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THE INTERACTION BETWEEN SiC AND Ni OR Fe AND THEIR ALLOYS

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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 predominant 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 and with the morphology of the reactions between SiC and four Fe-Ni alloys at 850°C. The experimental set-up and preparational procedure have been described extensively in ref. [1]. 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

Fe-Ni and Fe-Ni-Si alloys have been made by argon-arc melting the proper amounts of constituents (up to 10 gram) and equilibrating the resulting alloys during one week at 850°C. The diffusion couples were annealed in a vacuum furnace under a load of 20 kg (pressure 13 MPa).

The couples and alloys were both investigated by optical microscopy and electron probe micro analysis (Jeol Superprobe 733). In addition, the alloys were analysed by x-ray diffraction.

Results Fe-SiC

Qualitatively, at 850°C the reaction zones show 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. 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 α-(Fe,Si), whereas the SiC parts react in the same way as in the previously mentioned couples, forming α-(Fe,Si) + C (Fig. 4). The reaction of Fe with pure Si 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 α-(Fe,Si) is visible.

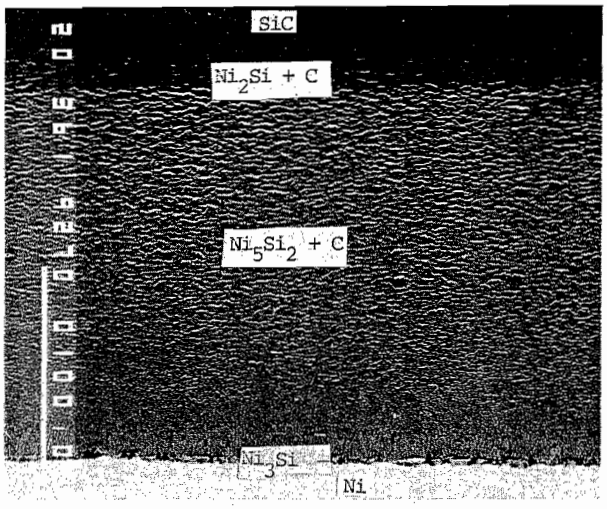

Fig. 1. Backscattered electron image of the diffusion couple SiC(w)-Ni, annealed for 44 hours at 850°C under 13 MPa (bar = 100 μm).

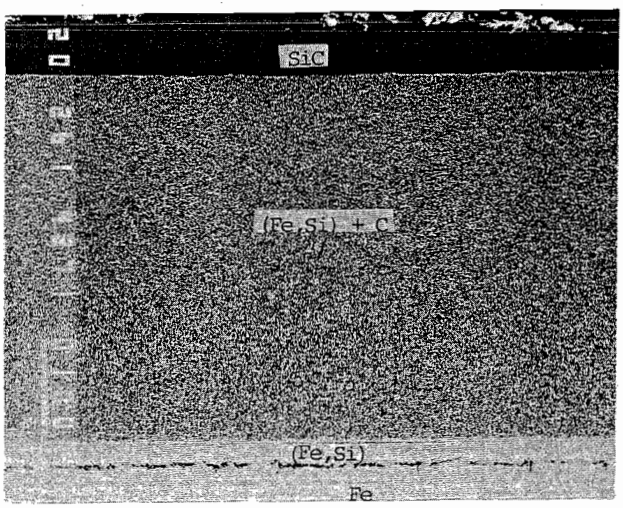

Fig. 2. Backscattered electron image of the diffusion couple SiC(w)-Fe, annealed for 44 hours at 850°C under 13 MPa (bar = 100 μm).

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 results in 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 we found the following phases 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.

