# The Interaction between SiC and Ni, Fe, (Fe,Ni) and Steel: Morphology and Kinetics

R. C. J. Schiepers, J. A. van Beek, F. J. J. van Loo & G. de With\*

Centre for Technical Ceramics, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

(Received 27 April 1992; accepted 12 June 1992)

#### Abstract

The interaction between SiC and metals based on Ni or Fe has been studied from a thermodynamic and kinetic point of view. In solid-state diffusion couples the reactions have been studied in the temperature range 700 to  $1035^{\circ}$ C. In SiC–Ni couples the phases Ni<sub>2</sub>Si, Ni<sub>5</sub>Si<sub>2</sub> and Ni<sub>3</sub>Si are formed. The carbon is present as precipitates in regular bands in the Ni<sub>2</sub>Si and Ni<sub>5</sub>Si<sub>2</sub> layers. In SiC–Fe couples the layers consist of  $\alpha$ -(Fe,Si) with random carbon precipitates.

In SiC-Fe<sub>x</sub>Ni<sub>100-x</sub> couples at 850°C a variety of phases has been found. Dependent on the value of x,  $\alpha$ -(Fe,Ni,Si),  $\gamma$ -(Fe,Ni,Si), (Fe,Ni)<sub>5</sub>Si<sub>2</sub>, (Fe,Ni)<sub>2</sub>Si and the ternary phase  $\tau$ -(Fe<sub>5</sub>Ni<sub>3</sub>Si<sub>2</sub>) are formed. Carbon is present, either as isolated particles (in Ferich layers) or in regular bands (in Ni-rich layers).

The interaction between SiC and steel 316 is also investigated. The reaction zone consists of Fe silicides, Ni silicides, Cr carbides, Cr silicides, Mo silicides and Mo carbides.

The kinetics of the foregoing reactions have been studied. The kinetics of the SiC-(Fe,Ni) reactions are not simply intermediate between the kinetics of SiC-Ni and SiC-Fe. The reaction layer in SiC-steel couples stops growing after a short time. This is attributed to the formation of the chromium carbides.

Das Verhalten von SiC gegenüber Ni- oder Fe-Basislegierungen wurde aus thermodynamischer und kinetischer Sicht betrachtet. Die Reaktionen wurden anhand von Festphasendiffusionspaaren im Temperaturbereich von 700 bis  $1035^{\circ}$ C untersucht. SiC-Ni-Paare bilden die Phasen Ni<sub>2</sub>Si, Ni<sub>5</sub>Si<sub>2</sub> und Ni<sub>3</sub>Si. Kohlenstoff tritt als regelmäßige, bandförmige Ausscheidung in den Ni<sub>2</sub>Si- und Ni<sub>5</sub>Si<sub>2</sub>-Schichten auf. Bei SiC-Fe-Paaren bestehen die Schichten aus  $\alpha$ -(Fe,Si) mit ungeregelten Kohlenstoffausscheidungen.

 $SiC-Fe_xNi_{100-x}$ -Paare bilden bei 850°C eine Reihe \*Also affiliated with Philips Research, Eindhoven, The Netherlands. von Phasen aus. In Abhängigkeit vom x-Wert werden  $\alpha$ -(Fe,Ni,Si),  $\gamma$ -(Fe,Ni,Si), (Fe,Ni)<sub>5</sub>Si<sub>2</sub>, (Fe,Ni)<sub>2</sub>Si und die ternäre Phase  $\tau$ -(Fe<sub>5</sub>Ni<sub>3</sub>Si<sub>2</sub>) gebildet. Kohlenstoff tritt entweder als isolierte Partikel (in Fe-reichen Schichten) oder als regelmäßige Bänder (in Nireichen Schichten) auf.

Ebenso wurde das Verhalten von SiC gegenüber Stahl 316 sowie die Kinetik der Reaktionen untersucht. Die Reaktionszone besteht aus Fe-Siliciden, Ni-Siliciden, Cr-Carbiden, Cr-Siliciden, Mo-Siliciden und Mo-Carbiden.

Die Kinetik der SiC-(Fe,Ni)-Reaktionen stellt nicht einfach ein gemitteltes Verhalten zwischen der Kinetik von SiC-Ni und SiC-Fe dar. Die Reaktionsschicht von SiC-Stahl-Paaren wächst nach kurzer Zeit nicht mehr weiter an. Dies wird auf die Bildung von Chromcarbiden zurückgeführt.

