The interaction between SiC and Ni or Fe

Defect and Diffusion Forum Vols. 66-69 (1989) pp. 1497-1502

THE INTERACTION BETWEEN SiC AND Ni OR Fe

R.C.J. Schiepers, F.J.J. van Loo and G. de With*
Centre for Technical Ceramics CTK, Eindhoven University of Technology
P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands
* also affiliated with Philips Research, Eindhoven, The Netherlands

Introduction

In a previous paper the authors have reported on the morphology and composition of the reaction layer between SiC and Ni or Fe at a temperature of 850°C [1]. In SiC/Ni diffusion couples, the compounds Ni_2Si, Ni_5Si_2 and Ni_3Si are formed in regular layers. Carbon precipitates are present in the Ni_2Si and Ni_5Si_2 layers as more or less regular bands parallel to the original interface (Fig. 1). By means of marker experiments nickel is found to be the predominantly diffusing component [1]. In SiC/Fe diffusion couples the ordered cubic compound Fe_3Si is formed, with carbon precipitates randomly dispersed in the layer except for a thin, carbon-free zone near the Fe/Fe_3Si boundary (Fig. 2). Fe turns out to be virtually the only diffusing component [1].

The present paper deals with the kinetics of these reactions in the temperature range between 700 and 925°C. The experimental set-up and preparational procedure have been described extensively in ref. [1]. The diffusion couples are annealed in a vacuum furnace under a load of 20 kg (pressure 13 MPa). The metals used in this investigation have a purity > 99.95 %. Various types of silicon carbide have been used as a starting material, viz.

a) hot isostatically pressed SiC without sinter additives: SiC(w)
b) hot isostatically pressed SiC with 0.2 wt% Al: SiC (.2 Al)
c) hot pressed SiC with 0.45 wt% Al: SiC (.45 Al)
d) reaction bonded SiC with 10 wt% free silicon: SiSiC

Results Fe-SiC

Qualitatively, at 850°C the reaction zones have the same morphology and composition independent of the presence of sinter additives if SiC without free silicon is used as a starting material. The thickness of the reaction layer, however, seems to be dependent on the type of SiC as shown in Fig. 3.

For SiC without any sinter additives the lowest growth rate is found. A parabolic layer growth is assumed after a large incubation time. In fact, from the measured data at 850°C it is difficult to decide whether this is true or not. On the other hand, experiments at 925°C clearly show an incubation time of about 18 hours. Up to that time a layer is formed with a thickness of only about 100 μm, whereas after a heat treatment of 24 hours the layer width is found to be about 800 μm.

For SiC with 0.2 or 0.45 wt% Al the incubation time t_o is shorter, and the parabolic rate constant $k_p = d^2/2(t-t_o)$ (d = layer thickness) is larger.

In the case of Fe/SiSiC the reaction layer is much thicker and has a different structure: the original Si parts of the starting material have transformed into Fe_3Si, whereas the SiC parts react in the same way as in the previously mentioned couples, forming Fe_3Si + C (Fig. 4). The reaction of Fe with pure Si to Fe_3Si is faster than the reaction of Fe with SiC. Therefore, towards the SiC side in the reaction layer (which is the last formed part) particles of SiC are found, which have not yet reacted completely. Next to the Fe starting material a carbon precipitate-free zone of Fe_3Si is visible.

Results for Ni-SiC

In couples where SiC without free silicon is used as a starting material, the morphology, composition and the layer thickness are independent of the presence of sinter additives. In Fig. 5 the d^2/t plot is shown for four temperatures. At 925, 775 and 700°C only SiC without sinter additives was used. At 850°C all types were used and a rather large scatter was found despite the very regular appearance of the reaction layers. This scatter could, however, not be attributed clearly to the use of various types of SiC. No incubation time was observed.

In Fig. 6 a plot of ln kp vs. 1/T is given, showing a non-linear relationship.

The use of SiSiC gives rise to a morphology as shown in Fig. 7. The original SiC-parts have reacted with Ni in the same way as in normal Ni-SiC couples. The original Si parts, however, do not behave in the same way as in normal Ni-Si couples. For instance, after 16 hours at 850°C the following phases are formed in a Ni-Si couple: Ni_3Si(20 μm), Ni_5Si_2(30 μm), Ni_2Si(80 μm), θ-Ni_3Si_2(800 μm) and NiSi + $NiSi_2$(traces).

