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Bonding of Si_3N_4 Ceramics and an Fe-26Cr Alloy Using Titanium Foils and a Nickel Interlayer

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Abstracts

A silicon nitride ceramic and an iron-26 mass% chromium alloy was bonded in an argon gas stream using a Ti-foil (20 μm) and Ni plate (1 mm). The fracture strength, obtained by bending tests at room temperature, was approximately 70 MPa for the bondings as-made at 1423 K for 3.6 ksec. By increasing the diffusion-annealing times the strengths were reduced rapidly, resulting in 40 MPa for 32 ksec, and then increased gradually up to 80 MPa for the bondings diffusion-annealed at 1373 K for 360 ksec.

The bonding layer was composed of two layers: One of them is an intermediate layer consisting of the TiN, Ti (Si, Ni), and oxides contained in the ceramics as the binder. The other is the intermetallic compounds such as TiNi, $TiNi_3$, and their mixture, as well as the Ni-Ti solid solution layers.

With the diffusion-annealing at high temperatures the TiNi layer was decomposed to the $TiNi_3$ and then to the Ni (Ti). In accordance with the decrement of the alloy layer thickness the fracture strengths were increased, in particular when the TiNi layer was thinned less than a few micronmeters.

It was found that the high fracture strengths were obtained for the surface-polished bondings, and were more than 200 MPa. This indicates that the surface flaws reduced significantly the fracture strength of the as-bonded specimens.

1. Introduction

Recently, non-oxide ceramics such as silicon-nitride and-carbide have received much attention because of their excellent properties on the heat-resistivity, anti-corrosion and -defacement. However, there exists at present a serious problem to be solved because of the brittleness of these fine ceramics. When the structual materials of ceramics are studied, it has been shown that combined systems with metals are best for many industrial appliances.

A number of the bonding techniques are being intensively investigated from this practical point of view, because the demands for the ceramic-metal bondings are increasing in automobile and other industries. On the bonding process of the silicon nitride ceramic and metals, many investigations[1] have been reported. These can be classified into three

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groups, namely, metallizing-solder, active metal filler, and solid state bondings. The fracture strengths of the bondings produced using these techniques are 200-250 MPa, which is 30% of the fracture strength of the ceramics themselves.

The two former processes, metallizing-solder and active metal filler, usually use aluminium and/or copper as interlayers in order to reduce the thermal residual stress. Because of these so-called soft metal interlayers these two bonding techniques are limited to the formation of relatively low temperature purposes. On the other hand, the solid state bonding, which appears to be one of the promising techniques because of the simplified bonding process without the solder and metal filler, is formed using the hot-and/or hot-isostatic presses. However, it is noted that these procedures increase the production costs. Thus in order to reduce the cost of bondings, the active metal filler method appears to be a candidate, in the present investigation the Ti-Ni filler was selected as a heat-resistive metal filler.

In this paper a bonding of the silicon nitride ceramics and an Fe-26Cr alloy was made using a Ti-foil and a nickel plate, which served as an alloy liquid formation with Ti-foil in addition to an interlayer for the stress relief. In the preliminary experiments flaws such as micro-cracks and non-bonded areas were found in the bondings, especially around the ceramic surface and in the vicinity of the bonding interface, and the bondings are also expected to reduce markedly the fracture strengths. The fracture strengths were measured of the surface polished bondings.

At high-temperatures the filler metals react with both ceramics and an alloy substrate to form an intermediate layer and intermetallic compounds. Several investigations[2),(3)] dealing with the solid state reaction of the ceramics and metal are reported, while little information is available for the compositional and structual changes during high temperature treatment of the bondings as well as their effects on the fracture strength. The composition profiles and fracture strength were investigated for the bondings, as-bonded and/or then were diffusion-annealed.

