# Joining of $Si_3N_4$ to 1.25Cr0.5Mo Steel Using Rapidly Solidified CuNiTiB Foils As Brazing Filler Metals

*A new brazing alloy was developed for joining ceramics with similar or superior properties to AgCuTi alloys*

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ABSTRACT. The joining of $Si_3N_4$ to 1.25Cr0.5Mo steel using a newly developed CuNiTi8 alloy in the form of rapidly solidified foils as the brazing filler metal was studied. The maximum joint strength (three point bend) at room temperature is 261 MPa. The value was maintained until 723 K (268 MPa). As the test temperature is raised, the joint strengths decreased.

By means of a scanning electron microscope with a wave dispersive spectrometer, the paper studied the interfacial metallurgical behavior between the brazing filler metal and $Si_3N_4$ or the interlayers and its effects on the joint strength. It was found that when the nickel (Ni) platelet is employed as the buffer layer next to the $Si_3N_4$, it is difficult to improve the joint strength, but if the steel platelet is employed as the interlayer instead of Ni, the joint strength can be greatly augmented.

## Introduction

In general, AgCuTi active brazing alloys are used for the joining of metal to ceramics (Refs. 1, 2). However, the brazing alloys contain a rather high quantity of expensive silver. In this study, the joining of $Si_3N_4$ to steel has been successfully accomplished by using a newly developed high-temperature brazing alloy that does not contain precious metals. To obtain a homogeneous brazing filler metal, the brazing alloys are fabricated into rapidly solidified foils.

A main factor in abating the metal to ceramic joint strength is the residual stresses produced by the mismatched thermal expansion of the two materials. To compensate for the thermal expansion mismatch, a wide variety of methods using interlayers has been developed for metal-ceramic joints, e.g., a soft metal interlayer as the buffer layer between the two different materials to release the residual stresses (Refs. 3–5). Although the use of Al, Al-Si and Cu interlayers relaxed the thermal stresses produced at the ceramic-metal interface, these joints are limited to use at lower temperatures. In the present study, the use of metal interlayers for joining $Si_3N_4$ to 1.25Cr0.5Mo steel for 723 K application has been examined.

The interaction between the buffer materials and the brazing filler metals sometimes plays a more important role on the joint strength than does the thermal expansion mismatch. This paper pays a great deal of attention to studying the effects of interlayers on the interfacial metallurgical behavior and the joint strength as well as to investigating the other relevant problems met when joining metal-ceramics.

## Materials and Experimental Procedures

The steel used in the study is 1.25Cr0.5Mo. Its mechanical properties are stable even at high temperatures between 773 and 823 K. The highest service temperatures can reach 848 K. The silicon nitride, $Si_3N_4$, with $\sigma_b \geq 800$ MPa, was supplied by the Shanghai Institute of Ceramics, Academia Sinica. The size of both the steel and the $Si_3N_4$ is 3 x 4 x 20 mm. The brazing filler metals used in the study were made from the newly developed brazing alloy HTB2, which is composed of Cu, 5–25% Ni, 16–28% Ti (at.-%) and a trace of B. The brazing alloy was fabricated into foils by a rapidly solidified technique with the following parameters: the diameter of the copper roller is 350 mm; rotary velocity V = 1800 r/min; pressure of the shielding gas Ar = 0.4 MPa. The obtained brazing alloy foils are 5–7 mm wide, 40–50 μm thick. After thinning by abrasive papers from both sides to about 20 μm thick, the foils were cut into rectangular sheets 3 x 4 mm in size. The interlayer platelet was prepared by electric spark machining and then thinned with abrasive papers from both sides to remove the surface pollution and the oxided layers.

The brazing alloy foils, interlayer platelets, ceramics and metals to be brazed were ultrasonically cleaned in acetone. After drying with an air blower, they were installed in an iron jig as shown in Fig. 1. The brazing temperature was 1353 K and the holding time 10 min. The pressure in the furnace was held between 3.0 and 5.0 x $10^{-5}$ torr. The heating rate was 15 K/min, and the cooling rate was 15 K/min until 673 K and 1.5 K/min afterward. The three-point bend strengths at room temperature were measured with 0.5 mm/min of cross-head speed. The interfacial microstructures and the element distributions were examined by scanning electron microscope (SEM) with wave dispersive spectrometer (WDS). Finally, the three-point bend strengths at high temperatures were measured with a heating rate of 12 K/min. After maintaining at determined temperatures for 10 min, the test samples were loaded with cross-head speed of 0.5 mm/min. The average values of three test results of bend strengths at room temperature and high temperature are reported in this paper.