The high-temperature phase θ-Ni_3Si_2 is clearly dominant. In the couples Ni/SiSiC, however, the layers and phases being formed under the same circumstances are (see Fig. 7): A(2 μm) = Ni_3Si; B(125 μm) = Ni_5Si_2 + (Ni_5Si_2 + C), formed from original SiC; C(25 μm) = Ni_5Si_2 + (Ni_2Si + C), formed from original SiC; D(50 μm) = Ni_2Si + SiC; and a very thin zone E, where traces of Ni_3Si_2, NiSi and $NiSi_2$ are found next to Si and SiC. The virtual absence of Ni_3Si_2 is conspicuous. The non-coexistence of Ni_5Si_2 and SiC is in line with the proposed phase diagram[1]. The width of layer (A + B + C) fits in with the plot of the total layer thickness vs. time in Ni-SiC couples as shown in Fig. 5.

Discussion

The reaction between Ni and SiC in a diffusion couple, using a pressure of 13 MPa, proceeds without an incubation time and follows a parabolic rate law. The effective activation energy of the process as determined from the ln kp vs. 1/T plot (Fig. 6) varies from about 50 kJ at 750°C to about 260 kJ at 900°C. This might be caused by a larger role of grain boundary diffusion at low temperatures. However, it might also be related to a change in the thermodynamics of the process, since the isothermal section of the phase diagram Ni-Si-C changes in this temperature range. Our results are in qualitative agreement with measurements by Yamada et al.[2], who report an activation energy of 180.5 kJ/mole.

In the reaction between Fe and SiC an incubation time is found, and the growth of the reaction layer depends on the sinter additives in SiC. A possible explanation is the occurrence of a barrier film on SiC, which hinders Fe diffusion (but not Ni-diffusion). At the moment experiments are going on to investigate this specific point and the further kinetic data on the Fe-SiC reaction. Also the difference in layer morphology between Ni-SiC and Fe-SiC couples (especially the layered and random carbon precipitates, respectively) is subject of further study.

References

1. R.C.J. Schiepers, F.J.J. van Loo and G. de With: J.Am.Ceram.Soc. 71, C-284, 1988
2. T. Yamada, H. Sekiguchi, H. Okamôto, S. Azuma, A. Kitamura: Proc. 2nd Int. Symp. on Ceramic Materials and Components for Engines, Eds.: W. Bunk and H. Hausner, Lübeck BRD 1986, p. 441-448.

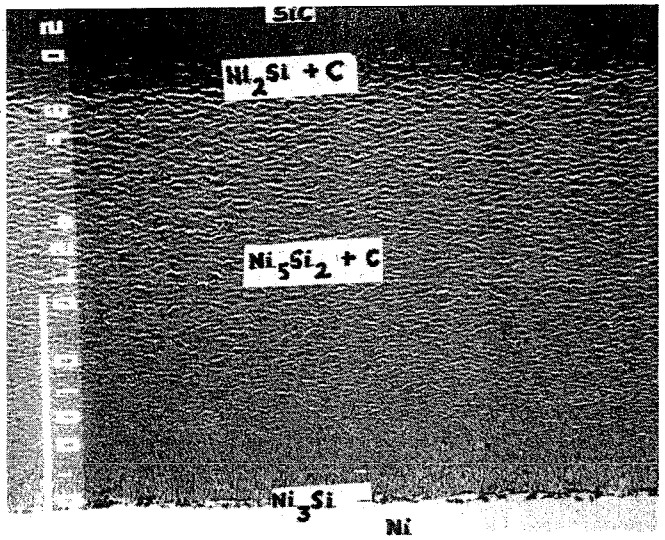

Fig. 1. Backscattered electron image of the diffusion couple SiC(w)-Ni, annealed for 44 hours at 850°C under 13 MPa (bar = 100 μm).