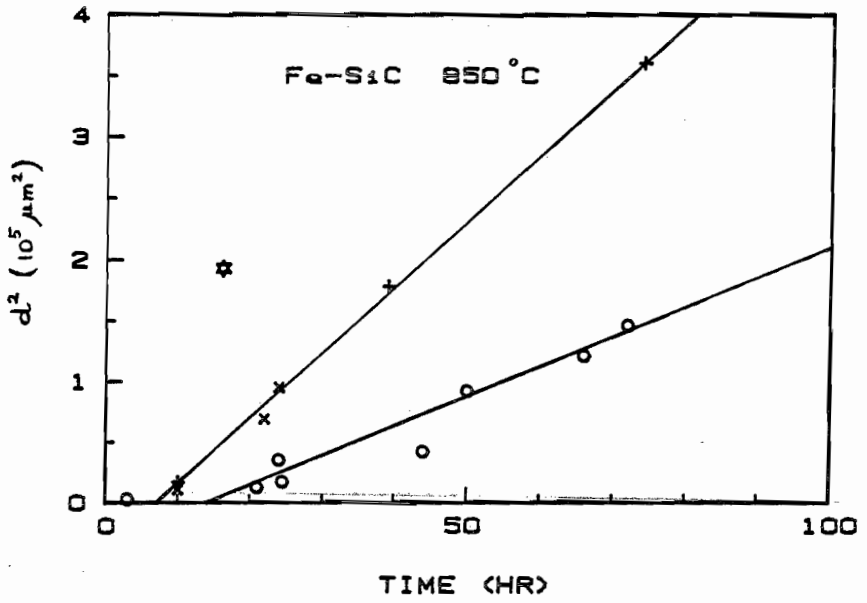

Fig. 3. Plot of the square of the total layer thickness d^2 (10^5 μm^2) versus time (hours) in Fe-SiC couples at 850°C. o = SiC(w); x = SiC(.2 Al); + = SiC(.45 Al); * = SiSiC.

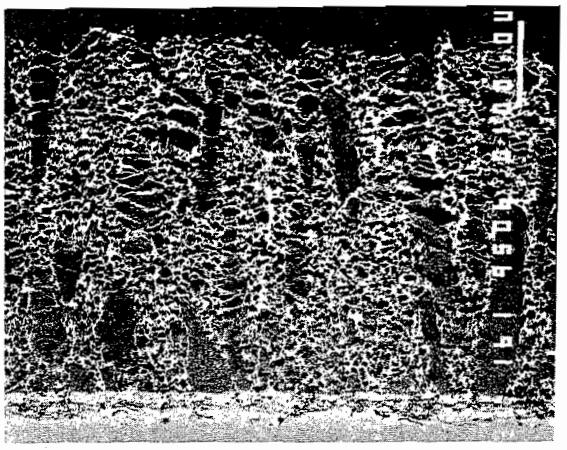

Fig. 4. Backscattered electron image of the diffusion couple Fe/SiSiC, annealed for 16 hours at 850°C under 13 MPa (bar = 100 μm).

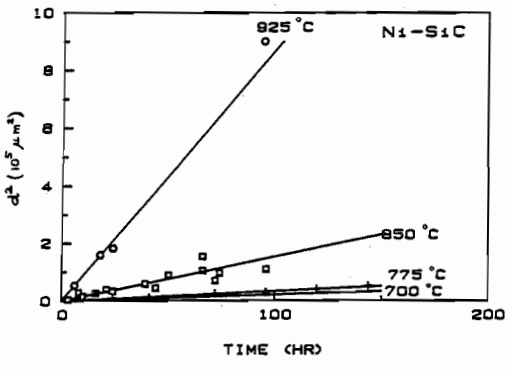

Fig. 5. Plot of the square of the total layer thickness d^2 (10^5 μm^2) versus time (hours) in Ni-SiC couples at various temperatures. o,+ = SiC(w); □ = SiC(w), SiC(.2 Al) and SiC(.45 Al); ■ = SiSiC.

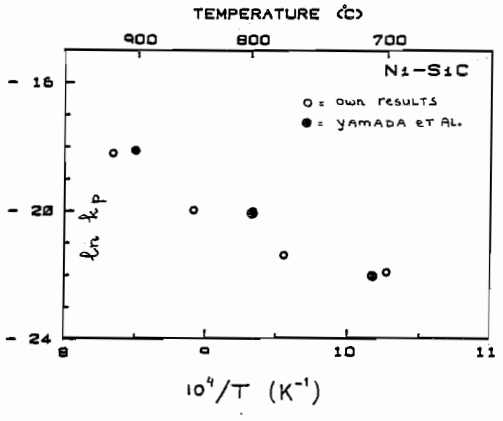

Fig. 6. Plot of ln kp (= $d^2/2t$ in cm^2/s) versus 1/T (K^{-1}) for the layer, grown in Ni-SiC couples. Black dots represent results of Yamada et al.[3].

