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Pattern formation in Pt–SiC diffusion couples

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Abstract

The morphology of reaction zones between platinum metal and silicon carbide ceramic at 973 and 1023 K is considered in detail. A periodic pattern of carbon bands embedded in Pt_3Si_2 is observed at both temperatures. The growth of platinum silicides at 973 and 1023 K is compared. Cross-sections of the Pt–Si–C phase diagram at those temperatures are presented. The periodic layered morphology is explained via a ‘repeated splitting’ mechanism.

Keywords: Silicon carbide; Metal/ceramic joint; Pattern formation; Diffusion couples

1. Introduction

Joining of metals to ceramics is an important field in engineering. The combination of malleable metal and strong corrosion- and wear-resistant ceramic is especially useful in high-temperature structural applications. A lot of attention has been paid to applications of silicon carbide, SiC, applied both as a coating and as a reinforcement fibre in composites. Moreover, SiC is a promising semiconductor for high-temperature and high-power electronic devices because of its high thermal and chemical stability and its wide band-gap (2.2 eV for β -SiC). Such devices need at least one low resistance ohmic contact, i.e. a joint with some metal.

Use at high temperatures puts high demands on the stability of the joint. The chemical, physical and mechanical properties of the joint might influence the

overall performance of the ensemble. It is thus useful to study growth and morphological development of the reaction zones between metal and ceramic.

SiC/transition metal joints have been the subject of study in our laboratory over a number of years. Schiepers [1] studied the interaction of SiC with iron, nickel and iron–nickel alloys and Wakelkamp [2] studied its interaction with titanium. It has been known since the beginning of the 1980s that reactions of SiC with Ni and Ni–Cr alloys produce a peculiar banded reaction zone [3,4]. This was later confirmed by Backhaus-Ricoult [5] and Chou et al. [6]. In the latter study, Chou et al. [6] also reported on the interaction between SiC and Pt over the temperature range 1173–1373 K, which produces a very pronounced ‘banding’ of the reaction zone. This periodic layered morphology (called by Chou a ‘modulated carbon precipitation zone’) was left largely unexplained, except for the general statement that the C precipitation behaviour depends on “...several competing kinetic processes, e.g., overall nucleation and growth rate of silicide phases, rejec-

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tion rate of C from the reaction front (...), growth (or condensation) rate of C clusters and diffusion rates of metals and Si."

The formation of periodic layered structures during solid state reactions is one of our research subjects. Since the reaction studied by Chou involved liquid, we decided to study the solid state interaction between Pt and SiC in the temperature range 973–1023 K. It turns out that annealing of Pt/SiC diffusion couples produces a very pronounced periodic layered reaction zone. Study of the reaction zone morphology and reaction kinetics of Pt/SiC diffusion couples demanded more knowledge about the growth kinetics in the binary Pt–Si system and the phase relations in the Pt–Si–C system at the temperatures of interest. Therefore, we also investigated the growth kinetics of silicides in Pt/Si diffusion couples and the isothermal cross-sections of the Pt–Si–C diagram at 973 and at 1023 K.

2. Experimental

The study was carried out using the conventional diffusion couple and pressed powder pellet techniques. Phase formation in the Pt–Si and in the Pt–SiC system and reaction zone morphology were studied using the diffusion couple technique. The materials for the diffusion couples were hot-isostatic pressed SiC with and/or without 0.25 wt.% alumina as a sintering aid (ESK, Germany), 0.25 mm platinum-foil (99.9%, ALFA products, Germany) and polycrystalline silicon (99.98%, Hoboken, Belgium). The same experimental results were obtained with both types of SiC. Before use in a diffusion couple, Pt-foils of approximately $6 \times 6 \text{ mm}^2$ were annealed in vacuum at 1400 K for 9 h to improve their ductility. The foils were pressed flat and polished to a final finish with 0.05 μm alumina slurry. SiC and Si were machined to planparallel slices and a final finish of 10 μm . Sandwich couples of the type SiC/Pt-foil/SiC and Si/Pt-foil/Si were annealed for various times in vacuum under an external load of 4 MPa. The couples were allowed to cool to room temperature, cut with a slow-speed saw and prepared for microscopic examination by standard metallographic techniques. Polarized light microscopy, scanning electron microscopy (SEM) and

electron probe microanalysis (EPMA) were used to investigate the samples.

