JOURNAL OF MATERIALS SCIENCE **37** (2002) 1179– 1182

The microstructure of ZrO_2-Ni-Si_3N_4 diffusion bonds

R. H. VEGTER*
Laboratory of Materials Science, Delft University of Technology, Rotterdamseweg 137, 2612 AL Delft, The Netherlands
E-mail: erik.vegter@skf.com

M. MAEDA, M. NAKA
Joining and Welding Research Institute, Osaka University, Mihogaoka 11-1, Ibaraki, Osaka, 567-0047, Japan

G. DEN OUDEN
Laboratory of Materials Science, Delft University of Technology, Rotterdamseweg 137, 2612 AL Delft, The Netherlands

In this paper the results are presented of work dealing with the microstructure of ZrO_2-Ni-Si_3N_4 diffusion bonds. Joints were made at 1050°C with bonding times between 22.5 and 360 minutes. The interfacial structure was studied using optical microscopy, scanning electron microscopy and transmission electron microscopy. The element concentrations in the joint were determined by electron probe microanalysis. It was found that at the ZrO_2-Ni interface no reactions take place, whereas at the Si_3N_4-Ni interface decomposition of Si_3N_4 occurs, resulting in a solid solution of Si in Ni and porosity due to the recombination of N to N_2.

1. Introduction

Diffusion bonding is one of the methods that can be used for joining ceramics. It is a technique in which two flat surfaces are pressed to each other at elevated temperature for a certain period of time until a bond is formed by diffusion of atoms of at least one of the materials to and into the other [1]. Generally speaking, diffusion bonding of ceramic materials is only possible when using a metallic interlayer. Under these conditions two metal-ceramic interfaces should be considered. At these interfaces, not only diffusion, but also chemical reactions may play a role. The reaction products can affect the strength of the bond. Beside this, reactions can influence the properties of the bulk of the ceramic or the metal adjacent to the interface. A study of the microstructure of diffusion bonds yields therefore important information about the applicability of this joining technique for specific material combinations. It also provides help in the selection of the optimal process conditions of the bonding procedure (temperature, time, pressure, furnace atmosphere).

This paper deals with the microstructure of ZrO_2-Ni-Si_3N_4 joints. Diffusion bonds were made under different process conditions and the microstructures of the bonds thus obtained were studied with various techniques. Emphasis is given to the ZrO_2-Ni interface, as not much is known about its bonding behaviour. The Si_3N_4-Ni interface has been studied extensively in earlier work [2–4].

2. Experimental

Circular discs of zirconia and silicon nitride were diffusion bonded using a nickel foil as interlayer. The chemical compositions of the used materials are given in [5]. The ceramic discs had a diameter of 6 or 10 mm and a height of 4 or 5 mm, respectively. Prior to bonding, the surface of the discs was polished until a surface roughness of $R_a = 0.02$ μm was obtained. The thickness of the nickel interlayer was 0.25 mm, its surface roughness about $R_a = 0.2$ μm. The materials were cleaned ultrasonically in ethanol.

Bonds were made in a diffusion bonding furnace. The materials were stacked in the furnace and pressed together using a hydraulic system. During the experiments the pressure was maintained at about 30 MPa. The furnace was heated inductively, using a water-cooled coil in which a graphite susceptor was placed. The temperature was measured with a pyrometer directly focused on the susceptor. The power was supplied by a high-frequency generator (400 kHz), which was controlled manually. The heating rate and cooling rate were about 100°C/minute. Experiments were carried out in a vacuum atmosphere ($p \approx 10^{-3}$ Pa), which was obtained by a combination of a rotary vane pump and an oil diffusion pump.

Examination of the microstructure was carried out using scanning electron microscopy (SEM, type Jeol JXA-8600) and transmission electron microscopy (TEM, types Philips CM30T and Hitachi H-800). The

---

*[*] *Present Address*: SKF Engineering and Research Centre, Postbus 2350, 3431 DT Nieuwegein, The Netherlands.

0022–2461

distribution of the elements in the samples was determined using electron probe microanalysis (EPMA), which was available on the SEM.

3. Results

To obtain insight in the development of the microstructure of the ZrO_2-Ni-Si_3N_4 diffusion bonds, experiments were carried out at 1050°C for bonding times varying from 22.5 to 360 minutes. First the ZrO_2-Ni interface was examined. It appears that the interface is sharp and undisturbed, which suggests that no reactions have taken place during the bonding process.