2. Experimental procedures

The Si_3N_4 ceramics [NTK: EC125], which were received as a square bar with 1 cm^2 and 10 cm length, were sliced with a diamond wheel for square tablets with 3 mm of thickness and the square surface as-sliced was used for the bonding experiment. An Fe-26Cr alloy (Showa Denko: SHORMAC RIVER 26-1), nickel plates of various thicknesses, and a titanium foil with 20 μm were commercially available. These materials were ultrasonically de-greased in the methanol-benzine solution prior to use for bondings.

Ti-foils, Ni-plates, and an Fe-26Cr alloy were overlayed on both sides of the ceramics in this sequence and fastened with a steel wire. The Ti-foil or TiH_2 powder was used to join the Ni-plate and an Fe-26Cr alloy. This set up was heated rapidly to bonding temperatures between 1423 and 1623K in an argon gas stream. After holding for desired periods from 1.8 to 18 ksec, the bondings were pulled up to the cold part of the reaction tubes. Diffusion-annealing experiments were carried out under a reduced pressure (10^{-2} Pa) at temperatures between 1173 and 1573 K up to 360 ks using the bondings, which were made at 1423 K for 3.6 ks. The mechanical properties of the bondings, as bonded and or diffusion-annealed, were determined from the three-or four-point fracture tests at room

temperature. The cross-head speed is 8.3×10^{-3} mm/sec, and a span is 30 mm for the three point bending test, and the lower and upper-spans are 40 and 18 mm, respectively, for the four point bending test.

The cross sections and concentration profiles across the ceramics, filler metals, and alloy substrate were investigated using an optical microscope (OP), scanning electron microscopy (SEM), and electron probe-micro analysis (EPMA). The inclined cutting method, which allows for enlargement of the sectioned area by five times of the normal sectioned area, was used for detailed observation of the ceramics/metal interface.

3. Results

It was found from the preliminary experiments that the optimum thickness of the nickel plate is approximately 1 mm. When using the nickel plates thinner or thicker than 1 mm, the bondings were self-broken during cooling because of the thermal residual stress.

Figure 1 shows the effect of bonding times at 1423 and 1523 K on the three-point fracture strengths. It was found that the fracture strengths plotted against bonding times indicated an upward concave curve at both bonding temperatures. The bonding time, at which the maximum strength was obtained, shifted from 3.6ksec at 1423 K to 1.8 ksec at 1523 K.

Figure 2 shows the three point fracture strengths of the bondings made at various temperatures for 1.8 ksec. From these results the bondings made at 1523 K for 1.8 ksec indicated the largest fracture strength (55 MPa).

Figures 3 A through C show the microstructures and the line analyses of Si, Ti, and Ni across the cross-sections of the bondings made at 1423 K for various times. In each photograph the left side is the ceramics, and from this side the Ti reacted zone, Ti-Ni alloy layers, and Ni substrate containing Ti were formed in this sequence. When the bonding was made at 1423 K for 1.8 ksec, Fig.3A, the total thickness of the intermetallic compound layers was approximately 40 μm and have a tendency to decrease gradually with the

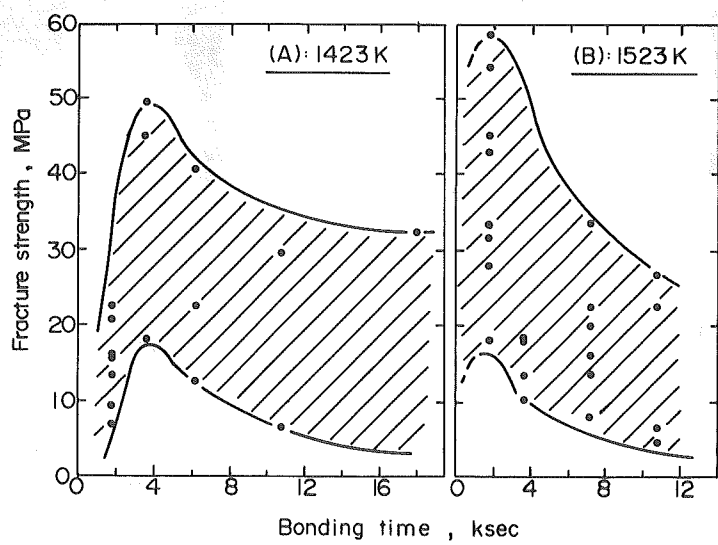


Figure 1 Changes in the fracture strengths with bonding thmes. (A) 1423 K, (B) 1523 K.