KEY WORDS

Ceramic-Metal Joining
High Temperature
Interlayer
Residual Stresses
Interfacial Reaction
Brazing Alloy
CuNiTiB

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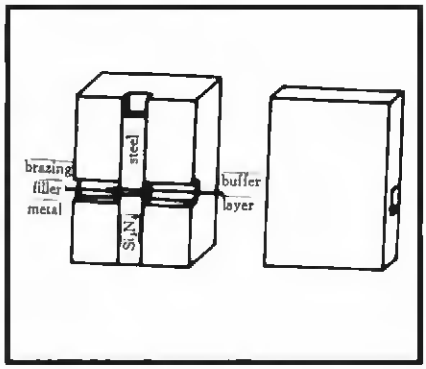


*Fig. 1 — The iron jig for the joining experiments.*

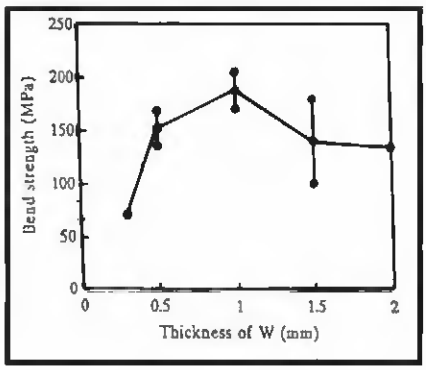


*Fig. 2 — When employing Ni-W-Ni laminate interlayers, the effects of the thickness of the W interlayer on the joint strength of $Si_3N_4$-Ni-W-Ni-steel is shown. The thickness of each nickel interlayer is 0.2 mm (T = 1353 K, t = 10 min).*

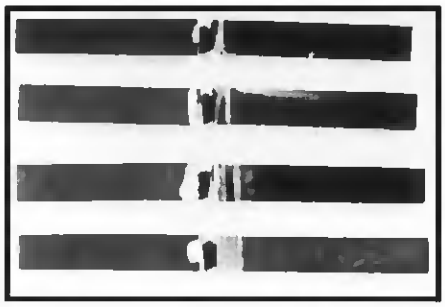

*Fig. 3 — Photograph of specimens for which ruptures occurred at the interface of $Si_3N_4$-Ni.*

**Table 1 — The Joint Strength of $Si_3N_4$-$Si_3N_4$ and Steel-Steel Using the HTB2 Brazing Filler Metal**

| Joint Strength (MPa) | | | |
|---|---|---|---|
| $Si_3N_4$-$Si_3N_4$ | | Steel-Steel | |
| 402 | 408[a] | 430 | 490[b] |

(a) The strength test temperature: 723 K; others: 293 K.
(b) The brazing temperature: 1413 K; others: 1353 K.

## Results and Discussion

### Effects of the Interlayers on the Joint Strength

The results of preliminary tests are shown in Table 1. The joint strengths of both $Si_3N_4$-$Si_3N_4$ and steel-steel using the HTB2 brazing filler metal are more than 400 MPa, but the joint strength for $Si_3N_4$-steel using the same filler metal is only 8 MPa as shown in Table 2 (refer to test No. 1). Due to the large difference in the coefficients of thermal expansion of the two materials, a significant magnitude of residual stress is produced during the cooling process after joining. As a result, the joint strength is lowered.

The influence of various interlayers on joint strength was examined. The interlayers were put into the joints as follows: $Si_3N_4$-brazing alloy-interlayers-brazing alloy-1.25Cr-0.5Mo steel. With a single interlayer of Ta, Mo or W as shown in Table 2 (Tests 2–4), the joint strengths are less than that without the buffer layer. However, with a single layer of Ni as the buffer, much better joint strengths are shown (Table 2, Tests 5–8). Table 3 shows that the coefficients of thermal expansion (CTE) of Ta, Mo or W are more similar to that of $Si_3N_4$ than Ni, but the yield strength of Ni is the lowest among the buffer materials. It is the low yield strength of Ni that released the residual stresses in the joint.