Powders used for pressing pellets were Pt powder of 0.5–1.2 μm particle size (99.9%, ALFA products) and SiC powder of about 45 μm particle size (>99.5%, ESK). Mixtures of the powders were cold-pressed into pellets and pre-sintered in vacuum at 973 K for 100 h and at 1023 K for 48 h. Further heat treatment was conducted in an electroresistance furnace in evacuated quartz ampoules at 973 and 1023 K for 400 h. After preparation, the pellets were investigated by EPMA and X-ray diffraction (XRD). The surface of the pellets was studied by cylindrical texture camera. Other pellets were crushed, ground to a fine powder and investigated by powder diffraction.

3. Results

3.1. Pt–SiC diffusion couples

Fig. 1 shows the reaction zone morphology of a SiC/Pt/SiC diffusion couple annealed in vacuum for 24 h at 1023 K. Pt_3Si , Pt_7Si_3 , Pt_2Si and carbon are the reaction products. A periodic layered morphology is clearly present. Bands of carbon are embedded in the Pt_7Si_3 phase up to the Kirkendall plane (see Section 4.2). A two-phase carbon-containing zone ($\text{Pt}_2\text{Si} + \text{C}$) is found adjacent to the SiC (Fig. 1b). Pt_2Si has a very irregular interface with Pt_7Si_3 . No carbon is found inside the Pt_3Si phase, which shows a wavy interface with Pt. Neither Pt_6Si_5 nor PtSi are present in Pt/SiC diffusion couples.

The band width and the band spacing increases from Pt towards SiC. The carbon is present in the form of densely packed plate-like grains embedded in a matrix of either Pt_7Si_3 or Pt_2Si . The two-phase carbon bands are continuous over almost the total reaction zone. When the thickness of the Pt_2Si layer exceeds the thickness of the carbon-containing zone, the formation of bands stops. The number of bands formed is the same in both reaction zones of the SiC/Pt/SiC couple (Fig. 1a).

The Kirkendall plane is situated inside Pt_7Si_3 , close to the interface with Pt_3Si , as is revealed by a row of pores (Fig. 1b). This proves that Pt is the fastest diffusing component inside Pt_7Si_3 at 1023 K.

Fig. 1. Diffusion zone of a SiC/Pt/SiC diffusion couple annealed for 24 h at 1023 K. (a) General view; (b) area near the end of the reacted part; (c) degradation of carbon bands in the old part of the reaction zone [back-scattered electron image (BEI)].

A rather peculiar ‘degradation’ of the carbon bands can be seen in Fig. 1c. The bands are broken up into tiny ribbons of carbon in a part of the reaction zone.

Fig. 2 shows the reaction zone morphology of the Pt/SiC diffusion couple annealed in vacuum for 25 h at the lower temperature of 973 K. A morphology

Fig. 2. Diffusion zone of a SiC/Pt diffusion couple annealed for 25 h at 973 K (BEI). (a) General view; (b) magnified area close to the SiC interface; (c) area near a crack that is parallel to the diffusion direction.

rather similar to the one previously described developed in this couple. Pt_3Si , Pt_7Si_3 and carbon are the directly visible reaction products. Again we find bands of carbon embedded in Pt_7Si_3 , with increasing spacing and thickness in the direction of SiC. A two-phase carbon-containing zone is found adjacent to the SiC. There is also degradation of bands in some part of the diffusion zone. In the vicinity of cracks in the diffusion zone, which run parallel to the diffusion direction, carbon is found as finely dispersed particles (Fig. 2c).

Although the growth of intermetallics in the reaction zone is irregular, the overall growth rate of the reaction zone is found to obey the parabolic law both at 973 and 1023 K (Fig. 3). This indicates that the reaction is diffusion-controlled.

An important feature of the band formation can be seen from Fig. 2. After the two-phase zone adjacent to SiC reaches a critical thickness, cracking in the interwoven graphite band occurs. The shape of the interface between Pt_7Si_3 and the newly formed mixed $\text{Pt}_7\text{Si}_3 + \text{C}$ band is an exact replica of the ($\text{Pt}_7\text{Si}_3 + \text{C}$) layer that remains at the SiC interface. This is true for all graphite-containing bands.

No single-phase Pt_2Si can be observed directly in the reaction zone of couples annealed at 973 K, even after long annealing times (121 h). However, the Pt–Si ratio (as measured by EPMA) inside the carbon-containing zone close to the SiC was found to be 2:1, while a ratio of 7:3 was measured within the same zone but close to the Pt_7Si_3 side. This indicates that Pt_2Si is also formed at 973 K, but as a thin layer. The $\text{Pt}_2\text{Si}/\text{Pt}_7\text{Si}_3$ interface is ‘hidden’ inside the carbon-containing layer.

Fig. 3. Square reaction layer width in SiC/Pt diffusion couples as a function of time.