Les auteurs ont étudié la thermodynamique et la cinétique de l'interaction entre SiC et des métaux à base de Ni ou Fe. Dans les couples de diffusion à l'état solide, les réactions ont été étudiées dans la gamme de température comprise entre 700 et  $1035^{\circ}$ C. Les phases  $Ni_2Si$ ,  $Ni_5Si_2$  et  $Ni_3Si$  sont formées pour les couples SiC-Ni. Le carbone est présent en tant que précipité en bandes régulières dans les couches de  $Ni_2Si$  et  $Ni_5Si_2$ . Dans les couples SiC-Fe, les couches consistent en (Fe,Si)- $\alpha$  avec le carbone précipité aléatoirement.

On a trouvé une grande diversité de phases pour les couples  $SiC-Fe_xNi_{100-x} a 850^\circ C$ . Selon la valeur de x,  $(Fe,Ni,Si)-\alpha$ ,  $(Fe,Ni,Si)-\gamma$ ,  $(Fe,Ni)_5Si_2$ ,  $(Fe,Ni)_2Si$  et la phase ternaire  $Fe_5Ni_3Si_2-\tau$  sont formées. Le carbone est présent, soit comme particules isolées (dans les couches riches en Fe) ou en bandes régulières (dans les couches riches en Ni).

L'interaction entre SiC et l'acier 316 a également été étudiée. La zone de réaction est constituée de siliciures de Fe, de Ni, de Cr et de Mo, et de carbures de Cr et de Mo.

Les cinétiques des réactions précédemment citées

Journal of the European Ceramic Society 0955-2219/93/\$6.00 © 1993 Elsevier Science Publishers Ltd, England. Printed in Great Britain

ont été examinées. Les vitesses des réactions SiC-(Fe,Ni) ne sont pas simplement intermédiaires entre celles des réactions SiC-Ni et SiC-Fe. La croissance de la couche réactionnelle des couples SiC-acier stoppe après un laps de temps court. Ceci est attribué à la formation de carbures de chrome.

#### **1** Introduction

Silicon-based structural ceramics, such as SiC, can have desirable properties like good corrosion resistance, high hardness and high strength up to high temperatures. In order to profit fully from the advantages of these ceramics in structures, ceramicmetal joints often have to be used. A good adherence between the metal and the ceramic is then required. However, severe reactions at the interface may negatively influence the quality of the joints.

Because of this practical importance, ceramicmetal interactions are being investigated in the authors' laboratory. In order to understand and to control the reactions, the thermodynamics and the kinetics of ceramic-metal interactions are subject to investigation. The programme started by studying the interactions between very pure, dense SiC and Ni and Fe.<sup>1</sup> The main results of this investigation can be summarized as follows.

In SiC–Ni diffusion couples at  $850^{\circ}$ C the compounds Ni<sub>2</sub>Si, Ni<sub>5</sub>Si<sub>2</sub> and Ni<sub>3</sub>Si are formed in regular layers. Carbon was present in the Ni<sub>2</sub>Si and Ni<sub>5</sub>Si<sub>2</sub> layers as regular bands parallel to the original interface (Fig. 1). By means of marker experiments nickel is found to be virtually the only diffusing component. The Ni–Ni<sub>3</sub>Si interface coincides, therefore, with the original (or Kirkendall) interface. The morphology and composition of the reaction layer are independent of the presence of aluminium, used as a sintering additive.

In SiC–Fe diffusion couples at  $850^{\circ}$ C the  $\alpha$ -(Fe,Si) solid solution was formed, with carbon precipitates



Fig. 1. Backscattered electron image of a SiC(0·2Al)–Ni couple annealed for 22 h at 850°C.



Fig. 2. Backscattered electron image of a SiC(0·2Al)–Fe couple annealed for 22 h at 850°C.

randomly dispersed in the layer, except for a thin, carbon-free zone of  $\alpha$ -(Fe,Si) (Fig. 2). Fe turns out to be virtually the only diffusing component. At 850°C the reaction zones show the same morphology and composition, independent of the Al content of the SiC ceramic. The isothermal sections of the Ni–Si–C and Fe–Si–C phase diagrams at 850°C have also been determined.<sup>1</sup>

In this paper the results of diffusion experiments between SiC and pure Ni, Fe, (Fe, Ni) alloys and steel 316 are presented, with emphasis on the kinetics and the morphology of the reaction layers.

