic precipitation during chemical reactions was first reported [13] in 1896. The periodic "Liesegang bands" were found in some gelatin systems in which the outer reactant diffuses into an initially homogeneous solution, reacts with only one component of the solution and gives rise to the forma-

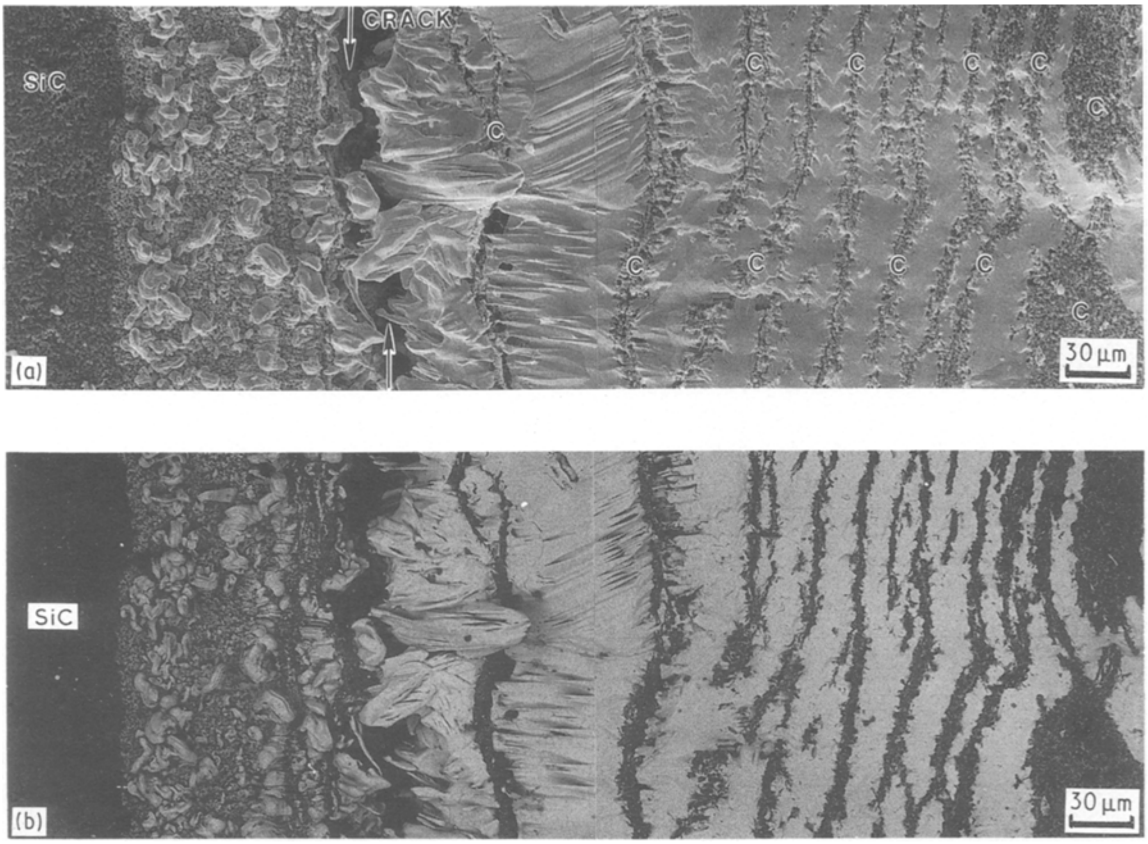

Figure 9 (a) Secondary electron images and (b) backscattered electron images showing the change of microstructure as a function of distance from the SiC reaction interface in an as-reacted Pt–SiC diffusion couple after annealing at 1000 °C for 5 h. The areas of low atomic density, i.e. SiC and carbon, are indicated and featured by the dark areas in the backscattered electron images. A crack due to shrinkage during solidification is indicated by arrows.

tion of precipitate. Since then, a few solid state material systems [14–18] have been reported to exhibit periodic structure during internal oxidation [15, 16], sulphidation [17], or interdiffusion between metals [18]. No periodic structure has ever been reported during metal–ceramic interactions.

