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Diffusion bonding of zirconia to silicon nitride using nickel interlayers

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The possibilities of diffusion bonding of zirconia to silicon nitride using a nickel interlayer were studied by carrying out bonding experiments under various processing conditions. The process parameters considered were temperature, bonding pressure and interlayer thickness. The optimal process conditions were determined by evaluating the mechanical strength using shear strength testing. It was found that the bonding is optimal in the temperature range 1000–1100°C. The bond strength appears to be independent of the bonding pressure and interlayer thickness if threshold values are exceeded (bonding pressure > 14 MPa, interlayer thickness > 0.2 mm). At the Si_3N_4–Ni interface, Si_3N_4 decomposes, forming a solid solution of silicon in nickel. At the ZrO_2–Ni interface, no reaction was observed. © *1998 Kluwer Academic Publishers*

1. Introduction

Diffusion bonding is a solid-state joining process, in which two flat surfaces are pressed together for a certain time at elevated temperature until a bond is formed. The initial interface between both materials disappears by deformation of the materials and diffusion of atoms across the interface. The bonding process takes place at temperatures below the melting temperature, T_m, of the materials, typically at 0.5–0.9 T_m. Often a ductile interlayer is used to bridge the difference in thermal expansion coefficient between the two materials, which always will give stresses during cooling of the joint from the bonding temperature down to the operation temperature. Another advantage of applying an interlayer is the decrease in process time if a fast-diffusing interlayer material is chosen.

In general, the diffusion bonding process is very suitable for the joining of similar and dissimilar combinations of ceramic materials. Of particular interest is the combination of zirconia with silicon nitride. In this system, the good mechanical strength of zirconia is combined with the wear resistance of silicon nitride. Diffusion bonding is expected to be possible when applying nickel as an interlayer material. At the silicon nitride–nickel interface, the silicon nitride reacts with the nickel [1]. In fact, decomposition of the silicon nitride to silicon and nitrogen is likely to occur. At the zirconia–nickel interface, relatively good bonding is expected [2,3]. However, the structure of this interface is not very well known.

This study deals with diffusion bonding silicon nitride to zirconia using nickel interlayers. Bonds were produced under various processing conditions. The optimal processing conditions were determined by measuring the shear strength of the joints obtained. An explanation of the observed behaviour is given in terms of interface phenomena.

2. Experimental procedure

2.1. Materials

The materials to be bonded were tetragonal (TZP) zirconia and hot isostatically pressed (HIP) silicon nitride in the form of cylindrical discs with a diameter of 10 mm and a height of 5 mm. The discs were cut from rods (Gimex b.v.). They were ground and polished with a diamond slurry until a smooth surface with roughness $R_s = 0.03\,\mu m$ was obtained. The chemical compositions of the zirconia and the silicon nitride are listed in Tables I and II. Foils of technically pure nickel were used as the interlayer; its chemical composition is given in Table III. Both ceramic materials and the nickel interlayer were cleaned ultrasonically in ethanol, after which the materials were stored in 2-propanol until their use.

TABLE I Chemical composition (wt %) of zirconia

ZrO_2	Y_2O_3	HfO_2	S	Al_2O_3	As_2O_3	SiO_2	CaO	K_2O
90.45	4.87	1.60	0.39	0.38	0.34	0.32	0.28	0.27

TABLE II Chemical composition (wt %) of Si_3N_4

Si	N	Mg	O	Fe	Ca	Al	Y	C
58	37	0.7	3.3	0.1	0.05	0.2	0.1	0.35

TABLE III Chemical composition (wt %) of the nickel used

Ni	Cu	Fe	Mg	Mn	S	Si
99.3	< 0.01	0.042	0.095	0.18	0.099	< 0.01

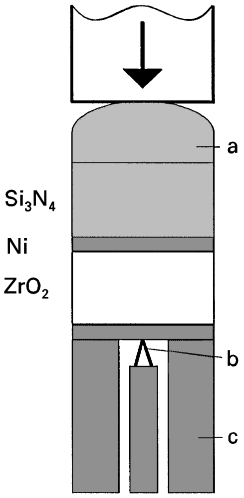

Figure 1 The diffusion-bonding furnace: (a) curved part for lining; (b) thermocouple; (c) table.