The soft buffer material Ni is able to release the residual stresses better, but its ability is very limited. A harder interlayer such as tungsten cannot effectively release the residual stresses but has a CTE closer to that of $Si_3N_4$. Therefore, it can reduce the gradient of residual stresses in the joint. If the advantages of the two types of interlayers can be taken to make laminate interlayers, the joint strength should be further augmented. The results of Tests 11 and 12 (Table 2) reveal that neither W-Ni nor Ni-W interlayers can fulfill the task. It was only with the laminate interlayer taking the form of Ni-W-Ni (Test 13) that the joint strength could be further augmented. The results show also that the adequate thickness of the nickel interlayer is 0.2 mm (Tests 13–15).

On the basis of the experimental results mentioned above, the effect of the thickness of the tungsten interlayer on the joint strength was investigated — Fig. 2. It can be seen that when the thickness of the W platelet was 1 mm, the joint strength arrived at the maximum value of 188 MPa. All fractures occurred at the interfaces of $Si_3N_4$-Ni as shown in Fig. 3.

**Table 2 — Strength of the Joints $Si_3N_4$-Interlayers-Steel (C-$I_1I_2I_3$-S)**

| Test No. | Interlayers ($I_1$) and thickness (mm) $I_1$ | | $I_2$ | | $I_3$ | | Joint strength (MPa) | Failure location |
|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | 8.0 | $Si_3N_4$-steel |
| 2 | Ta | 0.08 | | | | | ~0 | $Si_3N_4$-Ta |
| 3 | Mo | 0.2 | | | | | ~0 | $Si_3N_4$-Mo |
| 4 | W | 0.2 | | | | | ~0 | $Si_3N_4$-W |
| 5 | Ni | 0.2 | | | | | 84.0 | $Si_3N_4$-Ni |
| 6 | Ni | 0.5 | | | | | 104.0 | $Si_3N_4$ |
| 7 | Ni | 1.0 | | | | | 125.0 | $Si_3N_4$ |
| 8 | Ni | 1.5 | | | | | 20.0 | $Si_3N_4$ |
| 9 | Ni | 0.2 | Ta | 0.08 | | | 12.0 | $Si_3N_4$ |
| 10 | Ni | 0.2 | Mo | 0.2 | | | 27.0 | $Si_3N_4$ |
| 11 | Ni | 0.2 | W | 0.5 | | | 6.0 | W-steel |
| 12 | W | 0.5 | Ni | 0.2 | | | 24.0 | $Si_3N_4$-W |
| 13 | Ni | 0.2 | W | 0.5 | Ni | 0.2 | 152.2 | $Si_3N_4$-Ni |
| 14 | Ni | 0.5 | W | 0.5 | Ni | 0.5 | 46.0 | Ni-steel |
| 15 | Ni | 0.5 | W | 0.5 | Ni | 0.2 | 62.0 | Ni-W |

**Table 3 — Physical and Mechanical Properties of the Ceramic and Some Metals**

| Materials | Melting point (K) | Coefficient of thermal expansion, $\alpha \times 10^{-6}K^{-1}$ | Young's modulus E (GPa) | Yield strength $\sigma_{0.2}$ (MPa) |
|---|---|---|---|---|
| Ni | 1726 | 13.3 | 225 | 120 |
| Ta | 3269 | 6.5 | 190 | 344 |
| Mo | 2883 | 5.1 | 294 | 500–610 |
| W | 3653 | 4.6 | 380 | 720–830 |
| $Si_3N_4$ | 2193[a] | 3.5 | 284 | — |
| 1.25 Cr 0.5 Mo | — | 13.4 | 212 | 460 |

(a) Does not melt, but sublimes, decomposes or vaporizes.

