Carbon Fiber Silver-Copper Brazing Filler Composites for Brazing Ceramics

Short nickel-coated carbon fibers added to a brazing alloy provide a composite filler material that produces high-strength ceramic brazements

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ABSTRACT. The addition of 20 vol-% nickel-coated carbon fibers (400 μm long) to silver-copper alloy powder provided a mixture that was applied as a filler material for the brazing of ceramics. Ceramic joints were made by hot pressing at 830° to 870°C (1526° to 1598°F) and 10 MPa (1450 psi) for 40 to 60 min in a nitrogen atmosphere. The shear strength was ~300% higher than that of the corresponding joint without fibers. The nickel coating was needed to enhance the wetting of the fibers by the alloy.

Introduction

The ideal brazing filler metal for the joining of low thermal expansion materials (*e.g.*, ceramics) is thin, ductile and low in thermal expansion. The brazing community has for years emphasized the need for the filler metal to be thin and ductile, because 1) such properties are particularly critical for relieving the stress at the interface between the filler metal and the ceramic when the thermal expansion coefficient of the filler metal is high, and 2) the conventional filler metals all have high thermal expansion coefficients. On the other hand, when the thermal expansion coefficient of the filler metal is low, the need for the filler metal to be thin and ductile is far less severe. It is clear from basic stress analysis that a low thermal expansion coefficient for the filler metal is desirable for the joining of low thermal expansion materials. When a metal is joined to a ceramic by brazing, the weakest interface is that between the ceramic and the filler metal, because it is more difficult for the filler metal liquid to wet the ceramic than to wet the metal. Hence, improving the bonding between the filler metal and the ceramic results in strengthening of the ceramic-metal joint. Thus, the use of a filler metal of low thermal expansion will benefit ceramic-metal joints as well as ceramic-ceramic joints.

The thermal expansion mismatch between the ceramic and the metal parts being joined is another concern for ceramic-to-metal joints. A solution to this problem is to have a thin and ductile filler metal. Another solution is the use of a low thermal expansion interlayer (*e.g.*, Mo, Nb), as reported by Suganuma, *et al.*, (Ref. 1). Ideally, the filler metal is thin, ductile, and has a low thermal expansion coefficient. Unfortunately, low thermal expansion materials are seldom ductile, so the ideal filler metal described above is too hard to attain. This paper does not report such an ideal filler metal, but it does provide information on a filler metal of low thermal expansion. It further shows that a low thermal expansion in the filler metal indeed helps to strengthen the joint.

In this work, a filler metal of low thermal expansion is in the form of a metal-matrix composite obtained by adding carbon fibers to a brazing alloy. During brazing, the brazing alloy melts, while the carbon fibers do not.

Carbon fibers are particularly suitable for this application because they have a nearly zero thermal expansion coefficient, a high thermal conductivity, high temperature resistance (in the absence of oxygen), chemical inertness, a high tensile strength and a high Young's modulus. Furthermore, carbon fibers in the form of short pitch-based fibers are quite inexpensive, and the price is expected to decrease by 50% in less than five years.

Carbon fibers have not previously been used to form a composite brazing material, but carbon fibers in the form of continuous fibers have been used to form a composite solder with a low thermal expansion (Ref. 2).

The main drawback of using carbon fibers in metal-matrix composite brazing material is their poor wettability with molten metals in general. However, this problem can be much alleviated by using metal-coated carbon fibers (Ref. 2). Therefore, in this work, nickel-coated carbon fibers were used. Another way to alleviate this problem is to use an active brazing alloy in the composite brazing filler material.

Experimental

Materials

The brazing alloy used was the Ag-Cu eutectic alloy BAg 8a (71.7 wt-% Ag, 28 wt-% Cu and 0.3 wt-% Li) in the form of a powder of size –400 mesh. The solidus and liquidus temperatures are both 760°C (1400°F). The coefficient of thermal expansion is about 18.5 X 10^{-6}/°C. The maximum recommended brazing temperature is 870°C (1598°F). This alloy was chosen instead of an active brazing alloy because its relative chemical simplicity allowed it to serve as a model alloy for a basic study.