# 2 Experimental Procedure

The experimental set-up and preparational procedure have been described in detail in Ref. 1. The metals in this investigation have a purity >99.95 wt%. For SiC HIP-SiC without sintering additives (SiC(w)) and HIP-SiC with 0.2 wt% Al (SiC(0.2Al)) were used. As a steel austenitic stainless steel 316 was used. It contained max. 0.08% C, max. 2.00% Mn, max. 0.05% P, max. 0.03% S, max. 1.00% Si, 16-18% Cr, 10–14% Ni, 2–3% Mo and the remainder was Fe (wt%). (Fe,Ni) alloys were made by argon-arc melting the proper amounts of the constituents (up to 5 g), and the resulting alloys were annealed for 1 week in vacuum silica capsules at 850°C. The diffusion couples were annealed in a vacuum furnace at 10<sup>-4</sup> Pa under a pressure of 13 MPa for various times. The couples and the equilibrated alloys were investigated by optical microscopy, electron probe micro-analysis (JEOL Superprobe 733), scanning electron microscopy (JEOL JSM 840) and X-ray diffraction.

To reveal the morphology of the reaction layer in the SiC-(Fe,Ni) and SiC-steel diffusion couples the surface was etched with 10 ml HCl and 3.2 g FeCl<sub>3</sub> in 40 ml ethanol.

# 3 Interaction of SiC with (Fe,Ni) Alloys and with Steel 316

The alloys investigated contained 20, 40, 60, 80, 90, 95 and 99 at.% Fe. The diffusion paths can be plotted in the quaternary Fe–Ni–Si–C diagram at 850°C and can be projected on the Fe–Ni–Si phase diagram at 850°C<sup>2</sup> (Fig. 3). Using a model of van Loo *et al.*<sup>3</sup> it can be concluded that only phases at the right-hand side of the dotted line can be formed, since they have to be in equilibrium with carbon which is formed at the interface SiC–reaction layer. This is the reason that only a part of the Fe–Ni–Si–C diagram had to be investigated. The results for the experiments with the SiC without Al, SiC(w), are very similar to those with Al, SiC(0·2Al). Generally the undoped samples seem to yield somewhat thinner reaction zones. For



**Fig. 3.** (a) Fe-Ni-Si-C phase diagram at 850°C. The phases at the right-hand side of the dotted line are in equilibrium with graphite; those at the left are in equilibrium with SiC. (b) Projections of some diffusion paths on the Fe-Ni-Si diagram at 850°C.

the various SiC–(Fe,Ni) alloys interfaces the following observations were made.

# 3.1 SiC-Fe<sub>20</sub>Ni<sub>80</sub>

The reaction zone consists of alternating layers of  $(Fe,Ni)_2Si + C$  (d3),  $(Fe,Ni)_5Si_2 + C$  (d2) and  $\gamma$ -(Fe,Ni,Si)(d1)(Fig. 4). Carbon is present in more or less regular bands in the reaction zone, similar to the SiC–Ni system. Possibly a thin layer of  $\tau$ -(Fe<sub>5</sub>Ni<sub>3</sub>Si<sub>2</sub>) was also present.

# 3.2 SiC-Fe<sub>40</sub>Ni<sub>60</sub>

The reaction zone consists of  $(Fe, Ni)_2Si + C$  (d4), (Fe,Ni)<sub>5</sub>Si<sub>2</sub> + C (d3),  $\tau$  + C (d2) and  $\gamma$ -(Fe,Ni,Si) (d1) (Fig. 5). Here also bands of carbon are present in the reaction layer.

## 3.3 Si-Fe<sub>60</sub>Ni<sub>40</sub>

The reaction layer consists of  $(Fe,Ni)_2Si + C$ ,  $(Fe,Ni)_5Si_2 + C$ ,  $\alpha$ -(Fe,Ni,Si) + C,  $\tau$ - $(Fe_5Ni_3Si_2) + C$  and a thin layer of  $\gamma$ -(Fe,Ni,Si). The reaction zone contains random precipitates of C. Only in a small area near SiC is carbon formed in bands.