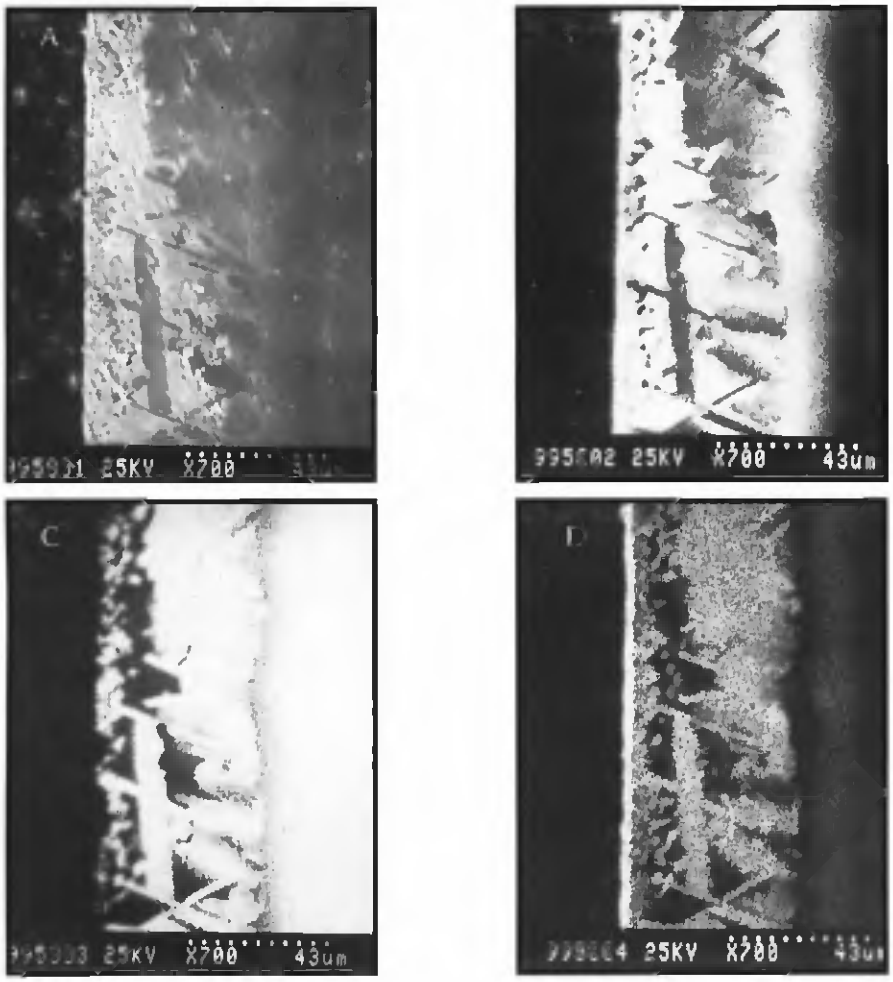


*Fig. 4 — Microstructure and element distributions of the cross section for the interfaces of the $Si_3N_4$-brazing filler metal-Ni interlayer. A — Microstructure; B — Cu; C — Ni; and D — Ti.*

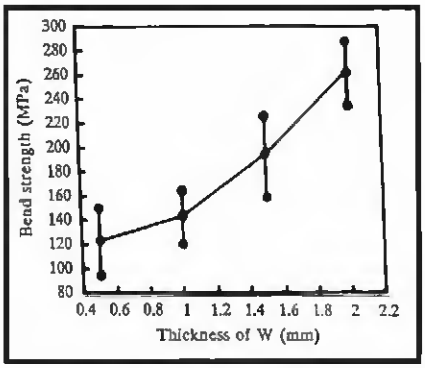


*Fig. 5 — Effect of the thickness of the tungsten interlayer on the joint strength of $Si_3N_4$-interlayers-steel, employing steel-W-Ni as laminate interlayers (the thicknesses of the steel and Ni interlayers are 0.2 mm each.*

**Table 4 — Heats of Solution of Liquid Nickel and Iron in Liquid Metal Solvents (Ref. 4)**

| Solvents | Heats of solution (kJ-mol) $\Delta H_{Ni}$ | $\Delta H_{Fe}$ |
|---|---|---|
| Cu | 26 | 60 |
| Ni | 0 | –6 |
| Ti | –140 | –70 |

**Effects of the Interfacial Metallurgical Behavior of the $Si_3N_4$-Brazing Filler Metal-Interlayer on the Joint Strength**

Figure 4 shows the microstructure and element distributions of a cross section for the joint with the bending strength of 188 MPa.