The formation of periodic structures of platinum silicides–carbon in the present experiment is believed to be attributed to the phase separation of carbon from platinum silicides. Carbon is believed to have a low solid solubility in platinum silicides, although no literature data are available, due to its presence as a free specie in the reaction zone. Carbon has been found [19, 20] to have a low solid solubility (0.25 to

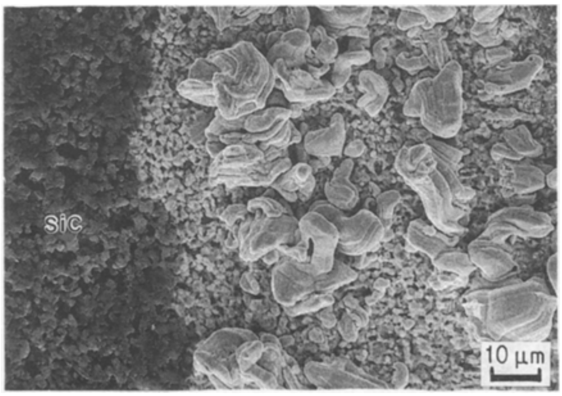

Figure 10 A high magnification SEM micrograph showing the microstructure from a region next to the SiC component in the as-reacted sample.

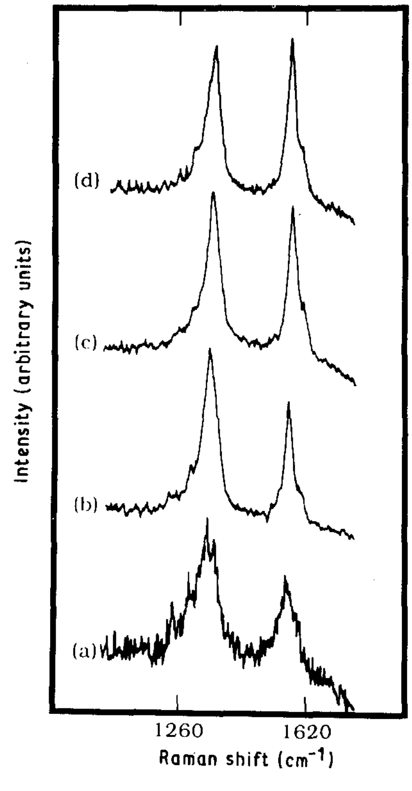

Figure 11 Raman spectra of the carbon bands, showing the change of carbon structure as a function of distance from the SiC reaction interface. The sample was annealed at 1100 °C for 4 h. It is noted that the carbon at the interface, (a), exhibits glassy character. The carbon starts to show ordered graphitic character as its location gets farther from the interface, (b) to (d). The carbon peaks occur at Raman shift of 1349 and 1591 cm^{-1}.