The milled carbon fibers used were pitch-based, unsized and produced by Ashland Petroleum Co. under the trademark Carboflex. Two kinds of fibers were

KEY WORDS

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Table 1—Properties of Bare Carbon Fibers

Filament diameter	10 μm
Tensile strength	690 MPa
Tensile modulus	48 GPa
Elongation at break	1.4%
Electrical resistivity	$3.0 \times 10^{-3}\ \Omega \cdot cm$
Specific gravity	1.6 g/cm^3
Carbon content	98 wt-%

Table 2—Shear Strengths of Alumina-to-Kovar Brazed Joints for Various Volume Fractions of Bare Carbon Fibers in the Composite Brazing Material

Volume Fraction Fibers	Debonding Strength (MPa)
0%	2.63 ± 1.0
12.0%	1.52 ± 0.18
15.9%	3.92 ± 1.0
19.8%	4.34 ± 0.02
24.0%	3.48 ± 0.7
28.0%	<0.67

Table 3—Shear Strengths of Alumina-to-Kovar Brazed Joints for Various Volume Fractions of Ni-Coated Carbon Fibers in the Composite Brazing Material

Volume Fraction Fibers	Joint Strength (MPa)
0%	2.63 ± 1.0
16.0%	5.28 ± 3.50
20.0%	8.86 ± 1.16
30.0%	3.94 ± 0.34

used: bare (uncoated) fibers (Carboflex P100, 100 μm long) and nickel-coated fibers (Carboflex P400, 400 μm long, coated with nickel by a vacuum coating process and containing 70 wt-% Ni and 30 wt-% C). The basic properties of the bare fibers are shown in Table 1.

The materials being joined were alumina (a sheet 0.500 in./1.27 cm thick, with a coefficient of thermal expansion 6.4×10^{-6}/°C at 25° to 100°C/77° to 212°F, and containing 96% alumina, as provided by Superior Technical Ceramics Corp., St. Albans, Vt., under the grade AL-96) and Kovar alloy (a sheet 0.010 in./0.25 mm thick, with a composition of 54 wt-% Fe, 29 wt-% Ni and 17 wt-% Co, and a coefficient of thermal expansion of 5.3×10^{-6}/°C at 25°C).

Joining Process

For joining alumina and Kovar, the brazing material (a mixture of carbon fibers and alloy powders) was placed between an alumina plate and a Kovar sheet. The joint was made by hot pressing at a temperature ranging from 830° to 870°C and a pressure of 10 MPa for 40 to 60 min. During the hot pressing, the composite filler metal was formed. The high pressure was used to promote the wetting between alumina and the brazing alloy. A nitrogen atmosphere was applied during joining to prevent the oxidation of the brazing alloy and the carbon fibers. The thickness of the brazing material was 0.02 in. (0.45 mm) in the joint. In one experiment, the facing surfaces of the alumina plate and the