As shown in Fig. 4, the rugged interface between the Ni interlayer and the brazing filler metal reveals that part of Ni is resolved into the brazing alloy, linked to the nickel in the brazing alloy and strongly combined with Ti to form the solid solution region m and the compound e, both of which are rich in Ni and Ti. In light of the analyzed WDS results, the compound of Ni-Ti should be $CuNi_8Ti_3$. While the great parts of titanium atoms combined with Ni, the others diffused bilaterally to $Si_3N_4$ and into the Ni interlayer for some micron (μm). These complicated reactions strongly interfered with the normal interfacial reactions between $Si_3N_4$ and the brazing filler metal and further weakened the joint strength. Therefore, the weakness of the joint is at the interface between $Si_3N_4$ and the Ni buffer.

The interlayer of Ni could be substituted with other metals, but not any metal with lower yield strength can substitute the Ni due to its superior high temperature properties. However, the steel to be brazed can be considered as a better candidate. It can be seen from Table 4 that the heats of the solution of liquid iron in the liquid metal solvents mentioned are almost all superior to those of liquid nickel. In particular, the heat of the solution of liquid iron in the liquid titanium is far higher than that of liquid nickel. So it can be reasoned that the reactions of Fe with relevant elements in the brazing filler metal, particularly with Ti, are evidently weaker than that of Ni, which is favorable to assuring the nominal interfacial reaction between $Si_3N_4$ and the brazing filler metal.

Based on the above analysis, the steel$_{(0.2mm)}$-W$_{(0.5–2.0\ mm)}$-Ni$_{(0.2\ mm)}$ laminate interlayers were employed to join $Si_3N_4$-steel. As shown in Fig. 5, the joint strength is increased up to 261 MPa with increasing the thickness of the W interlayer up to 2 mm. The rupture occurred at the steel-W interface. A comparison of Fig. 5 with Fig. 2 reveals that the effect of the laminate interlayers of Ni-W-Ni on the joint strength is better than that of steel-W-Ni when the thickness of the W interlayer is small (less than 1.3 mm), because the low yield strength of nickel played a more important role. The effect of the laminate interlayers of steel-W-Ni is better than that of Ni-W-Ni when the thickness of the W interlayer is more than 1.3 mm, because the favorable interfacial metallurgical reactions have started to play a more important role.

Figure 6 shows the interfacial microstructure and the element distributions of the sample with 261 MPa joint strength. It can be seen that the distribution of Fe is similar to that of Ni and Ti, in particular to that of Ni. Part of Ni has been substituted with Fe in the interfacial metallurgical reactions. The reaction of Fe with Ti is less strong than that of Ni, as mentioned above. There is no great block of Ti compound existing in the brazing filler metal layer. Thus, the joint strength could be improved.