2.2. Diffusion-bonding equipment

Diffusion-bonding experiments were carried out in a diffusion-bonding furnace. The samples to be bonded were pressed together with an air pressure cylinder. To obtain a well-lined system, a curved piece of silicon nitride was placed on top of the stacked sample combination, guaranteeing a homogeneous pressure on the interfaces (Fig. 1). The applied bonding pressure on the sample can be varied between 14 and 37 MPa, assuming a circular cross-section with diameter 10 mm. The materials were heated by a susceptor, which was heated inductively by a high-frequency current, delivered by a high-frequency generator (Himmel). The temperature of the sample combination was measured with a W(Re5 wt %) to W(Re 26 wt %) thermocouple, located under the zirconia disc. The temperature profile was programmable: the standard profile for the experiments was chosen as follows:

30 min evacuation;

heating to 50 °C below the process temperature at a rate of 25 $^{\circ}$C min^{-1};

continued heating at a rate of 5 $^{\circ}$C min^{-1};

maintaining the process temperature for 90 min;

cooling down to room temperature at a rate of 10° C min^{-1}.

Experiments were carried out in vacuum ($p \approx 4 \times 10^{-4}$ Pa), which was obtained by a combination of a rotary vane vacuum pump and a turbomolecular pump.

2.3. Mechanical testing

The strength of the bonds obtained was measured by means of shear strength testing. In this testing method, the alignment of the specimen is relatively easy and accurate results are obtained. Tests were performed with a shear test device which was mounted in a Tira test 2300 tensile and compressive testing machine. Generally, the applied forces on the standard samples were of the order of 2–10 kN. The shear stress was calculated by dividing the measured force by the nominal surface area (78.54 mm^2).

TABLE IV Initial values of bonding parameters

Parameter	Value
Temperature	1050 °C
Bonding pressure	30 MPa
Interlayer thickness	0.2 mm

2.4. Analysis

To examine the structure of the joints, cross-sections were studied with a Leitz Neophot 2 optical microscope. The joint structures were examined in more detail by electron probe microanalysis (EPMA), using a Jeol JXA 733. A wavelength-dispersive spectrometer was used for this measurement, which was fully automated with the Tracor Northern system TN 5500. A number of line scans was made to determine the element distribution profiles.

3. Results and discussion

To investigate the possibilities of bonding the combination silicon nitride–nickel–zirconia, a number of diffusion-bonding experiments was carried out. To determine the optimal bonding conditions, the influence of the different parameters (temperature, bonding pressure, interlayer thickness) was studied by varying each of these parameters separately, while keeping the others constant. The initial values of the bonding parameters are listed in Table IV.

3.1. Temperature dependence

The most important variable of the diffusion process is the temperature. To determine the optimal bonding temperature, a series of experiments was carried out with temperatures between 900 and 1275 °C. The results of these experiments are given in Fig. 2. In this figure, the strength of the bonds is plotted as a function of temperature. It can be seen that the bonds have a maximum strength in the range 1000–1100 °C. During shear testing, nearly all welds failed at the Si_3N_4–Ni interface or in the silicon nitride in the vicinity of this interface. A combination of failures was sometimes observed in the form of cracks partially along the interface and partially through the ceramic. In most cases, a piece of ceramic remained attached to the nickel foil (Fig. 3). The dependence of the strength on temperature can be explained by considering the behaviour of the materials in the vicinity of both interfaces (Si_3N_4–Ni and Ni–ZrO_2). Because most welds fail at the silicon nitride–nickel interface, the