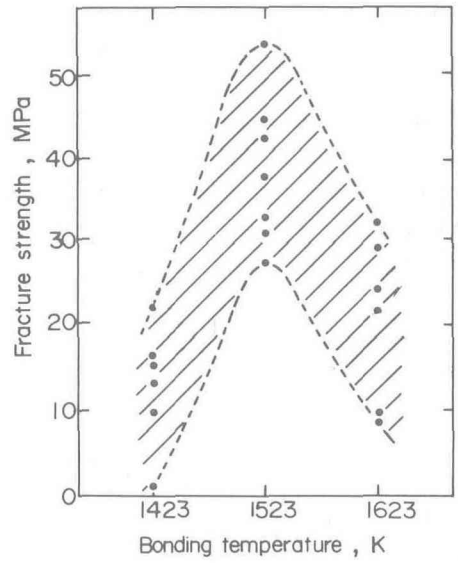
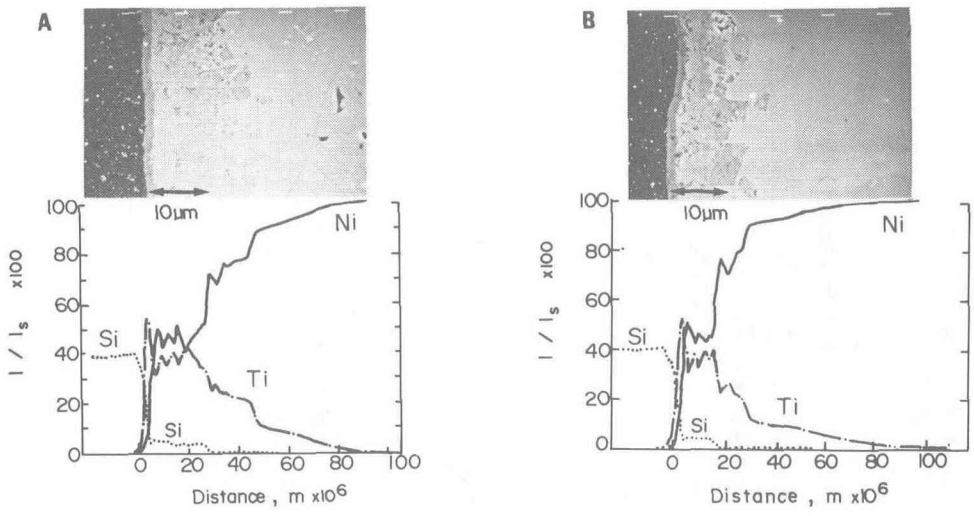


Figure 2 Temperature dependences of the fracture strengths of the bondings made for 1.8 ksec at temperatures of 1423, 1523, and 1623 K.

increasing bonding times and eventually became 15 μm for 18 ksec. It was found that the width of the alloy layer containing silicon was reduced in accordance with the decrease in the alloy layers. This will be discussed in the latter section, based on the reaction and diffusion kinetics between the ceramics and titanium.



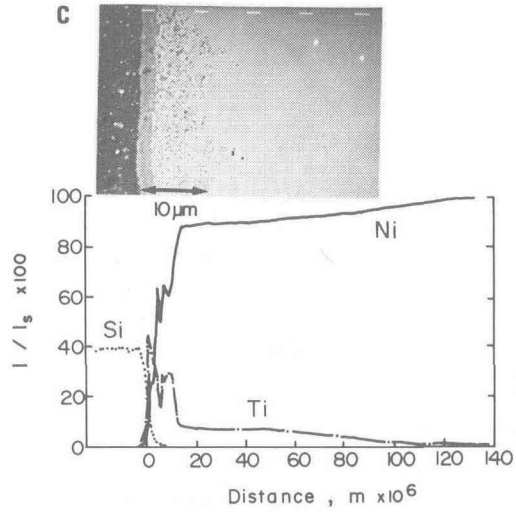


Figure 3 Microstructures and line analyses of Ti, Si, and Ni across the ceramic/metal bondings made at 1423 K for various times. A : 1.8 ksec, B : 3.6 ksec, and C : 18.0 ksec.