According to [7], two modifications of Pt_2Si exist; high-temperature (HT) $\beta\text{-Pt}_2\text{Si}$ and low-temperature (LT) $\alpha\text{-Pt}_2\text{Si}$, with a transition temperature of 968 ± 5 K. The HT phase has the hexagonal crystal structure, whereas the LT phase is tetragonal [8]. Thus, the conspicuous difference in the growth kinetics of Pt_2Si in the present case might be due to the formation of the β -modification at 1023 K and the formation of the α -modification at 973 K.

In order to study the growth kinetics of Pt_2Si , binary platinum/silicon diffusion couples were annealed at 973 and 1023 K. In Fig. 4, two couples annealed at these respective temperatures, for 4 h, are compared. It is clear that at 1023 K, Pt_2Si is the predominant compound in the diffusion zone, whereas, at 973 K, it grows very slowly. In the latter case, PtSi is the predominant compound. In both cases, the Kirkendall plane is found inside Pt_7Si_3 . The growth

Fig. 4. Binary bulk Pt/Si couples annealed for 4 h; (a) at 1023 K and (b) at 973 K.

of most of the intermetallics in those Pt/Si diffusion couples is rather irregular, i.e. no straight interfaces are observed.

In order to interpret the presence (or absence) and sequence of the phases in the diffusion couples, knowledge about the Pt–Si–C diagram is needed. This diagram will be discussed in Section 4.2.

3.2. Isothermal cross-sections of the Pt–Si–C phase diagram

A first attempt at describing the phase relations in the Pt–Si–C system was published by Searcy and Finnie ([9], reproduced in [10]). Their data are rather uncertain. No temperature was specified and not all binary Pt–Si compounds (as we know them nowadays) are present, i.e. Pt_6Si_5 and Pt_7Si_3 are missing. There is still some uncertainty as to the composition of the latter platinum silicide, which may also be found in literature as $\text{Pt}_{12}\text{Si}_5$, e.g. in [8]. A metastable phase, Pt_2Si_3 , is also known [8].

The three binary phase diagrams involved in the Pt–Si–C system provide us with a specific type of cross-section. There are no binary Pt–C compounds and between Si and C, only the line-compound, SiC, exists. Since platinum is a non-carbide-forming metal, it is highly unlikely that ternary platinum-carbosilicides are present in the Pt–Si–C system. Moreover, in the studies of Chou et al. [6], it was shown by Raman spectroscopy that pure carbon is formed in the reactions between Pt and SiC, either in an amorphous state or in the form of graphite and no ternary phases were reported. This topology of the cross-section allows us to determine the isothermal cross-section of the Pt–Si–C phase diagram using just one well-equilibrated pellet with a nominal composition of $\text{Pt}_{30}\text{Si}_{35}\text{C}_{35}$ (Pt:SiC = 6:7), as shown in Fig. 5. Then it is only necessary to determine which platinum silicide is in equilibrium with both carbon and silicon carbide.

Cylindrical texture camera measurements [11] revealed the presence of coarse SiC particles, α - Pt_2Si and graphite at both annealing temperatures. The data were corroborated by the powder diffraction measurements. Pt_2Si was the only silicide phase present in the pellets.

Fig. 6 shows the cross-section of equilibrated pellets. Coarse-grained SiC is visible together with

Fig. 5. Diagram showing the right choice of composition of a Pt/SiC pellet in order to determine the complete isothermal cross-section of the Pt–Si–C phase diagram.

single-phase Pt_2Si and two-phase (Pt_2Si + graphite) regions. Only SiC, carbon and Pt_2Si were found both at 973 and 1023 K. We conclude that PtSi , Pt_6Si_5 and Pt_2Si are in equilibrium with SiC, and Pt_7Si_3 , Pt_3Si and Pt_2Si are in equilibrium with carbon at both temperatures. This confirms the presence of Pt_2Si in the Pt/SiC diffusion couples annealed at 973 K. No ternary phases have been found. The experimentally determined cross-section of the phase diagram is given in Fig. 7.

4. Discussion

4.1. Behaviour of carbon

The stability of carbides is known to decrease in the direction Fe_3C (cementite) $\rightarrow$ Co_3C $\rightarrow$ Ni_3C . Accordingly, the carbon has a tendency to cluster and form graphite (graphitization). Such graphitization may also be expected for reactions of the platinum-group metals with SiC, since those metals form stable silicides but no carbides. During the reaction of non-carbide-forming metals with SiC, carbon is formed on the SiC side, together with a metal silicide. The metal silicides that are not in equilibrium with carbon, usually silicon-rich, will not form

Fig. 6. Cross-sections of the equilibrated Pt/SiC pellets annealed in vacuum for (a) 448 h at 1023 K and (b) 500 h at 973 K.