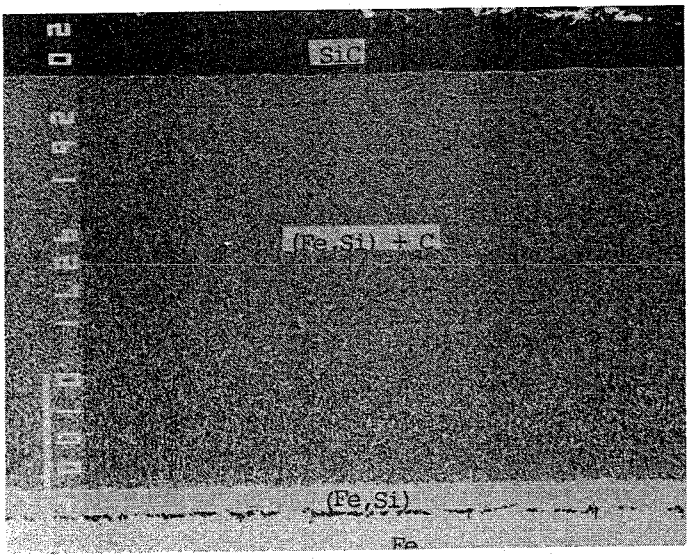

Fig. 2. Backscattered electron image of the diffusion couple SiC(w)-Fe, annealed for 44 hours at 850°C under 13 MPa (bar = 100 μm).

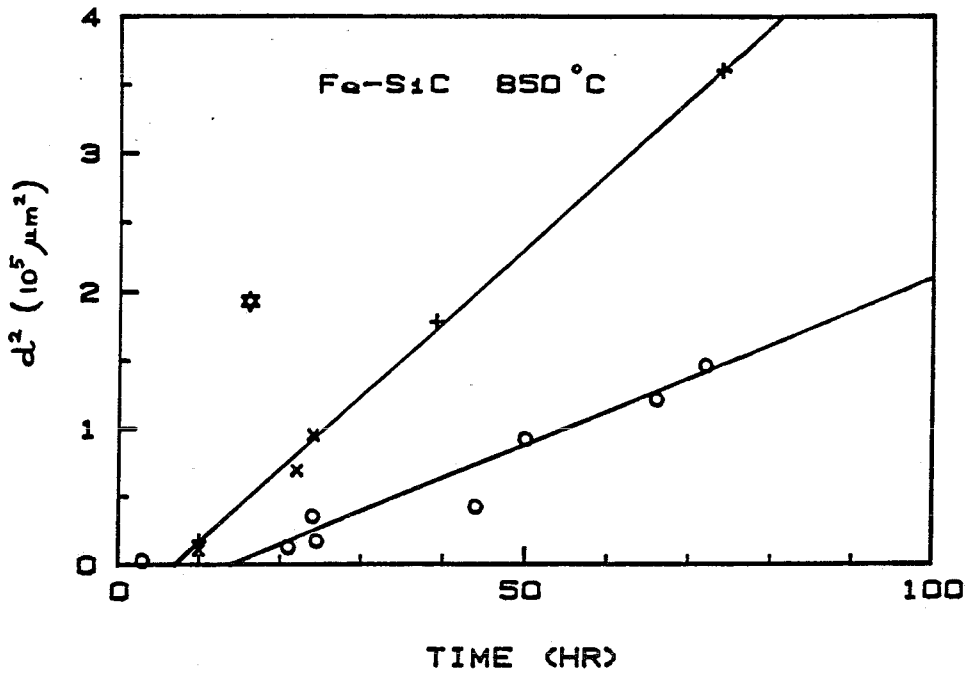

Fig. 3. Plot of the square of the total layer thickness d^2 (10^5 µm^2) versus time (hours) in Fe-SiC couples at 850°C. o = SiC(w); x = SiC(.2 Al); + = SiC(.45 Al); * = SiSiC.

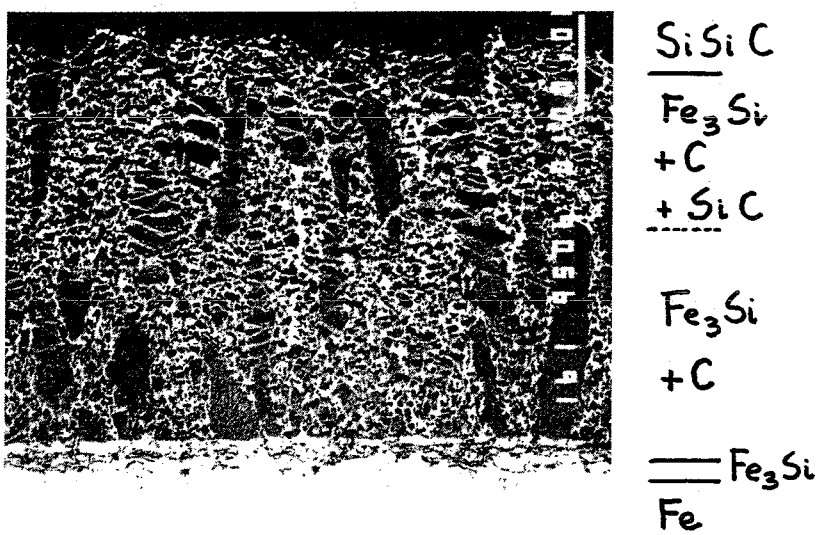

Fig. 4. Backscattered electron image of the diffusion couple Fe/SiSiC, annealed for 16 hours at 850°C under 13 MPa (bar = 100 µm).