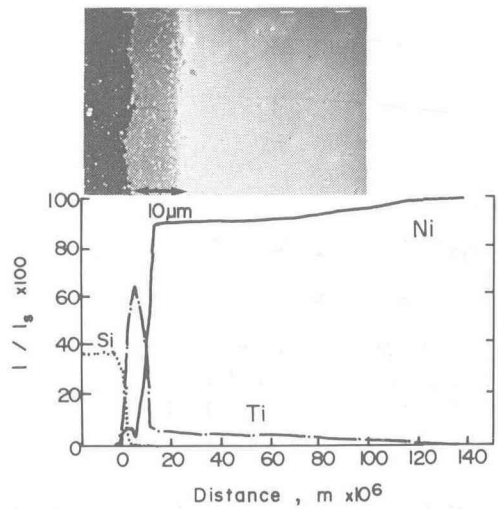


Figure 4 Microstructure and line analyses of Ti, Si, and Ni across the ceramic/metal bonding made at 1523 K for 1.8 ksec.

Figure 4 shows the cross-sectional microstructure of the bonding made at 1523 for 1.8 ksec. It was clearly demonstrated that the TiNi layer disappeared from the bonding alloy layer. This seems to be due to the rapid diffusion in the alloy layer, resulting in the decomposition from the TiNi phase to $TiNi_3$ and then further to a nickel-titanium solid solution.

Fracture modes of the bondings could be classified into two groups. One of them is the failure through the ceramics at high temperatures for lengthy bonding times, and the other is the interfacial failure at low temperatures for short bonding times. The failure through the ceramics demonstrated that the cracks started at the ceramic surface near the interface, which was followed by propagation through the ceramics and then terminated at the other surface near the interface, leaving the ceramics with upward concave curve on the metals. These two types of fracture modes are given in Fig.5.

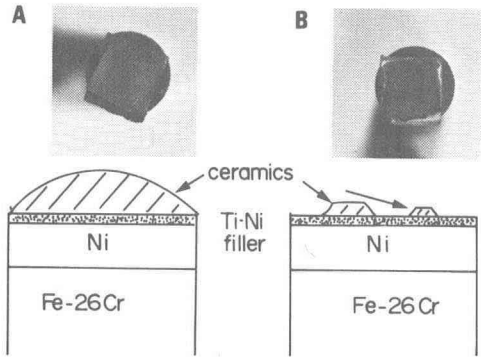


Figure 5 Morphologies of the fractured surfaces of the bondings and their schematic structures. A: failure through ceramics and B: interfacial failure.

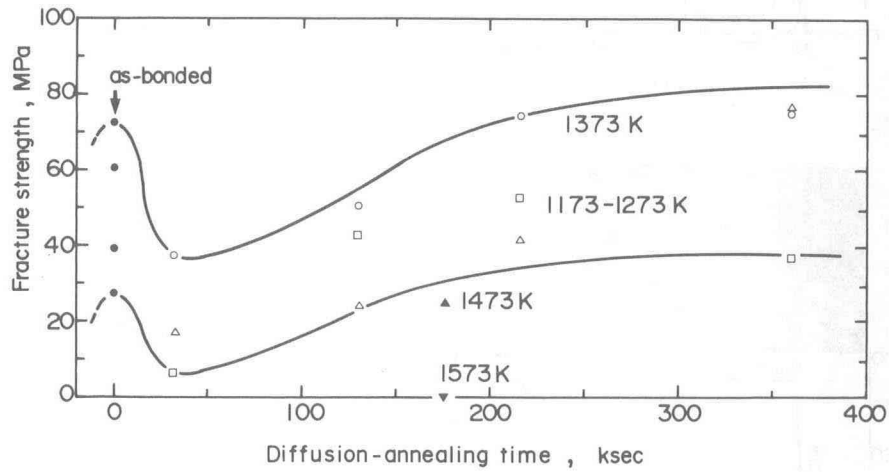


Figure 6 Variations of the fracture strengths with diffusion-annealing times at temperatures between 1173 and 1573 K, where the bonding has been made at 1423 K for 3.6 ksec.