Fig. 7. Experimentally determined cross-section of the Pt–Si–C phase diagram. Pt_2Si is present as α at 973 K and as β at 1023 K.

during such a reaction. Since pure carbon has unit activity, and its activity in SiC is lower, it cannot diffuse through the reaction layer towards the metal and may thus be seen as an inert side-product. The bands of carbon just drift in the direction of Pt and may thus be considered as ‘markers’ (see below).

The ‘sintering behaviour’ of carbon may be expected to change, depending on the other reaction products that form a matrix for carbon. That this is indeed so can be seen from a comparison of reactions between Fe/SiC [12], Co/SiC [6], Ni/SiC [12] and Pt/SiC. Whereas in Fe/SiC and Co/SiC diffusion couples, carbon appears as finely dispersed particles, in Ni/SiC couples, the carbon particles are present in the form of parallel but rather diffuse bands, while in the reaction zone of Pt/SiC couples, the carbon is formed in quite compact and distinct bands. The same kind of carbon behaviour can be observed in equilibrated pellets.

4.2. Mobility of Pt and Si; the Kirkendall effect

In diffusion couples with components of unequal diffusivities, mass flow occurs relative to the original interface. This is the so-called Kirkendall effect, named after its discoverer [13]. The Kirkendall effect may be considered as the addition of atomic planes on one side of the interface and removal of them on the other side (see, e.g. Ref. [14]), which causes the original interface (also called the Kirkendall plane) to wander relative to the laboratory frame of reference. The position of the Kirkendall plane relative to its original position (the Matano plane) gives information about the relative mobilities of the components. This is especially true for binary diffusion couples, but also for higher order systems. In practice, the position of the Kirkendall plane is usually marked by inert marker particles or wires that are placed at the interface between the original diffusion couple halves before annealing. Even if no markers are used on purpose, the Kirkendall plane may be detected as a row of pores or a line separating two areas with differing morphologies inside the reaction zone. This role of ‘natural marker’ may also be played by sintering additives or polishing debris.

The Kirkendall plane, i.e. the original contact surface between Pt and SiC, was found to lie within the Pt_7Si_3 phase, close to Pt_3Si . From this, we

conclude that, in Pt_7Si_3 , platinum is by far the most mobile element. In Pt/SiC diffusion couples, a periodic layered structure is exclusively found in Pt_7Si_3 . Since no periodic layers were found in Pt_2Si , the question arose whether the ratio of the mobilities of Pt and Si in this phase differed appreciably from that in Pt_7Si_3 . In order to gain qualitative information about the relative mobilities of Pt and Si in Pt_2Si , a many-foil couple of platinum with silicon was annealed. The use of this technique is described in [15]. Four foils of platinum (of about 200 μm) were clamped and annealed at 1023 K between two slices of silicon. Since the contact between foils can never be perfect, pores existing prior to annealing may serve to identify the original contact interfaces. The photomicrograph in Fig. 8 shows one half of the diffusion couple. The first foil of Pt is already completely consumed by the reaction. The second foil has been partly consumed. Pt_2Si is the dominant phase in the diffusion zone, the other four Pt–Si intermetallics are present as very thin layers. The original interface between the first and second Pt-foil was determined by extrapolating the straight interface between the unreacted ends of the couple. This interface is marked M. The original interface between Pt-foils two and three is marked by B. The row of pores marked by K constitutes the second Kirkendall plane, i.e. the plane which was originally situated at M. It shows that this plane has shifted just a few microns from its original position, in the direction of Si. We conclude from this that, in Pt_2Si , the mobility of Si is somewhat higher than that of Pt. This observation supports the fact that the formation

of a periodic layered reaction zone needs components with widely different mobilities inside this zone.

Considering the flux-balance at the $\text{Pt}_2\text{Si}/\text{Pt}_7\text{Si}_3$ interface in connection with these observations, we note that this interface must be a source of vacancies.

4.3. On the periodic layered morphology

This periodic layered structure bears a resemblance to the well-known Liesegang bands which form when, e.g., a drop of silver nitrate solution is placed on a gelatinous medium containing potassium bichromate [16]. The accepted explanation for this phenomenon is based on Ostwald's supersaturation theory [17], which was quantified by Wagner [18]. Although systems are known that do form Liesegang bands in the solid state [19–22], the formation of bands in the Pt/SiC diffusion couples cannot be explained in the same way. First, the Liesegang mechanism needs two counter-diffusing species to form bands. In the Pt/SiC couples, the bands are formed by carbon which cannot diffuse, but only drift inside the diffusion zone. Moreover, a new Liesegang band is not formed until a critical supersaturation has been built up. From Fig. 2 we can see that a two-phase ($\text{Pt}_2\text{Si} + \text{C}$) layer is still present at the SiC 'substrate' after a band has been released. Thus, we exclude a Liesegang mechanism.