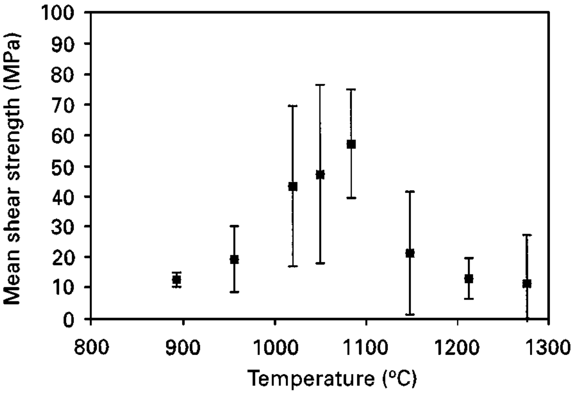

Figure 2 Shear strength as function of bonding temperature: $p = 30\,\mathrm{MPa}$, $d = 0.2\,\mathrm{mm}$, $t = 90\,\mathrm{min}$.

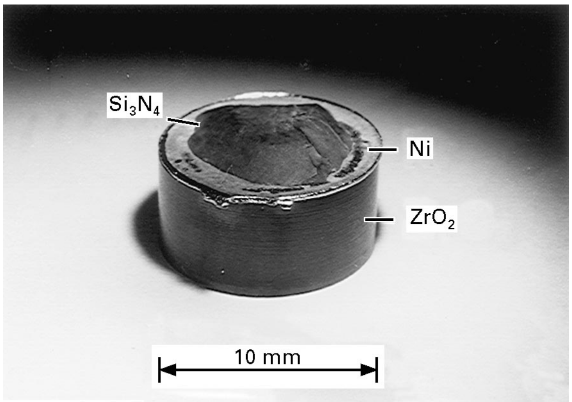

Figure 3 Typical fracture showing a piece of Si_3N_4 remaining on the surface of the nickel layer.

strength of the bond is mainly determined by the phenomena occurring at this interface.

The occurrence of low strength at low temperature can be understood in terms of the exponential temperature dependence of the diffusion rate. If the temperature is low, the diffusion rate is small, and void shrinkage by diffusion of atoms is also small. Consequently, voids will remain behind along the interface, causing lack of contact between the two surfaces. Hence, low strength is obtained.

At higher temperatures, the solid-state reaction between silicon nitride and nickel has to be considered. This reaction can be written as

$$Si_3N_4 \rightarrow 3[Si]_{Ni} + 2N_2 \tag{1}$$

Under atmospheric conditions (partial nitrogen pressure $\approx 0.8 \times 10^5\,\mathrm{Pa}$) the Gibbs' free energy of the reaction is positive ($57.5\,\mathrm{kJ\ mol^{-1}}$) at $T = 1000\,^\circ\mathrm{C}$, assuming that the activity of silicon in nickel is equal to the concentration of silicon in nickel, which is estimated to be 0.01 mol%. Lowering of the partial nitrogen pressure leads to a lower value of the Gibbs' free energy [1]. Under the present experimental conditions, the nitrogen pressure is $\approx 4 \times 10^{-4}\,\mathrm{Pa}$. At this pressure, the Gibbs' free energy is negative ($-46.3\,\mathrm{kJ\ mol^{-1}}$). As a consequence of this, the reaction will take place and the nitrogen which is formed by this reaction causes some porosity [4]. This can be illustrated with Fig. 4. Along the interface, the nickel shows pores, which are due to the recombination of atomic nitrogen to molecular nitrogen. It is not exactly known how these pores influence the bond strength, but it is evident that they will give rise to a decrease in strength, because of the reduction of bonded area. Another reason for the low strength at high bonding temperatures is the influence of silicon on the melting point of the silicon–nickel solid solution. In the Ni–Si phase diagram (Fig. 5), it can be seen that with increasing silicon content in nickel, the melting point decreases. A eutectic point exists at 13 wt% silicon in nickel. If the bonding temperature exceeds the melting temperature of this eutectic (1143 °C), the molten nickel will be pushed out by the applied pressure. In the case when all nickel is pushed out, no bond will be formed. If some nickel remains behind, bonds of low strength are formed.