Figure 6 shows the four point bending strength obtained for the bondings, which were at first joined at 1423 K for 3.6 ksec and then diffusion-annealed at temperatures from 1173 to 1573 K for various intervals up to 360 ksec. At each temperature the fracture strengths decreased gradually with the diffusion times, from 73 MPa as-bonded to 40 MPa for 32 ksec. With further diffusion-annealing the strengths increased again and became 80 MPa at 1373 K for 360 ksec, whereas the fracture strengths increased slowly at temperatures of 1273 and 1173 K. At temperatures higher than 1373 K the fracture strengths decreased, that is to say, at 1473 K the strength was relatively low, 26 MPa, and the bondings diffusion-annealed at 1573 K were self-broken during cooling. This is due to the rapid formation of the intermediate layer composed of TiN, Ti-Ni alloys, and oxides as binders in the ceramics.

Figures 7 A and B show the variations of the TiNi layer, $TiNi_3$ layer, and a mixture of these two phases as well as total thickness with diffusion annealing times at 1173 and 1373 K, respectively. At 1173 K the thickness of the TiNi layer decreased gradually with

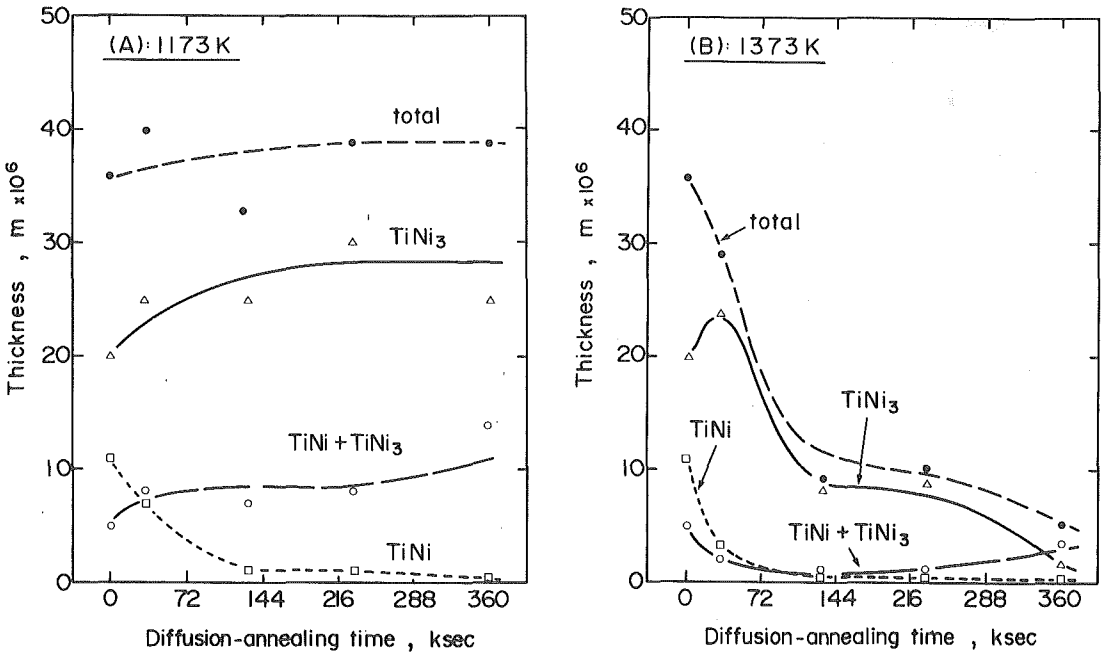


Figure 7 Changes in the layer thicknesses of the $TiNi_3$, TiNi, a mixture of TiNi and $TiNi_3$, and total of them with diffusion-annealing times. A : 1173 K and B : 1373 K.