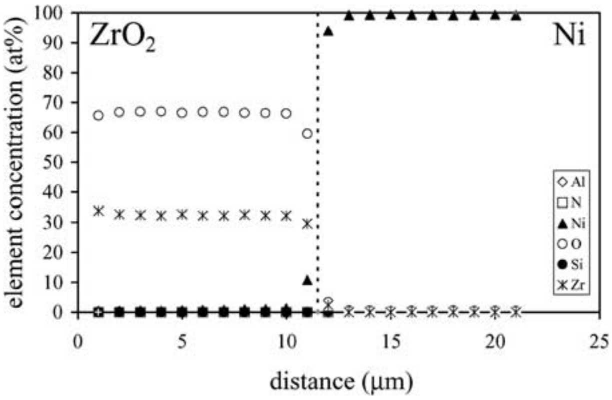

Figure 1 EPMA line scan across ZrO_2-Ni interface. $T = 1050°C$, $t = 90$ minutes.

To determine the element distribution in the vicinity of the interface, EPMA line scans were made. A typical scan made across the ZrO_2-Ni interface is given in Fig. 1. The figure shows that the interface is very sharp and that no reaction layers or diffusion zones are formed. The apparent deviations from perfect stoichiometry at the interface are due to the fact that the element distribution is measured in a circular area with a diameter of about 1 μm. Since the step size of the measurement is 1 μm, this implies that in a zone of about 1 μm at either side of the interface both materials are included in the measurement.

To obtain additional information about the ZrO_2-Ni interface, thin slices of the ZrO_2-Ni-ZrO_2 joints normal to the interface were studied by means of TEM. A TEM micrograph of the ZrO_2-Ni interface is shown in Fig. 2. It can be seen that the Ni consists of large grains, whereas the ZrO_2 consists of small ($\approx$0.5 μm) and a few medium size ($\approx$5 μm) grains.

A high-resolution TEM micrograph of the interface is shown in Fig. 3. In this picture, an image of the atomic planes can be observed. It can be seen that the atomic planes of both ZrO_2 and Ni continue into an interfacial zone in which both crystals can not be distinguished any more. On the basis of this picture, it can be concluded that within an interfacial zone of about 0.3 nm width, contact between the two crystal lattices is achieved. Obviously, it is not possible to determine the character

Figure 2 TEM micrograph of ZrO_2-Ni interface. $T = 1050°C$, $t = 90$ minutes.

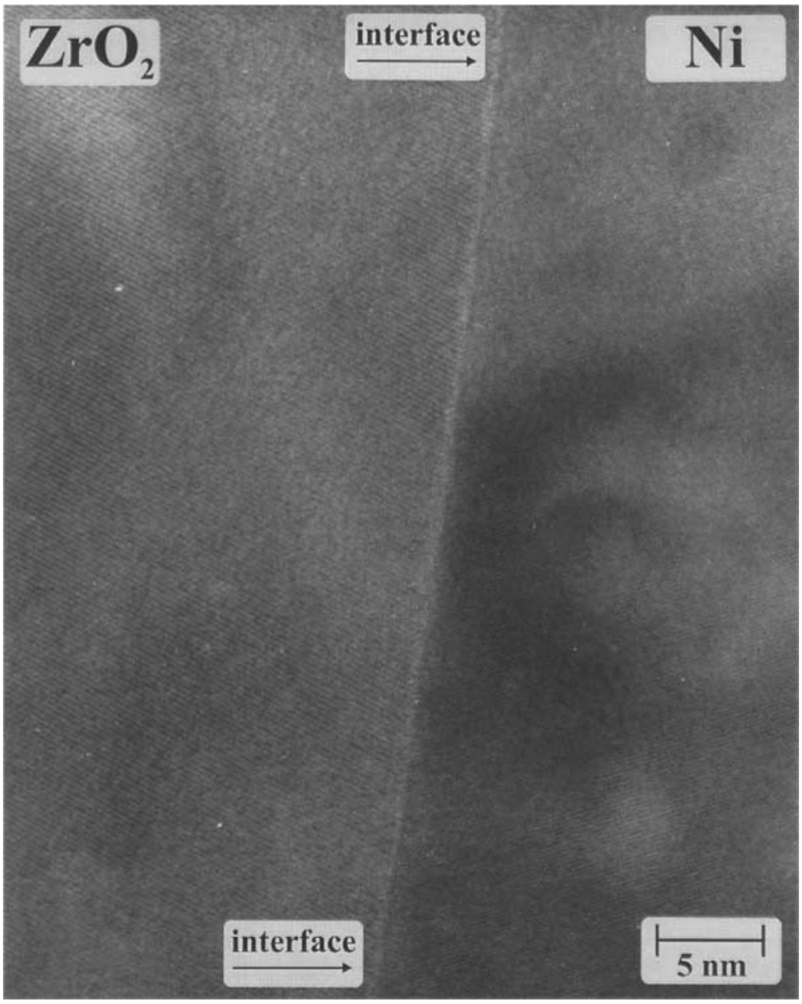

Figure 3 High-resolution image of ZrO_2-Ni interface. Plane spacing of ZrO_2 is 0.253 nm, plane spacing of Ni is 0.203 nm. $T = 1050°C$, $t = 90$ minutes.