# 3.4 SiC with $Fe_{80}Ni_{20}$ , $Fe_{90}Ni_{10}$ , $Fe_{95}Ni_5$ and $Fe_{99}Ni_1$

The reaction zones for the couples  $Fe_{80}Ni_{20}$  to  $Fe_{95}Ni_5$  consist of  $\alpha$ -(Fe,Ni,Si) + C and a thin layer



Fig. 4. Optical micrograph of a SiC(0.2Al)-Fe<sub>20</sub>Ni<sub>80</sub>-SiC(w) couple annealed during 72 h at 850°C.



Fig. 5. Optical micrograph of a SiC(0.2AI)-Fe<sub>40</sub>Ni<sub>60</sub>-SiC(w) couple annealed during 24 h at 850°C.

of  $\gamma$ -(Fe,Ni,Si). Carbon is present as random particles. For Fe<sub>99</sub>Ni<sub>1</sub> the reaction zone consists of  $\alpha$ -(Fe,Ni,Si) + C and a layer of  $\alpha$ -(Fe,Ni,Si) without C, as in couples formed between pure Fe and SiC.

#### 3.5 SiC-steel 316

In the reaction zone nickel silicides, iron silicides, chromium carbides, chromium silicides, molybdenum silicides and molybdenum carbides are formed.

# 4 Periodic Layers in SiC-Ni and SiC-(Fe,Ni) Reaction Zones

In SiC-Ni couples periodic layers in the form of regular bands are present. The layers consist of precipitates of C in Ni<sub>2</sub>Si and Ni<sub>5</sub>Si<sub>2</sub> layers. The same type of periodic layer was found in all SiC-Fe<sub>x</sub>Ni<sub>100-x</sub> couples for  $x \le 60$ . In all of these couples the band formation is found on the SiC side of the interface, whereas in the Fe-rich silicides random precipitation of C is found on the metal side (Fig. 4). Since the reaction front is at the SiC-layer interface (Ni and Fe are the only diffusing species) the bands, formed in the Ni-rich silicides, are, during further layer growth, overtaken by the Fe-rich silicides, and then disintegrate into small random particles. In Table 1 the average distance between the carbon bands is given for the system SiC-Ni.

From a thermodynamic model by van Loo *et al.*<sup>3</sup> the layer sequence in SiC–Ni can be predicted. The sequence SiC–C–SiNi<sub>x</sub>–Ni follows from the phase diagram proposed by the present authors.<sup>1</sup> The attacking element Ni diffuses through the reaction layer towards the substrate (SiC) and reacts with Si, leaving the carbon behind in pure form. This initial layer sequence is not only governed by the phase relations. Other factors like the relative mobilities of the elements in the various phases are also of importance.<sup>3</sup> Mechanical stress built up during the reactions is probably the most important requisite for the formation of a periodic structure.<sup>4</sup>

### 5 Kinetics

In this section the results of the kinetic experiments for the various couples are discussed.

 Table 1. The average distance between carbon bands for the system SiC-Ni

$T(^{\circ}C)$	$Ni_2Si + C \ (\mu m)$	$Ni_5Si_2 + C \ (\mu m)$
650	3	3
800	3	4
850	2	3
1025	14	16



**Fig. 6.** Plot of the square of the total layer thickness  $d^2$  versus time *t* in SiC–Ni couples at various temperatures:  $\bigcirc$ , SiC(w) at 700°C;  $\triangle$ , SiC(w) at 775°C;  $\bigtriangledown$ , SiC(w) at 850°C;  $\square$ , SiC(w) at 925°C;  $\bigcirc$ , SiC(w) at 1035°C; +, SiC(0·2Al) at 850°C; +, SiC(0·2Al) at 925°C.



**Fig. 7.** Plot of  $\ln k_p$  versus 1/T for the SiC–Ni system:  $\bigcirc$ , SiC(w); +, SiC(0·2Al);  $\triangle$ , Kurokawa;  $\square$ , Yamada. Data for 650 and 800°C are included in this graph (but not in Table 2); they represent a  $k_p$  value derived from a single thickness measurement.