time from 11 μm of the as-bonded to a few μm for 130 ksec. Meanwhile, both layers of the $TiNi_3$ and a mixture of the TiNi and $TiNi_3$ thickened slowly during the diffusion-annealing up to 360 ksec. When the bondings were diffusion-annealed at 1373 K, each layer of the TiNi, a mixture of FiNi and $TiNi_3$, and the $TiNi_3$ reduced rapidly. In particular, the thickness of the TiNi layer decreased to less than 1 μm after 130 ksec.

4. Discussion

It was found that the silicon nitride ceramic was successfully joined with an Fe-26Cr alloy using the Ti-Ni filler and the Ni interlayer, although there were large scattering in fracture strengths. This seems to be due to the following reasons; the ceramics joined slipping somewhat with metal from the normal position, and non-bonded areas were formed in the pheriphery. These surface flaws appear to act as the so-called notch-effect, leading to the decrease in the fracture strength accompanied by their scattering.

The surface of the bondings was polished by about 1 mm with a diamond whetstone in order to remove the above mentioned flaws. The results obtained for the surface-polished bondings were summarized in Table 1. It was clearly shown that the fracture strength became two or three times more larger than those of the as-bonded specimens, being over 200 MPa. It was noted that the fracture strength should be measured using the

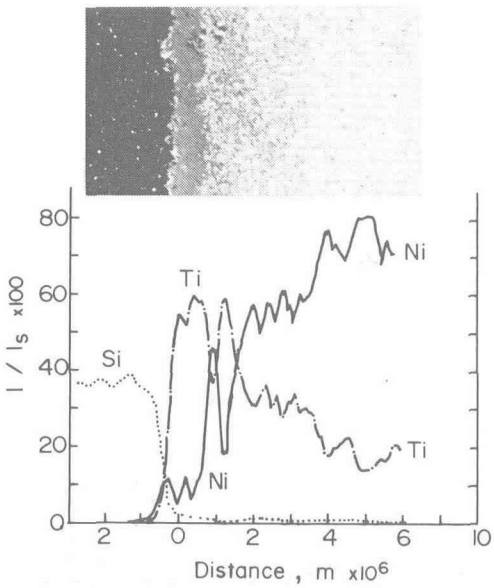


Figure 8 Enlarged microstructures of the ceramic-filler metal interface and concentration profiles of Ti, Si, and Ni.

Table 1 Summary of the fracture strengths obtained for the surface polished bondings, made at 1423 K for 3.6 ksec.

(A)	$Fe-26Cr/Si_3N_4/Fe-26Cr$: $\sigma_{3b}=120$MPa, (max.$=208$MPa) $\sigma_t = 46$MPa,
(B)	$Fe-26Cr/Si_3N4$: $\sigma_{3b}=100$MPa, (max.$=118$MPa)

notes ; σ_{3b} : three-point bending test
σ_t : tensile test

sound bondings without any surface flaws, and in particular for the quantitative analysis of the results.

The chemical reaction between the silicon nitride ceramics and metals is one of the possible mechanisms for the bonding and could be given by

$$Si_3N_4+4Ti=4TiN+3Si \quad \cdots\cdots(1)$$

The silicon released by eq. (1) should be alloyed with titanium and nickel. The free energy change for the reaction (1) is-387 kcal/mol Si_3N_4 at 1423 K, and therefore the reaction could be expected to occur spontaneously. The possibility of the chemical reaction of the Si_3N_4 with nickel is unknown, because of the lack of themochemical deta on a TiN compound.

According to the recent investigation[3),(4)] the Si_3N_4 and nickel was found to join in a solid state. This was explained on the basis of the combined process of two reactions : one of them is the thermal decomposition of the silicon nitride, and the other is the diffusion of silicon into the nickel, forming the alloys.