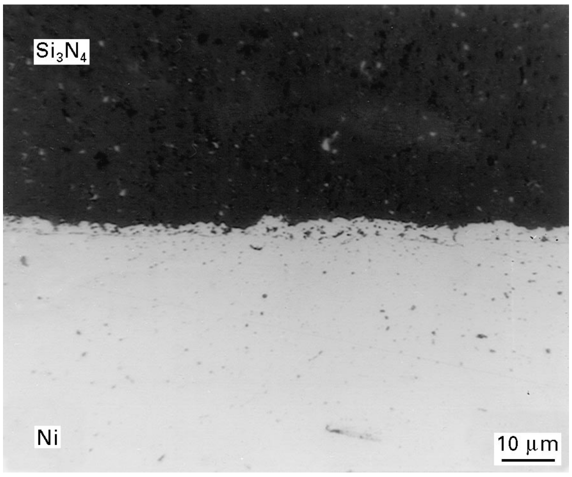

Figure 4 The Si_3N_4–Ni interface: $T = 1050\,^\circ\mathrm{C}$, $p = 25\,\mathrm{MPa}$, $d = 0.2\,\mathrm{mm}$, $t = 90\,\mathrm{min}$, × 1000, unetched.

In the foregoing, it is assumed that no nickel silicides are formed at the Si_3N_4–Ni interface. Although thermodynamically possible, the formation of these silicides has not so far been observed in diffusion-bonding processes, which justifies this assumption [6–9].

At the ZrO_2–Ni interface, the most probable reaction is the reduction

$$2Ni + ZrO_2 \rightarrow 2NiO + Zr \tag{2}$$

However, this reaction is thermodynamically not possible, as the change in Gibbs' free energy is positive ($\Delta G = 62.8\,\mathrm{kJ\,mol^{-1}}$) at 1027 °C [10]. Consequently, no change in interface structure is expected. This is confirmed by the results of microscopical examination.

To obtain more detailed information about the chemical composition of the material in the vicinity of both interfaces, a line scan of a bonded Si_3N_4–Ni–ZrO_2 combination was made by microprobe analysis. The results are depicted in Fig. 6. In this figure the relative element concentrations along a line from the Si_3N_4 across the nickel interface into the ZrO_2 is plotted. The plot shows that at the Ni–ZrO_2 interface, no diffusion of nickel into ZrO_2 or zirconium into

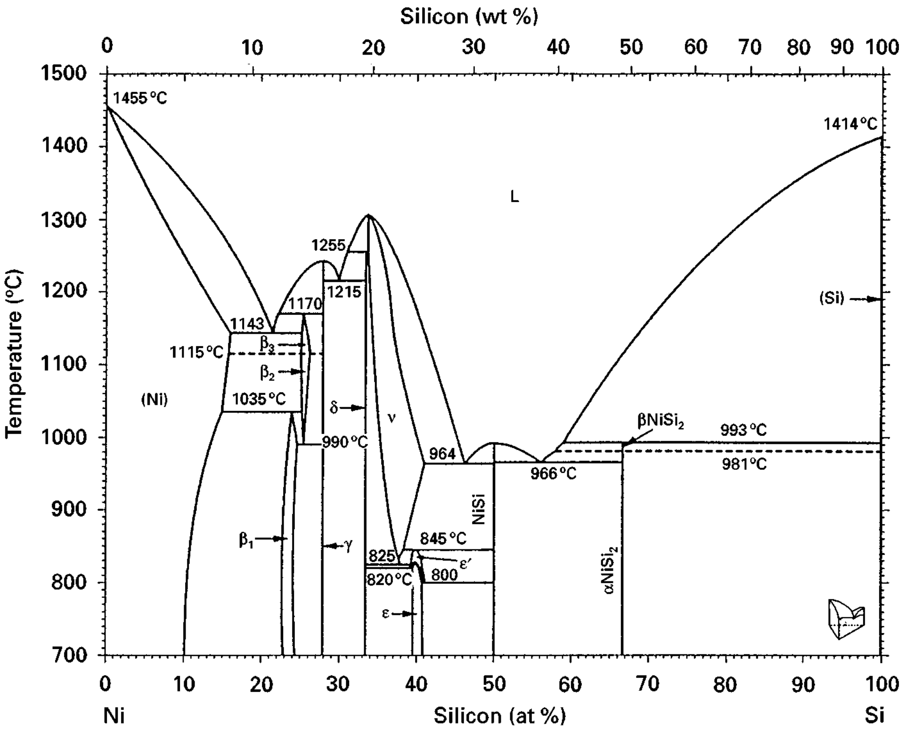

Figure 5 The nickel-silicon phase diagram [5].