# 5.1 SiC-Ni

The kinetics of the reaction between silicon carbide and nickel have been studied between 650 and 1035°C. The results are shown in Figs 6 and 7. SiC reacts with Ni without an incubation time. In the Alcontaining diffusion couples thicker reaction zones are formed.<sup>5</sup> The layer growth follows the parabolic growth law  $d^2 = 2k_p t$ , where d denotes the thickness of the layer,  $k_p$  the rate constant and t the time. In Table 2 the  $k_p$  values ( $\mu$ m<sup>2</sup>/h) for both types of SiC are listed, as calculated by the non-weighted, leastsquares method, constrained to give a line through the origin.

From Fig. 7  $E_{act} \pm \sigma(E_{act})$  (kJ/mol), the activation

**Table 2.** Rate constants  $k_p$  for SiC–Ni couples

<i>T</i> (° <i>C</i> )	$k_{p} (\mu m^{2}/h)^{a}$		
	SiC(w)	SiC(0·2Al)	
700	105 (3)		
775	170 (4)	_	
850	439 (55)	924 (87)	
925	3 640 (260)	6100 (120)	
1035	23 700 (310)		

"Value and estimated standard deviation (in parentheses) as obtained from constrained least-squares fit.

energy and its standard deviation, can be calculated using the equation

$$\ln k_{\rm p} = (-E_{\rm act}/RT) + \ln k_{\rm p}^0$$

and the non-weighted, unconstrained least-squares method. As usual R and T denote the gas constant and absolute temperature, respectively. This results in a value for  $E_{act}$  for SiC-Ni of  $177 \pm 29$  kJ/mol. The activation energy, as calculated from  $k_p$  values resulting from  $d^2$  versus t plots where an unconstrained fit was used, is  $181 \pm 22$  kJ/mol. The temperature dependence of the ln  $k_p$  values of both types of SiC versus Ni is nearly the same. So the same value of  $E_{act}$  is obtained. These values are in good agreement with those reported by Yamada *et al.*:<sup>6</sup>  $E_{act} = 181 \pm 3$  kJ/mol. The  $k_p$  data as given by Kurokawa & Nagasaki<sup>7</sup> also fit well in the graph.

#### 5.2 SiC-Fe

In the kinetics of the SiC-Fe diffusion couples an irreproducible incubation time is present, probably caused by a reaction barrier at the initial interface. The free energy change at 850°C for the reaction  $3Fe + SiC \rightarrow Fe_3Si + C$ ,  $\Delta G^{\circ} = -11 \text{ kJ}$ , is much less negative than the value for the corresponding reaction with Ni,  $\Delta G^{\circ} = -85 \text{ kJ}$ . Any barrier, such as a small oxide film, can easily hinder the reaction with Fe more than with Ni. After this incubation time a parabolic layer growth is found (Fig. 8). In the Alcontaining samples again thicker reaction zones are formed. Due to the presence of the irreproducible incubation time, the authors were not able to find reliable growth rate values at other temperatures and, therefore, could not determine a value for the activation energy in SiC-Fe couples.



**Fig. 8.** Plots of  $d^2$  versus time for various SiC–(Fe,Ni) diffusion couples. (a) SiC–Fe at 850°C:  $\bigcirc$ , SiC(w); +, SiC(0·2Al); (b) SiC–Fe<sub>20</sub>Ni<sub>80</sub> at 850°C:  $\bigcirc$ , SiC(w); +, SiC(0·2Al); (c) SiC–Fe<sub>40</sub>Ni<sub>60</sub> at 850°C:  $\bigcirc$ , SiC(w); +, SiC(0·2Al); (d) SiC–Fe<sub>80</sub>Ni<sub>20</sub> at 850°C:  $\bigcirc$ , SiC(w); +, SiC(0·2Al); (e) SiC–Fe<sub>90</sub>Ni<sub>10</sub> at 850°C:  $\bigcirc$ , SiC(w); +, SiC(0·2Al); (f) SiC(0·2Al)–Fe<sub>95</sub>Ni<sub>5</sub> at  $\bigcirc$ , 750°C; △, 850°C; and +, 925°C. Data for SiC(w) at 850°C indicated by  $\bigtriangledown$ .

#### 5.3 SiC-(Fe,Ni)

The kinetics of the interaction between SiC and (Fe,Ni) alloys or steel were measured at 850°C. It is difficult to follow experimentally the kinetics of the SiC–(Fe,Ni) interaction. A number of disturbing effects occurs.