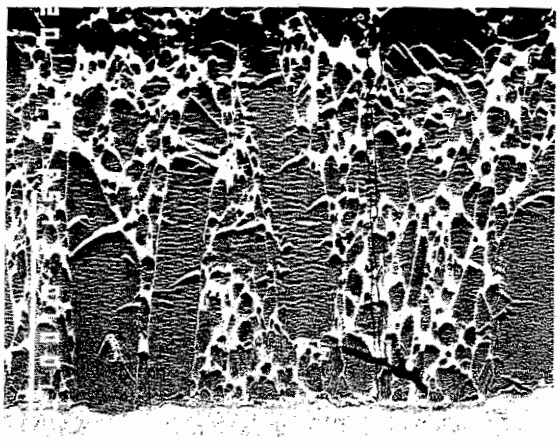

Fig. 7. Backscattered electron image of the diffusion couple Ni/SiSiC, annealed for 16 hours at 850°C under 13 MPa (bar = 100 μm). Legend at right-hand side is explained in text.

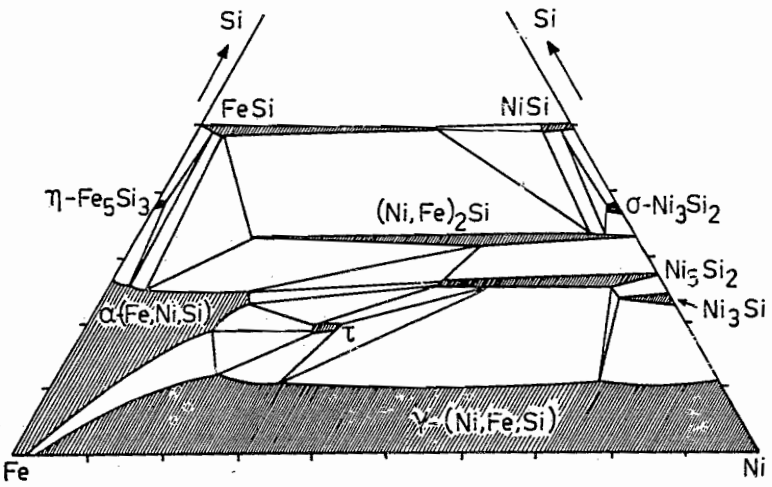

Fig. 8 Phase relations in the Fe-Ni-Si system at 850°C, based on the work of Inden[2] and adapted to our results.

Reactions between SiC (.2 Al) and Fe-Ni alloys

The alloys investigated contained 20, 40, 60 and 80 at% of Nickel respectively. The main results are plotted on the ternary Fe-Ni-Si Gibbs triangle of Fig. 8, given by Inden[2] and on the analysis of twelve equilibrated alloys in the present investigation.

- $Fe_{80}Ni_{20}$. A very thick layer of an α-Fe solid solution containing 22-25 at% Si and 15-16 at% Ni was formed. Carbon precipitates were present as random particles in a large part of the layer; in a narrow part of the layer at the boundary with SiC the precipitates originated as regular bands, whereas a small carbon-free zone was found near the alloy.
- $Fe_{60}Ni_{40}$. Four layers were found: the ternary compound τ at the alloy side, the α-Fe solid solution, $(Ni, Fe)_5Si_2$ and $(Ni, Fe)_2Si$. Carbon was mainly present as bands, except for a thin carbon-free zone near the alloy.
- $Fe_{40}Ni_{60}$. The layers formed are τ with random precipitates of carbon (except near the alloy) and the phases $(Ni, Fe)_5Si_2$ and $(Ni, Fe)_2Si$ with bands of carbon.
- $Fe_{20}Ni_{80}$. The reaction layer consists of the phases $(Ni, Fe)_5Si_2$ and $(Ni, Fe)_2Si$ with bands of carbon (except for a narrow region near the alloy).

Further investigations are necessary in order to understand the exact reaction mechanism. It will be clear that Fig. 8 only gives projections of the compositions which exist in a four-component, three-dimensional configuration (carbon axis perpendicular to the isothermal Fe-Ni-Si Gibbs triangle). The exact phase relations remain to be solved.

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/mole at 750°C to about 260 kJ/mole 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.[3], 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. The kinetics and further morphological evaluation of the reaction between SiC and Fe-Ni alloys are also still in progress, together with an investigation into the quaternary phase relations in the Fe-Ni-Si-C system.

Acknowledgement

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