In the present investigation it was assumed that the silicon contained in the alloy layer was formed according to eq. (1), rather than the thermal decomposition of the ceramics, because it disappeared gradually with the increasing time, as shown in Figs.3A-C.

Figure 8 shows the microstructures and the concentration profile across the section enlarged with the inclined cut method. The intermediate layer formed by the reaction between the ceramics and alloys was found to be composed of a mixed phase of a TiN with golden color, Ti-Ni intermetallic compounds, and a gray phase. The latter phase seems to be the oxides added to the ceramics as binders.

According to the investigation[5] on the solid state reaction between the silicon nitride and titanium, the reaction zone, composed of the TiN and a mixture of the Ti_5Si_3 and Ti,

grew parabolically. This parabolic growth could be maintained by the dissolution of silicon into a titanium plate to make the Ti-Si binary alloy. This titanium plate seems to act as a silicon absorber. On the other hand, when a Ti-foil was used as was in the present investigation, the formation of Si and TiN will cease after a complete reaction of the titanium foil, because of its limited amount. Accordingly, for a long duration at high-temperatures the concentration of silicon, contained in the Ni-Ti-Si layer formed at the initial stage of the bonding, tended to decrease by diffusion of silicon toward the nickel substrate.

As mentioned above, a reaction between the silicon nitride and titanium is the most important bonding process. However, the TiN formation according to eq.(1) does not seem to be the necessary condition for the bonding of Si_3Ni_4 and metal, because the TiN compound has a relatively high thermal expansion coefficient and a fragile property.

The variation of the fracture strength with bonding times has been investigated, and the results obtained indicated that the strength increased with times at an initial stage of the bonding and then decreased. The proposed mechanism[6] explained the time dependency of the fracture strength as follows: At the initial stage of the reaction the fracture strength increased owing to the improvement of contact, whereas with further holding at high temperatures the intermediate layer grew thick, leading to low fracture strengths.

In the present investigation a similar time dependence was observed for the fracture strength of the bondings formed up to 15 ksec. Although the reason why the strengths decreased after passing a certain critical value is still an open question, it is likely that the decrease in fracture strengths is not due to the formation of the brittle intermediate layer, because the fracture strength increased again with the prolonged diffusion-annealing treatment.

Figure 9 shows the over-all thickness of the Ti-Ni intermetallic compound layers

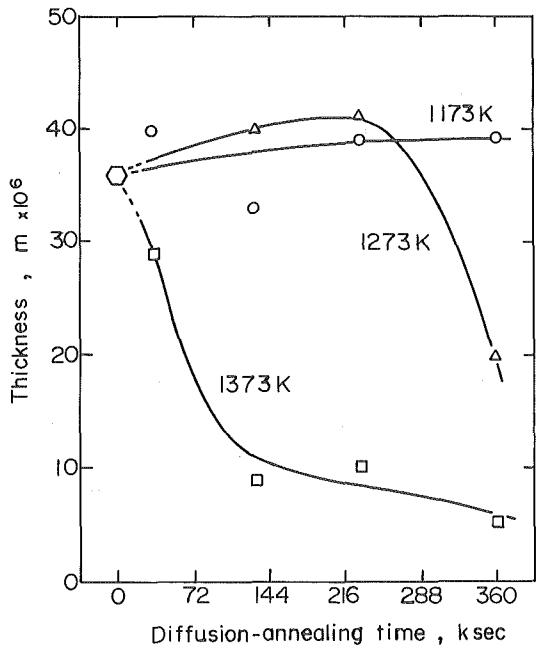


Figure 9 Changes in the total thickness of the intermetallic compounds with the diffusion-annealing times at 1173, 1273, and 1373 K.