- (a) The presence of oxide barrier films leading to an irreproducible incubation time.
- (b) On the various  $Fe_{1-y}Ni_y$  alloys different oxide films may be present. For instance, the oxides in thermodynamic equilibrium with the various alloys at 1000°C are<sup>3</sup>

for 
$$y < 0.80$$
 $Fe_{1-\delta}O(\delta \ll 1)$ 

 for  $0.80 < y < 0.95$ 
 $(Fe, Ni)_3O_4$ 

 for  $0.95 < y < 1$ 
 NiO

- (c) The formation of the ternary compound  $\tau$ -(Fe<sub>5</sub>Ni<sub>3</sub>Si<sub>2</sub>) seems to diminish the reaction rate. In the diffusion couples SiC-Fe<sub>80</sub>Ni<sub>20</sub>, SiC-Fe<sub>90</sub>Ni<sub>10</sub> and SiC-Fe<sub>95</sub>Ni<sub>5</sub> the compound  $\tau$ -(Fe<sub>5</sub>Ni<sub>3</sub>Si<sub>2</sub>) is not formed, so the reaction rate is high.
- (d) There is a relation between the thickness of the  $(Fe,Ni)_2Si$  and  $(Fe,Ni)_5Si_2$  layers and the reaction rate. When these layers are thin compared with the total thickness of the reaction layer, the experiment is reliable. But when these layers are thicker than usual, the experiment is not reliable, since then they are formed at the expense of other phases when the contact between the end members is not optimal. The relative thickness of the various layers formed at a certain temperature has to be independent of time, therefore this verification has always been made for the various (Fe,Ni) alloys.

5.4 SiC-Fe<sub>20</sub>Ni<sub>80</sub>, SiC-Fe<sub>40</sub>Ni<sub>60</sub> and SiC-Fe<sub>60</sub>Ni<sub>40</sub> For the couples SiC-Fe<sub>20</sub>Ni<sub>80</sub> and SiC-Fe<sub>40</sub>Ni<sub>60</sub> the experiments are considered to be reliable according to remark (d) in the previous section. In Fig. 8 the  $d^2$  versus *t* plot for SiC-Fe<sub>20</sub>Ni<sub>80</sub> and SiC-Fe<sub>40</sub>Ni<sub>60</sub> at 850°C are given.

In SiC-Fe<sub>60</sub>Ni<sub>40</sub> diffusion couples the contact between the alloys and the reaction zones was not always maintained at the alloy (= Kirkendall) interface so that the Si-rich layers could grow at the expense of the others and thinner total layers are found. The data from these experiments are not considered to be reliable.

#### 5.5 Remaining couples

For the systems SiC-Fe<sub>80</sub>Ni<sub>20</sub>, SiC-Fe<sub>90</sub>Ni<sub>10</sub>, SiC-Fe<sub>95</sub>Ni<sub>5</sub> and SiC-Fe<sub>99</sub>Ni<sub>1</sub> such a verification is not possible, because a single-phase layer is formed. Here the same disturbing features as in SiC-Fe

**Table 3.** Rate constants  $k_p$  for SiC-Fe<sub>x</sub>Ni<sub>100-x</sub> couples

Couple	$T(^{\circ}C)$	$k_{p} (\mu m^2/h)^a$	
		SiC(w)	SiC(0·2Al)
Ni	850	439 (55)	924 (87)
Fe <sub>20</sub> Ni <sub>80</sub>	850	295 (7)	309 (7)
Fe <sub>40</sub> Ni <sub>60</sub>	850	242 (9)	272 (8)
Fe <sub>60</sub> Ni <sub>40</sub>	850	2 500 (750)	3 1 50 (640)
Fe <sub>80</sub> Ni <sub>20</sub>	850	15 900 (1 300)	36 200 (1 400)
Fe <sub>eo</sub> Ni <sub>10</sub>	850	2 900 (590)	6 570 (350)
Fe <sub>95</sub> Ni <sub>5</sub>	750		37 (5)
Fe <sub>95</sub> Ni <sub>5</sub>	850	3 900 (250)	2 780 (330)
Fe <sub>9</sub> ,Ni,	925		19 100 (1 600)
Fe	850	890 (70)	2 280 (160)

"Value and estimated standard deviation (in parentheses) as obtained from constrained least-squares fit.

couples are probably present, which causes the large variation of the experimental values (Fig. 8). In the case of  $Fe_{80}Ni_{20}$ ,  $Fe_{90}Ni_{10}$  and  $Fe_{95}Ni_5$  the incubation time is, however, much smaller and a reasonable value of  $k_p$  can be obtained. This makes it possible to extrapolate to the case of pure Fe. In the case of  $Fe_{99}Ni_1$  a highly irreproducible and varying reaction layer thickness is obtained and these data are not considered further.