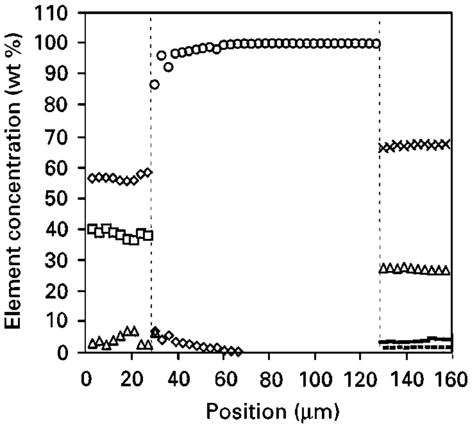

Figure 6 Element scan of a Si_3N_4–Ni–ZrO_2 diffusion bond: $T = 1050\,^\circ C$, $p = 30\,MPa$, $d = 0.1\,mm$, $t = 90\,min$. (□) N, (△) O, (◇) Si, (○) Ni, (—) Y, (–) Zr, (–) Hf, (- - -) interface.

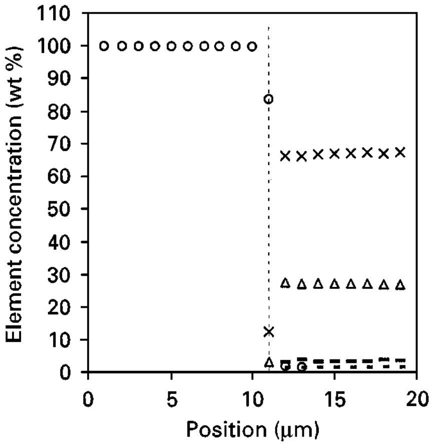

Figure 7 Element scan of the Ni–ZrO_2 interface: $T = 1050\,^\circ C$, $p = 30\,MPa$, $d = 0.1\,mm$, $t = 90\,min$. (△) O, (○) Ni, (—) Y, (×) Zr, (–) Hf, (- - -) interface.

nickel has occurred. A detailed scan across this interface confirms this observation (Fig. 7). At the Si_3N_4–Ni interface, a concentration gradient of silicon in nickel is observed, due to the decomposition of Si_3N_4 at the bonding temperature and the diffusion of the resulting silicon into nickel.

3.2. Bonding pressure

As a second step in the determination of the optimal process conditions, the influence of the applied bonding pressure on the obtained bonding strength was studied. A number of experiments was carried out with different pressures, varying between 14 and 37 MPa. The results are shown in Fig. 8, in which the measured shear strength is plotted versus the bonding pressure.

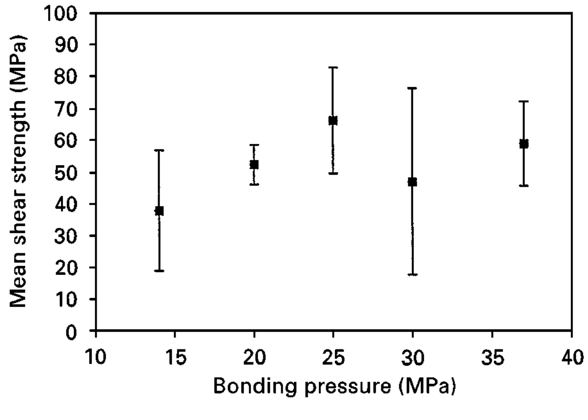

Figure 8 Shear strength as a function of bonding pressure: $T = 1050\,^\circ C$, $d = 0.2\,mm$, $t = 90\,min$.