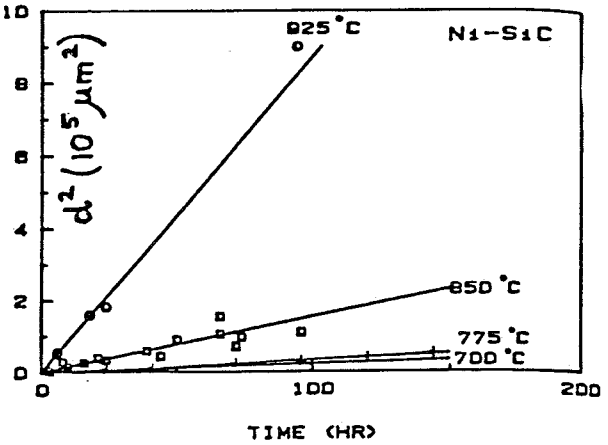

Fig. 5. Plot of the square of the total layer thickness d^2 (10^5 µm^2) versus time (hours) in Ni-SiC couples at various temperatures. o,+ = SiC(w); □ = SiC(w), SiC(.2 Al) and SiC(.45 Al); ■ = SiSiC.

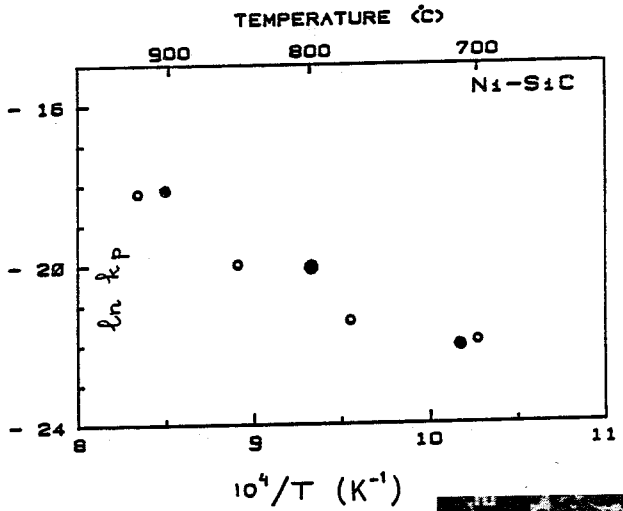

Fig. 6. Plot of ln kp (= $d^2/2t$ in cm^2/s) versus $1/T$ (K^{-1}) for the layer, grown in Ni-SiC couples. Black dots represent results of Yamada et al.[2].

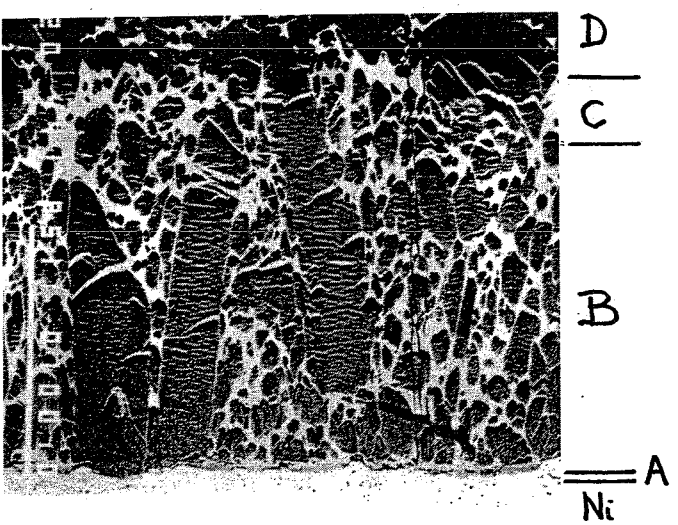

Fig. 7. Backscattered electron image of the diffusion couple Ni/SiSiC, annealed for 16 hours at 850°C under 13 MPa (bar = 100 µm). Legend at right-hand side is explained in text.