For the SiC-steel interaction after a short annealing time a more or less constant reaction zone thickness is observed, independent of the annealing time. This might be explained by the formation of a chromium carbide layer which completely stops diffusion and further reaction.

From the  $d^2$  versus t plots the  $k_p$  values can be determined (Table 3). In this case again a constrained fit through the origin was used, except for the SiC-Fe couples. It is seen from Table 3 that the variation in  $k_p$  values is large. Unconstrained fits yielded comparable values.

In Fig. 9 the rate constant  $k_p$  versus atomic per cent  $x_{Fe}$  is plotted for the SiC–(Fe,Ni) system in the range  $80 \le x_{Fe} \le 100$  at.%. By extrapolation the  $k_p$ 



Fig. 9.  $k_p$  versus  $x_{Fe}$  for  $80 \le x_{Fe} \le 100$  at.% for SiC-(Fe,Ni) systems:  $\bigcirc$ , SiC(w); +, SiC(0.2Al).



Fig. 10.  $\ln k_p$  versus 1/T plot for SiC(0·2Al)-Fe<sub>95</sub>Ni<sub>5</sub>.

values for SiC–(Fe, Ni) (without incubation time) are compared with the experimental values for  $k_p$  for pure Fe versus SiC (with incubation time). It is seen that the agreement is quite good.

Some experiments were performed to determine the kinetics of SiC(0·2Al)–Fe<sub>95</sub>Ni<sub>5</sub> couples at different temperatures, as shown in Fig. 10. The activation energy thus obtained,  $367 \pm 33$  kJ/mol, can probably be used as a value for the pure SiC–Fe couples in view of the comparable value of  $k_p$  for both couple types at 850°C. The influence of the fitting method is again minor. The activation energy as calculated from  $k_p$  values resulting from  $d^2$  versus *t* plots where an unconstrained fit was used is  $375 \pm 23$  kJ/mol.

# 6 Concluding Remarks

#### 6.1 Periodic structures

The banded reaction zone found in SiC–Ni and SiC–Fe<sub>x</sub>Ni<sub>100-x</sub> for  $x \le 60$  has many similarities with those found in the systems Fe–Si–Zn and Co–Si–Zn which were investigated by Osinski and coworkers.<sup>4,8,9</sup> In a recent publication by Backhaus-Ricoult<sup>10</sup> the periodic structure was also reported and discussed. The present results on morphology are in good agreement with those in Ref. 10. Moreover, Backhaus-Ricoult points out that the carbon precipitates show the fibrous structure of turbostratic graphite.

# 6.2 Kinetics of the SiC-(Fe,Ni) interaction

In SiC-Fe<sub>x</sub>Ni<sub>100-x</sub> couples a ternary compound,  $\tau$ -(Fe<sub>5</sub>Ni<sub>3</sub>Si<sub>2</sub>), is present for 20 < x ≤ 60 at.%. The kinetics in these couples, therefore, cannot be described as simply intermediate between the kinetics of SiC-Ni and SiC-Fe. When  $\tau$ -(Fe<sub>5</sub>Ni<sub>3</sub>Si<sub>2</sub>) is formed, the reaction seems to be hindered so that the reaction zone is relatively small. In SiC-Fe<sub>80</sub>Ni<sub>20</sub> the zone is very thick because  $\tau$ -(Fe<sub>5</sub>Ni<sub>3</sub>Si<sub>2</sub>) is not present. The sharp decrease in reaction rate going from Fe<sub>80</sub>Ni<sub>20</sub> to pure Fe is very remarkable, in view of the fact that the same phases are formed.