of the bonding at the interface, but the distance between ZrO_2 and Ni atoms is small enough to make sharing of electrons possible, which would result in a chemical type of bonding. However, as the width of the interfacial zone is still larger than the atomic radius (≈ 0.15 nm), it should be expected that Van der Waals forces will also play a role [6].

Attention was also given to the Si_3N_4-Ni interface. Initially, this interface is flat, due to the surface polishing of the Si_3N_4, but during the diffusion bonding process, the interfacial structure changes. A SEM micrograph of the interface is depicted in Fig. 4. In this figure, an irregularly shaped interface and small voids can be seen. The location of the original interface is situated on the lower side of the irregular zone, which means that the silicon nitride was affected by some interfacial reaction. To determine the element distribution in the material adjacent to the interface, an EPMA line scan was made perpendicular to the interface. The result is given in Fig. 5. It can be seen that the bulk of the silicon nitride remained unaffected, but that some Si diffused into the Ni. As it is assumed that this Si originates from the decomposition of Si_3N_4, it might be expected that also N would be present. However, no nitrogen was detected in the nickel interlayer. This suggests that the atomic nitrogen either escaped to the surface or is trapped in molecular form in pores. In the latter case, it will not be detected with the applied analysis method, as it escapes during cutting of the specimen. In Fig. 5, it can also be seen that no oxygen is present in the nickel, which indicates that no oxides are formed during the bonding process.

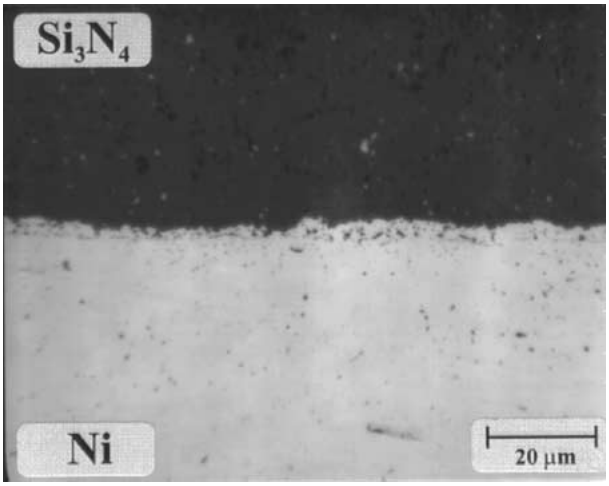

Figure 4 SEM micrograph of Ni-Si_3N_4 interface. $T = 1050°C$, $t = 90$ minutes.

4. Discussion

To optimise the diffusion bonding process, knowledge of the physical and chemical phenomena taking place at the interface of the materials to be joined is required.

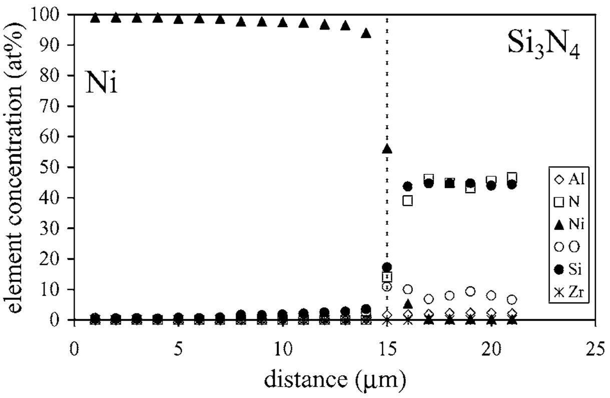

Figure 5 EPMA line scan across Ni-Si_3N_4 interface of specimen shown in Fig. 4.