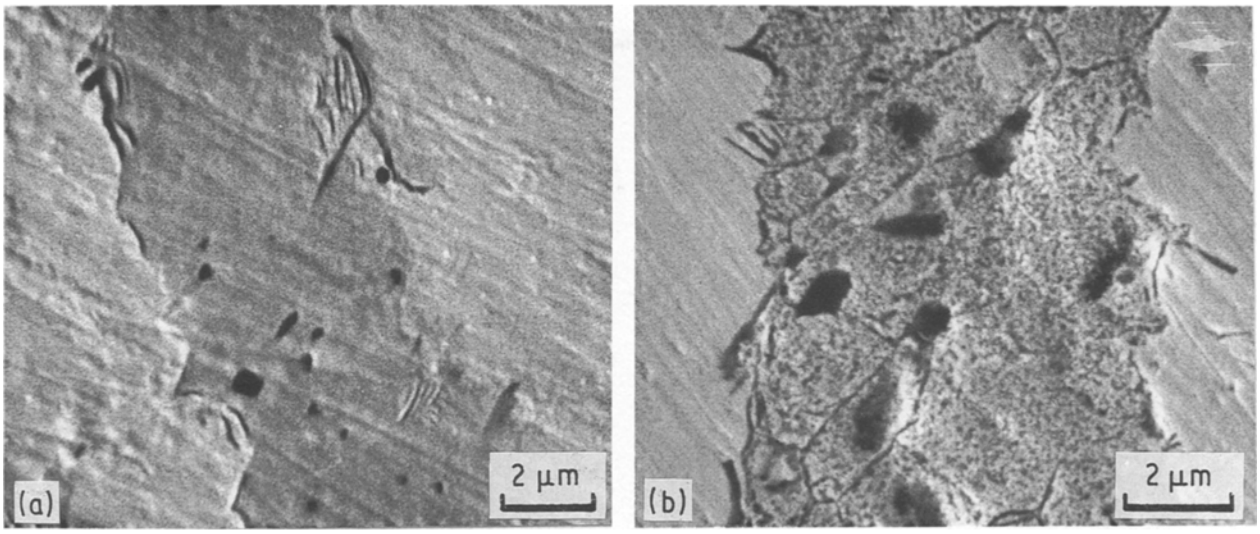

Figure 12 SEM micrographs showing the microstructures of the (a) glassy carbon, and (b) graphitic carbon layers. The sample was annealed at 900 °C for 5 h.

1.45 wt %) in molten platinum. More importantly, no diffusion of carbon in platinum was observed [21] at 800–900 °C. Limited by its low solid solubility in platinum silicides, the decomposed carbon atoms separate from Pt-silicide matrix, aggregate, and form precipitates in the reaction zone. As a result, the carbon clusters which separate out at an early stage (i.e. the ones located farther from the SiC reaction interface) experience a longer heat treatment and show primarily graphitic nature. The driving force for the carbon aggregation is suggested to originate from the reduction of the total interfacial energy between the carbon and Pt-silicide.

The distribution pattern of the carbon precipitates, and changes of spacing and thickness of the periodic layers as a function of distance from the SiC reaction interface are suggested to be attributed to the balance among the interdiffusion kinetics of the constituents, the decomposition rate of SiC and rejection rate of the carbon, and the nucleation and growth kinetics of Pt-silicides during the solid state reactions. All these aforementioned kinetic properties are known to be strongly dependent upon the location, composition and temperature of the reaction zones. The present periodic structure should be differentiated from the eutectic lamellae in view of the pre-existence of the solid state carbon in those temperature regimes. Moreover, the formation of periodic structure has been demonstrated to be independent of its cooling rate, suggesting that the structure has evolved during the reaction.

4. Conclusions

Solid state reactions between SiC and platinum, at temperatures ranging from 900 to 1100 °C, produce carbon and Pt-silicides as reaction products. The formation of Pt-silicides gives rise to localized interfacial melting between the platinum and SiC at temperatures as low as 900 °C. Limited by its low solid solubility in Pt-silicide phases, the carbon atoms form clusters and precipitate out in the Pt-silicide matrix either randomly or periodically, depending upon their location from the SiC reaction interface. Laser Raman microprobe analysis identified that the carbon precipitates existed in two different crystalline states; glassy carbon were located close to the SiC reaction interface while graphitic carbon was located farther away. The thermodynamic driving force for the SiC–Pt reactions is suggested to be the highly negative Gibbs free energy of the platinum silicide formation.

Acknowledgements

I am grateful to J. Patchett for the arc melting work, to R. Moore at Perkin–Elmer for Auger analysis and to F. Adar at Instruments SA for Raman analysis. Technical support from the analytical group at Engelhard Corporation is acknowledged.

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Received 13 November
and accepted 1 December 1989