The variations of the joint strength

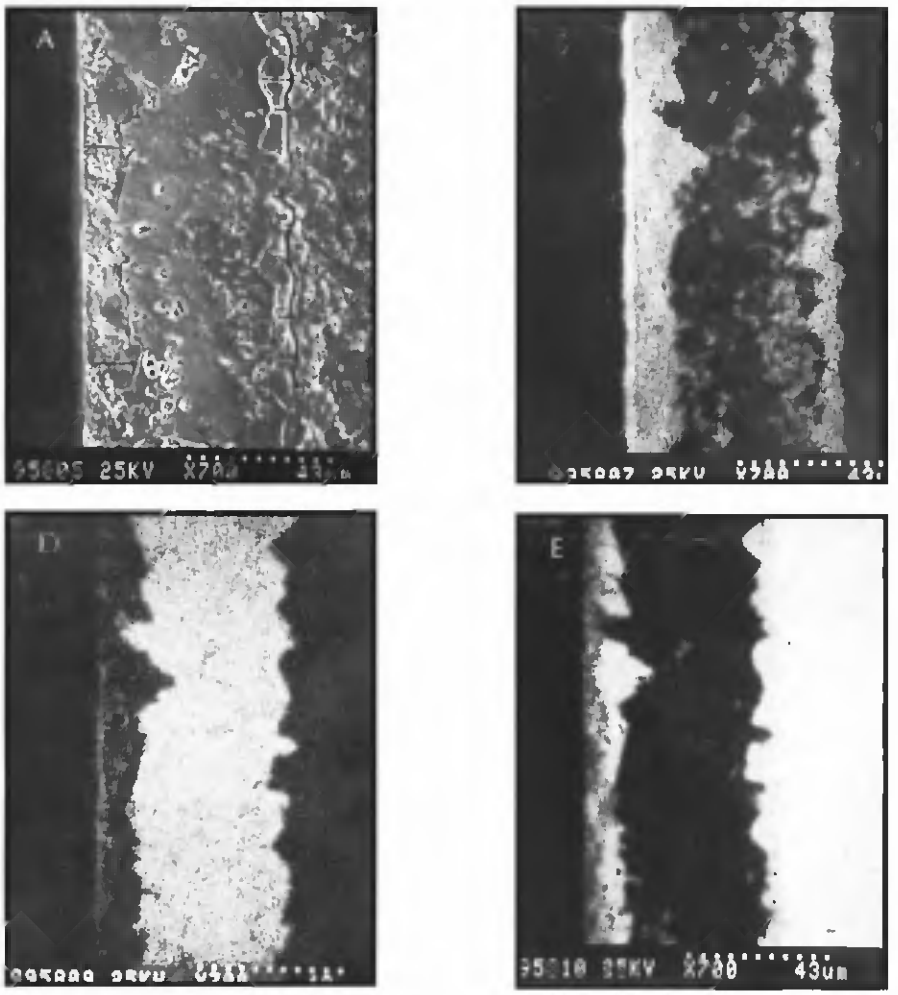


*Fig. 6 — Cross-section microstructure and element area distributions for the interfaces among the $Si_3N_4$-brazing filler metal-steel interlayer, using steel$_{(0.2\ mm)}$-W$_{(2.0\ mm)}$-Ni$_{(0.2\ mm)}$ as the laminate interlayers. These were etched by a water solution of 5% FeCl3, followed by (HF+NHO3). A — Microstructure; B — Ti; C — Ni; D — Cu; and E — Fe.*

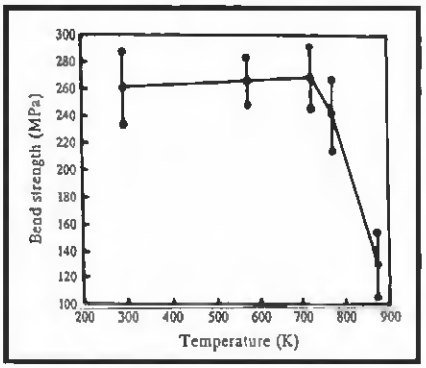


*Fig. 7 — Variations of the joint strength for $Si_3N_4$-interlayers-steel with the test temperatures, taking steel$_{(0.2\ mm)}$-W$_{(2.0\ mm)}$-Ni$_{(0.2\ mm)}$ as the laminate interlayers.*

with the temperature are shown in Fig. 7. It can be seen that the joint strength could be maintained to 723 K (268 MPa). With a continuing increase in the test temperatures, the joint strengths still hold adequate values, *e.g.*, 240 MPa at 773 K, 130 MPa at 873 K. Fractures occurred at the interface of the Ni interlayer, *i.e.*, W-Ni or Ni-steel, etc.

## Conclusions

1) Ni plates can release the residual stresses that exist in the joint by the elastic, plastic and creep deformation.

2) The interfacial metallurgical reactions between Ni and Ti results in weakening of the joint strength.

3) By using the steel as the buffer layer next to $Si_3N_4$ instead of Ni, the joint strength can be further improved owing to the weaker reaction of Fe with Ti than that of Ni.

4) The maximum joint strength at room temperature is 261 MPa and it maintains the value up to 723 K. When continuing to raise the temperature, the joint strength presents a decreasing trend.

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