The figure shows that the bond strength is scarcely affected by the applied bonding pressure. Because the ceramics are assumed to be stiff, even at elevated temperature, the only material which can deform is the nickel. The pressure independence can therefore be ascribed to the low yield point of nickel at high temperature; at the bonding temperature, the yield point is of the order of the applied pressure [11]. Near the yield point, the deformation of the nickel during the diffusion-bonding process is sufficiently large to bring the metal into contact with the ceramic on an atomic scale. Once full contact is made, further increase of the pressure does not contribute to the diffusion, which is needed to eliminate voids on a nanoscale.

The applied force could also help to break up oxides, which may be present at the interfaces. Although nickel is not very corrosive in air, the presence of oxides cannot be excluded, because no special treatment to remove these oxides is given to the interlayers. Silicon nitride is also covered by an oxide layer, which can form a barrier for diffusion, giving rise to an incubation time for the decomposition reaction at the Ni–Si_3N_4 interface. However, quantitative data of the strength of the oxide layer and the pressure needed to promote diffusion through this layer are lacking at present.

3.3. Interlayer thickness

Experiments were also carried out to determine the influence of the interlayer thickness on the bond strength. The results of these experiments are given in Fig. 9. The figure shows that for interlayer thickness > 0.1 mm, the bond strength is independent of interlayer thickness. The shear strength of the bonds with interlayer thickness 0.1 mm is significantly lower than the strength obtained for other values of the layer thickness. The majority of the fractures takes place at the Ni–Si_3N_4 interface or in the Si_3N_4 as shown in Fig. 2.

This behaviour can be explained as follows. The difference in thermal expansion coefficient between nickel ($13.6 \times 10^{-6}\,K^{-1}$) and Si_3N_4 ($3 \times 10^{-6}\,K^{-1}$) is relatively large, whereas the difference between zirconia ($10.0 \times 10^{-6}\,K^{-1}$) and nickel is much smaller. The highest residual stresses are therefore present around the Ni–Si_3N_4 interface. These stresses cause fracture in the vicinity of this interface. Another possible cause for fracture is the formation of reaction products at this interface, which also weakens the bond. Both effects are independent of interlayer thickness, which implies that the strength of the bond is also independent of interlayer thickness. Only at low thickness of the interlayer, could the zirconia play a role in the stress distribution at the nickel–silicon nitride interface. This could be a reason for the low strength obtained in bonds with 0.1 mm interlayer thickness.

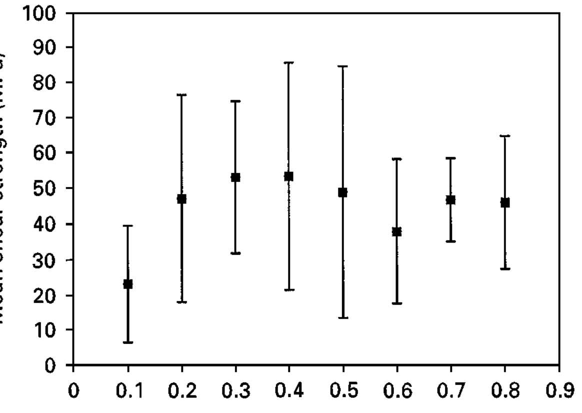

Figure 9 Shear strength as function of interlayer thickness: $T = 1050\,°C$, $p = 30$ MPa, $t = 90$ min.

3.4. Optimal processing conditions

To use the results presented in the foregoing for the production of diffusion bonds on an industrial scale, a choice of the best processing conditions has to be made. It is evident that, when making this choice, the design specifications of the application have to be taken into account. Three parameters have to be selected: process temperature, bonding pressure and interlayer thickness. The chosen bonding temperature is 1050 °C, which lies in the range 1000–1100 °C, where the strength reaches its maximum (Fig. 4). For the bonding pressure, a value of 30 MPa is chosen, which is well above the yield point of nickel at high temperature. The optimal processing conditions are listed in Table V.