# 6.3 Incubation time in SiC-Fe and SiC-(Fe,Ni) interactions

In the SiC-Fe kinetic plot an incubation time is present. The addition of 5 at.% of Ni prevented this incubation time to a large extent. Extrapolation of the kinetics for x from 80 to 100 at.% gives values for  $k_p$  which are comparable to those found in actual SiC-Fe couples.

#### 6.4 Future studies

To join (Fe,Ni) alloys to SiC ceramics it is necessary to use barrier layers to prevent too fast a diffusion resulting in thick reaction layers. In order to obtain thin reaction layers, a small amount of Fe and/or Ni can be used as a reactive solute in the barrier alloy. From the present kinetic data, optimum concentration, bonding time and temperature can be estimated. Barrier layers are also necessary to diminish the mechanical stresses arising from the thermal expansion mismatch. In future experiments attempts will be made to combine the chemical and mechanical requirements of the metal-ceramic combination in order to obtain reliable joints.

# Acknowledgements

This investigation has been partly supported by the Commission for the Innovative Research Program Technical Ceramics (IOP-TK) of the Ministry of Economic Affairs in The Netherlands (IOP-TK research grant 86.B033).

#### References

- Schiepers, R. C. J., van Loo, F. J. J. & de With, G., Reactions between α-silicon carbide ceramic and nickel or iron. J. Am. Ceram. Soc., 71 (1988) C-284-C-287.
- Schiepers, R. C. J., van Beek, J. A., van Loo, F. J. J. & de With, G., The interaction between SiC and metals. In *Proc. Int. Conf. Euro-Ceramics*, ed. G. de With, R. A. Terpstra & R. Metselaar. Elsevier Applied Science, London, 1989, pp. 3.424–8.
- van Loo, F. J. J., van Beek, J. A., Bastin, G. F. & Metselaar, R., The role of thermodynamics and kinetics in multiphase ternary diffusion. In *Diffusion in Solids, Recent Developments*, ed. M. Dayananda & G. E. Murch. TMS, Warrendale, USA, 1985, pp. 231–59.
- van Loo, F. J. J. & Osinski, K., Periodic structures in multicomponent diffusion couples. In *Fundamentals and Applications of Ternary Diffusion, 29th Ann. Conf. of Metall.* of CIM, ed. G. R. Purdy. Pergamon, New York, 1990, pp. 109–18.
- Schiepers, R. C. J., van Beek, J. A., de Giacomoni, E., Valla, B., van Loo, F. J. J. & de With, G., The interaction between SiC and Ni or Fe and their alloys. In *Metal-Ceramic Interfaces, Acta/Scripta Metallurgica Proc. Series*, Vol. 4, ed. M. Rühle, A.G. Evans, M. F. Ashby & J. P. Hirth. Pergamon, Oxford, 1990, pp. 138–43.
- 6. Yamada, T., Sekiguchi, H., Okamoto, H., Azuma, S. &

Kitamura, A., Diffusion bonding of SiC or Si<sub>3</sub>N<sub>4</sub> to metal. In Proc. 2nd Int. Symp. Ceramic Materials and Components for Engines, ed. W. Bunk & H. Hausner. Verlag Deutsche Keramische Gesellschaft, Lübeck-Travemünde, FRG, 1986, pp. 441-8.

- 7. Kurokawa, K. & Nagasaki, R., Reactivity of sintered SiC with metals. In Proc. Int. Inst. Sci. of Sintering Symp., ed. Sh. Somiya, M. Shimada, M. Yoshimura & R. Watanabe. Elsevier Applied Science, Tokyo, 1987, pp. 1397–402. 8. Osinski, K., Vriend, A. W., Bastin, G. F. & van Loo, F. J. J.,

Periodic formation of FeSi bands in diffusion couples Fe

- (15 wt% Si)-Zn. Z. Metallkde, 73 (1982) 258-61.
  9. Osinski, K., The influence of aluminium and silicon on the reaction between iron and zinc. PhD thesis, University of Technology, Eindhoven, The Netherlands, 1983.
- 10. Backhaus-Ricoult, M., Physicochemical processes at metalceramic interfaces. In Metal-Ceramic Interfaces, Acta/ Scripta Metallurgica Proc. Series, Vol. 4, ed. M. Rühle, A. G. Evans, M. F. Ashby & J. P. Hirth. Pergamon, Oxford, 1990, pp. 79–92.