In the case of ZrO_2-Si_3N_4 bonding using a Ni interlayer, two interfaces have to be taken into consideration. On one side, ZrO_2 is bonded to Ni. Using SEM, TEM and element analysis (EPMA), no reaction products could be detected at the ZrO_2-Ni interface. The high-resolution image, depicted in Fig. 3, shows that the lattice fringes of ZrO_2 and Ni meet within a distance of $\approx$0.3 nm. A reaction layer of a few atomic planes can therefore not be excluded. However, such a narrow layer can hardly be thought of as a separate phase. This suggests that both materials coexist at 1050°C, which is consistent with the fact that reactions between ZrO_2 and Ni at that temperature are thermodynamically forbidden. More specifically, it appears that the reaction $ZrO_2 + 2Ni \rightarrow Zr + 2NiO$ has a positive Gibbs free energy (604.3 kJ/mole) [7], which means that this reaction will not take place at the process temperature (1050°C). Thus, it might be concluded that the ZrO_2-Ni interface is directly bonded, without the formation of an intermediate layer of another phase. This observation differs from the results of other research [8, 9], which suggests that a nickel oxide layer is needed to achieve bonding between the Ni and the ZrO_2. The findings on the absence of the reaction products at the ZrO_2-Ni interface are confirmed by [10], although here no proof at the nanometer scale is given.

The fact that during the bonding process no reaction products or intermediate phases are formed at the ZrO_2-Ni interface, indicates that the choice of the process conditions during bonding is not critical. The only important point is that full contact between ZrO_2 and Ni is reached. This means that each of the process parameters (temperature, time, pressure) has to exceed a minimum value, but once full contact between the ZrO_2 and the Ni is established, bonding is completed and the process can be stopped.

Contrary to the ZrO_2-Ni interface, the Si_3N_4-Ni interface is well described in literature [2–4]. During the diffusion bonding process, decomposition of Si_3N_4 occurs, leading to a solid solution of Si in Ni and the generation of free N along the interface. The solid solution of Si in Ni results in a thin diffusion layer [11]. The free N diffuses into the Ni and concentrates along the interface, where it can recombine to N_2, resulting in pore formation (Fig. 4). The formation of the layer with high silicon content and porosity leads to a decrease of the mechanical strength [11]. This implies that the bonding time should be restricted. A certain time is needed to bring the Si_3N_4 in full contact with the Ni on an atomic scale, but after this the bond quality will deteriorate by the formation of a porous layer.

From the results presented here, it is also clear that the physical and chemical phenomena that take place at the individual interfaces do not interfere with each other. From Figs 1 and 5, it can be concluded that no diffusion of the elements from the ceramic materials from one interface to the other occurred. This validates the assumption that both interfaces, although present in one combination, can be studied separately, as carried out in this research.

5. Conclusions

The microstructure of ZrO_2-Ni-Si_3N_4 diffusion bonds has been investigated. Diffusion bonding experiments were carried out at $T = 1050°C$ for bonding times between 22.5 and 360 minutes. Based on the results obtained, the following conclusions can be drawn. At the ZrO_2-Ni interface, no chemical reactions take place. This implies that the ZrO_2 is directly bonded to the Ni and that no separate NiO phase is needed to make bonding possible. At the Si_3N_4-Ni interface, decomposition of Si_3N_4 occurs, resulting in a solid solution of Si and N in Ni and the presence of N along the interface. The latter recombines to N_2 and causes porosity along the interface.

Acknowledgement

The authors would like to thank T. Nakatsuka of the Joining and Welding Research Institute of Osaka University for their help with the scanning electron microscopy. F. D. Tichelaar of the National Center for HREM at Delft University of Technology is acknowledged for help with the TEM investigations.

References

1. B. DERBY, in "Joining of Ceramics," edited by M. G. Nicholas (Chapman and Hall, London, 1990) chap. 6.
2. S. D. PETEVES, G. CECCONE, M. PAULASTO, V. STAMOS and P. YVON, *Joining of Materials* (1996) 48.
3. L. ESPOSITO, A. BELLOSI and G. CELOTTI, *Acta Mater.* **45**(12) (1997) 5087.
4. J. T. KLOMP, in "Joining Ceramics, Glass and Metals," edited by W. Kraft (DGM, Oberursel, Germany, 1989) p. 55.
5. R. H. VEGTER and G. DEN OUDEN, *J. Mater. Sci.* **33** (1998) 4525.
6. J. ISRAELACHI, in "Surface and Interfacial Forces" (Wiley & Sons, New York, 1991) p. 83.
7. I. BARIN, in "Thermochemical Data of Pure Substances" (VCH, Weinheim, Germany, 1989).
8. T. YAMANE, Y. MINAMINO, K. HIRAO and H. OHNIISHI, *J. Mater. Sci.* **21** (1986) 4227.
9. J. G. DUH and W. S. CHIEN, *ibid.* **25** (1990) 1529.
10. C.-D. QIN and B. DERBY, *J. Mater. Res.* **7**(6) (1992) 1480.
11. B. T. J. STOOP and G. DEN OUDEN, *Met. Trans.* A **24A**(8) (1993) 1835.

Received 5 February
and accepted 18 September 2001