In order to evaluate the optimal processing conditions, 16 bonds were made using the selected parameters. The strength of each bond was measured by shear strength testing. The results are plotted in a Weibull graph, presented in Fig. 10. The Weibull modulus, m, of these data is 1.6, the characteristic strength, σ_0, is 57 MPa. The value of m of the bonds is relatively low compared to the value of the bulk material (≈ 25). One of the reasons for this widespread distribution of strength might be the occurrence of irregularities at the ceramic–metal interface in the vicinity of the surface. In particular, imprecise alignment of the sample combination can result in a crevice between the ceramic and the metal, which facilitates crack initiation during shear testing. This behaviour has also been recognized by other investigators [12].

The determination of the optimal processing parameters was carried out starting from a fixed set of initial values of T, p and d, which was based on preliminary experiments and literature [4, 13]. Obviously, this yields only approximate values of the optimal process parameters. More accurate values can be

TABLE V Optimal values of the processing parameters

Parameter	Optimal values
Heating rate	5–25 °C min^{-1}
Temperature	1000–1100 °C
Bonding pressure	20–37 MPa
Interlayer thickness	0.2–0.8 mm
Cooling rate	10 °C min^{-1}

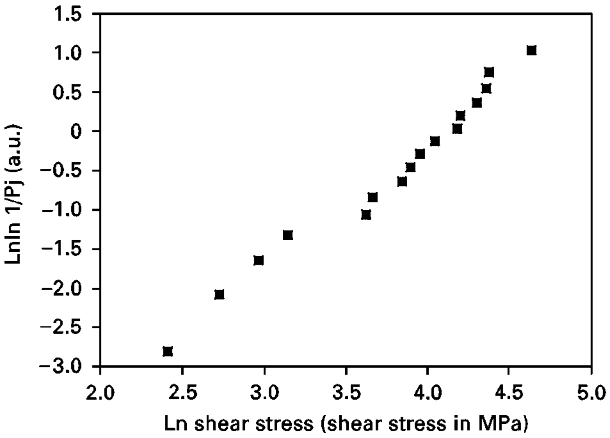

Figure 10 Weibull diagram of 16 experiments: P_j is the specimen survical probability, $T = 1050\,°C$, $p = 30\,\text{MPa}$, $d = 0.2\,\text{mm}$, $t = 90\,\text{min}$.

obtained by carrying out additional experiments with other combinations of T, p and d.

In general, diffusion bonding experiments are very time consuming. This is not a real problem in research, but will become a serious drawback when applying the technique on a larger scale. The bonding time should therefore be kept as short as possible. In the present study, a value of 90 min was chosen for the bonding time. Considering only diffusional aspects, the bonding process can be accelerated by using higher temperatures, because time and temperature are exponentially related. However, it should be realized that, at high temperatures, other phases and reaction products can be formed than at low temperatures, which might deteriorate the bond strength. In these situations longer processing times rather than higher temperatures should be applied.

4. Conclusions

Diffusion bonding of zirconia to silicon nitride using a nickel interlayer was studied. The optimal processing parameters were determined by evaluating bonds made under various processing conditions, with constant bonding time (90 min) and constant gas pressure ($\approx 4 \times 10^{-4}$ Pa). The strength of the bonds was measured by means of shear strength testing. On the basis of the results obtained, the following conclusions can be drawn.

1. At the Si_3N_4–Ni interface, Si_3N_4 decomposes, forming free silicon and nitrogen. The silicon diffuses into the nickel, whereas the nitrogen atoms recombine to molecular nitrogen, which escapes to the surroundings and/or forms pores along the interface.
2. At the ZrO_2–Ni interface, no reaction is observed.
3. The bond strength is maximal for bonding temperatures in the range of 1000–1100 °C.
4. The bonding pressure and the interlayer thickness do not affect the bond strength.
5. The characteristic strength of bonds made under optimal conditions is 57 MPa. The Weibull modulus is 1.6.
6. Failure occurs almost always at the Si_3N_4–Ni interface, which therefore turns out to be the weakest link of the system.

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