The appearance of a periodic pattern originates rather from a repeated separation ('cracking') of the interwoven part of the two-phase layer formed close to the substrate, as is well illustrated by the Pt/SiC reaction zone morphology (Fig. 2).

Osinski [23] has proposed a model for periodic layer formation in the diffusion couples $\text{Fe}_3\text{Si}/\text{Zn}$ and $\text{Co}_2\text{Si}/\text{Zn}$, based on the assumption of a periodic build-up and relaxation of stresses at the interface. When the growing band has reached a critical thickness, the stress developed in the diffusion zone becomes so large that it may cause blistering of the bands. After that, the reaction can start afresh, forming the intermetallic and another band.

Another model for periodic layer formation was proposed by Kao and Chang [24]. They considered periodic thermodynamic instability of the substrate/product interface with subsequent new nucleation of the reaction layers. However, this model requires

Fig. 8. Many-foil couple of Pt and Si, annealed in vacuum for 4 h at 1023 K.

single-phase reaction layers and single-phase bands, contrary to the experimental observations. Their model might be applied to the Ag/Ti-foil/Si couple, in which a periodic layered reaction zone was also found [22], if we consider the thermodynamic instability to occur not at the interface but inside the reaction product layer.

It seems reasonable to link the appearance of a periodic layered structure to the large difference in mobilities of the components inside the diffusion zone, and thence to a large vacancy flux in the direction of the fast component. This requires that vacancies are created on one side of the diffusion zone, while they are annihilated on the other side. Dunaev and Zver'kov [25] considered periodic layer formation to have its origin in different deposition rates of atoms at vacancy sources inside the diffusion zone. This would cause composition fluctuations leading to the nucleation of a new phase. However, in Pt/SiC couples, new nucleation of phases is not required, because the silicides and carbon are already present when a band is formed.

It is the creation and annihilation of vacancies that cause the Kirkendall effect. The problems associated with phase interface migration and the Kirkendall effect in binary two-phase systems have already been

considered in detail [26]. An important conclusion from this work is that, depending upon the intrinsic diffusion coefficients in each newly formed phase and the interfacial compositions in the diffusion couple, the phase interface must be able to create or annihilate vacancies.

In the case of Pt/SiC, we have shown that the $\text{Pt}_2\text{Si}/\text{Pt}_7\text{Si}_3$ interface must act as a source of vacancies. The diffusion zone containing the periodic bands is adjacent to this interface. As was noted before, the bands may be considered as inert markers, formed in situ inside the diffusion zone. They are drifting in the direction of Pt inside the Pt_7Si_3 and in the direction of SiC inside Pt_2Si . Therefore, a band of inert carbon markers can be split as a result of opposite vacancy fluxes inside the reaction zone. Such a phenomenon has been observed by Bastin and Rieck [27]. In a multiphase Ti/Ni diffusion couple, they demonstrated the actual rupture of a tungsten marker wire as a result of opposite intrinsic fluxes in the various phases. The diffusion zone of a Pt/SiC couple and the expected fluxes are schematically shown in Fig. 9. If the interwoven carbon band is completely situated within the Pt_2Si phase (Fig. 1a), no stresses will occur in the carbon-containing layer, because of the nearly

Fig. 9. Concentration profile (schematic) and expected intrinsic fluxes in the vicinity of the Pt_2Si – Pt_7Si_3 interface in a SiC/Pt diffusion couple (K^* denotes the original metal ceramic contact surface).

zero vacancy-flux, and there will be no driving force for splitting. Hence, the periodic formation of bands is stopped. The increasing thickness of the bands reflects the growth of the Pt_2Si phase.

A difference in vacancy fluxes on both sides of a reaction interface necessitates local climb processes involving misfit and/or misorientation dislocations [28]. These processes support the annihilation or creation of vacancies. The annihilation of vacancies tends to contract the solid, thereby subjecting this region of the diffusion zone to elastic tensile stress, because the adjacent material opposes contraction. By the same constraint, the creation of vacancies leads to elastic compressive stress on the other side of the diffusion zone. At a critical stress, the interwoven carbon band will crack, thereby relaxing the stress in the diffusion zone. As the growth of the reaction layer continues, the newly formed band will drift off, and a new build-up of stresses is expected in the layer adjoining the SiC . In this way the reaction zone morphology will demonstrate a periodic layered pattern.

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