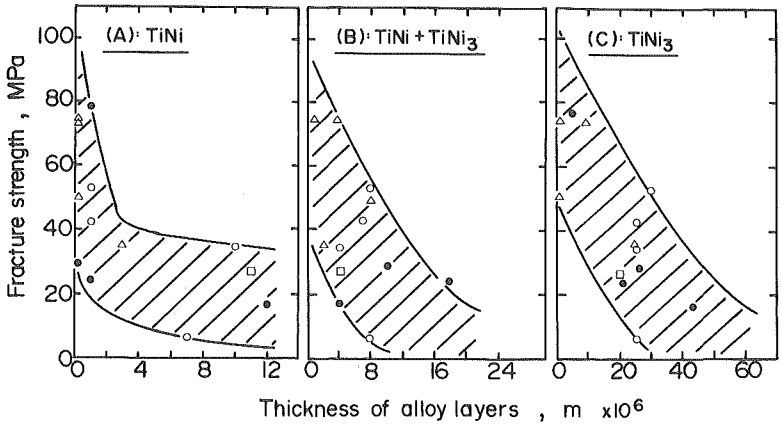


Figure 10 Changes in the fracture strengths with the layer thicknesses of (A) TiNi, (B) a mixture of TiNi and $TiNi_3$, (C) $TiNi_3$.

plotted against the diffusion-annealing times at 1173, 1273, and 1373 K. At a temperature of 1173 K the thickness tended to increase slowly up to 360 ksec. This could be explained by assuming that the TiNi phase decomposed rapidly into the $TiNi_3$ phase in contrast to the slow decomposition of the $TiNi_3$ to the nickel containing titanium. After the TiNi layer was completely transformed into the $TiNi_3$ phase, the alloy layer reduces rapidly because of the decomposition of the $TiNi_3$ into the Ni(Ti) phase. The critical time, at which the alloy width decreased rapidly, became shorter with increasing temperatures, 216 ksec at 1273 K and 72 ksec at 1373 K.

Figure 10 shows the changes in the fracture strength with the layer thicknesses of the TiNi, $TiNi_3$, and a mixture of TiNi and $TiNi_3$. From these results the fracture strengths were found to be strongly dependent on the alloy layer thickness, in particular on the TiNi layer. It is worthwhile to note that the fracture strength increased when the TiNi layer was thinner than a few micronmeters. The diffusion-annealing at high-temperatures is effective to reduce rapidly the alloy layers. However, if the diffusion temperature is too high, the intermediate layer could be formed thicker and thus reducing significantly the bonding strength, as demonstrated in Fig.6.

5. Summary and Conclusion

The results obtained are summarized as follows:

(1) Using the Ti-Ni filler and nickel plates as an interlayer, the silicon nitride ceramics was bonded to stainless steels and fracture strength of 73 MPa was obtained.

(2) The bondings were diffusion-annealed in vacuum at temperatures from 1173 to 1573 K up to 360 ksec. The fracture strength decreased with diffusion time in a short period and became 40 MPa. With further diffusion-annealing treatment the fracture strength tended to increase gradually again and became 80 MPa, larger than that of the as-bonded specimen at 1373 K for 360 ksec. This is due to the decomposition of the Ti-Ni intermetallic compound layers into the nickel solid solution containing titanium. At temperatures of 1173 and 1273 K the fracture strength increased slowly, because of the slow decomposition

rates of the metallic compounds, whereas the TiN compound was formed thicker at temperatures higher than 1373 K, resulting in the low fracture strength or self-breaking during cooling.

(3) The fracture strength could be correlated with the thickness of the Ti-Ni alloy layers. In particular, the fracture strength increased rapidly when the thickness of the TiNi layer was reduced down to a few micronmeters.

(4) The intermediate layer, which was formed by the reaction of ceramics and alloy filler containing titanium, was found consist of the TiN, Ti-Ni alloys, and the oxides phases.

(5) The principle process is the reaction of titanium and silicon nitride to form TiN and silicon. However, the formation of the TiN seems to be not necessary for the bonding, but titanium acts as a scavanger to render clean ceramic surfaces.

(6) Fracture strength increased significantly and attained up to 200 MPa when the bonding surface was polished away by 1 mm. The low fracture strength of the as-bonded specimens is due to the so-called notch effect of the micro-cracks, non-bonded area and other flaws.

Acknowledement

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