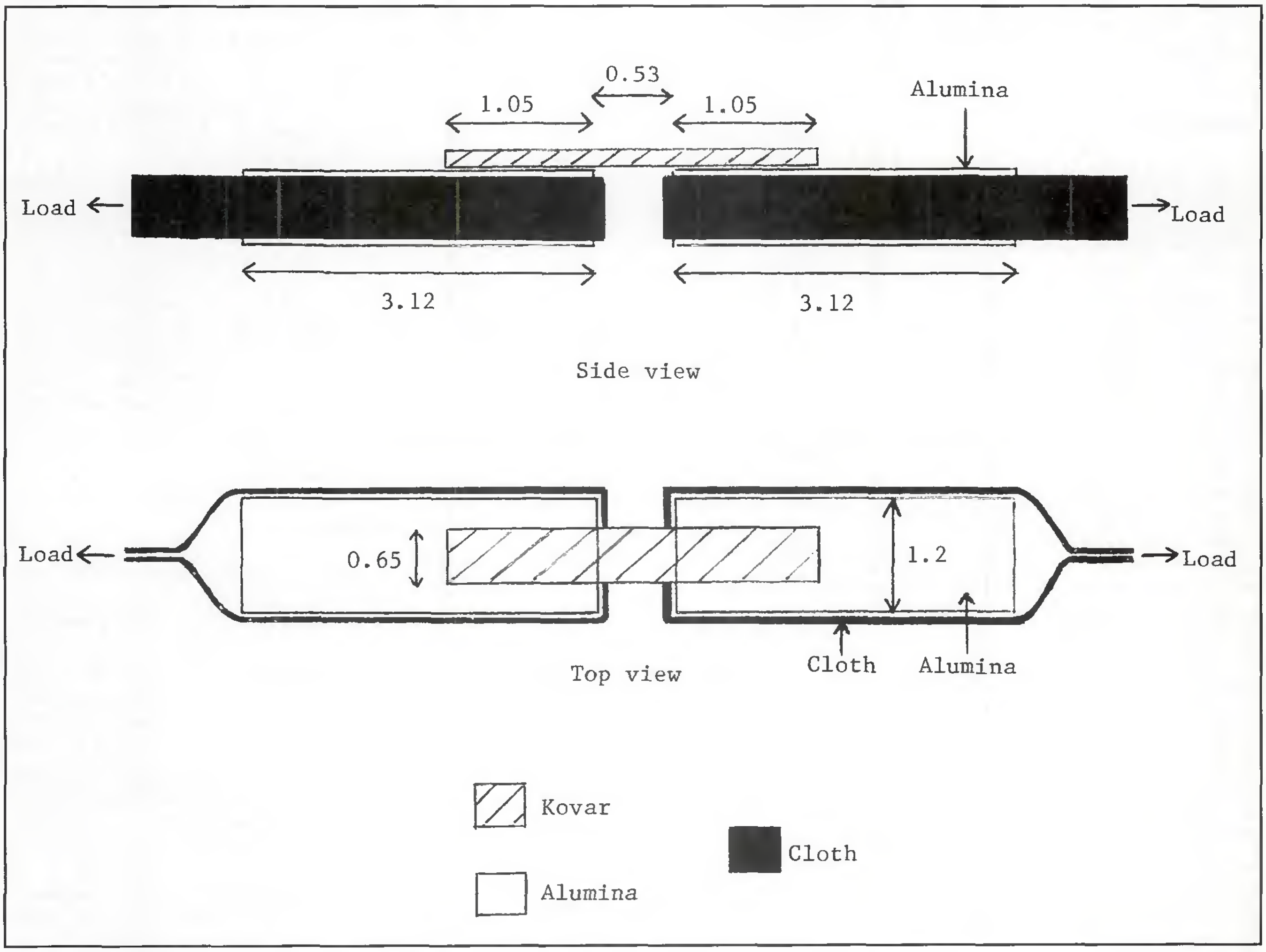

Fig. 1 — Sample configuration for joint strength measurement under shear load. Dimensions shown are in cm.

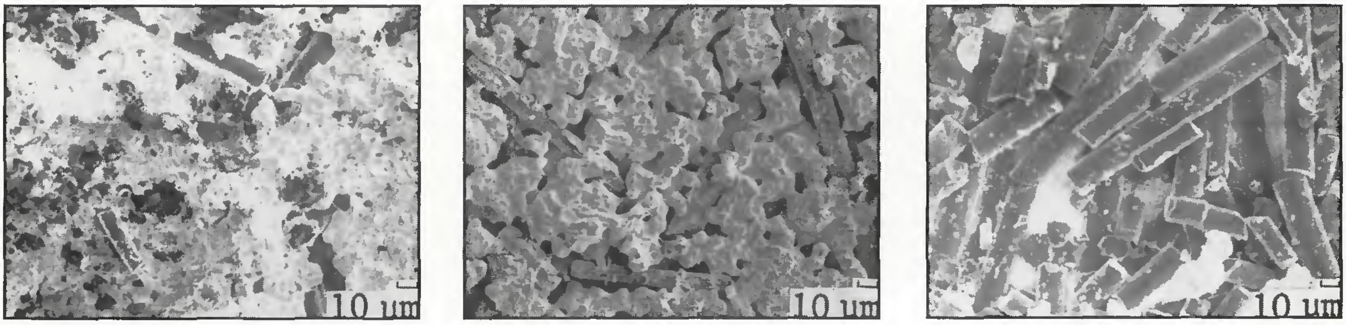

Fig. 2 — SEM photographs of shear surfaces on the Kovar side for joints brazed by using Ag-Cu with 12 vol-% bare carbon fibers (left), 20 vol-% bare carbon fibers (center), and 28 vol-% bare carbon fibers (right).

Kovar sheet were coated with a film of gold (450 Å thick) by sputtering to increase the wettability (Ref. 3). In spite of the coating, high pressure was still necessary during brazing, probably because of the pressure required to form a sound composite filler material during the hot pressing. Since the gold coating makes the joining process more complex and expensive, it was not used for the results reported here.

Joint Strength Measurement

In order to examine the joint strength between alumina and Kovar, a shear strength test was made using the sample configuration shown in Fig. 1, where two pieces of alumina each 3.12 cm long and 1.2 cm wide (1.23×0.47 in.) were brazed to one piece of Kovar 2.63 cm long and 0.65 cm wide (1.03×0.26 in.). The longer edge of each of the three pieces was parallel to one another and each piece of alumina overlapped one end of the Kovar piece by a distance of 1.05 cm (0.41 in.) along the longer edge of the Kovar piece. Hence, the area of the brazed joint was twice 1.05×0.65 cm^2. The shear strength was calculated on the basis of the test load and the overlap area. In order to minimize the bending moment, each alumina piece was wrapped with a cloth ribbon to which force was applied during testing. The load was measured by a tensile tester (Vishay BT-1000 bench-type testing machine).

Tables 2 and 3 give the shear strengths of joints for different brazing material compositions. Each value is the average of the data on two or three samples. The location of failure was between the brazing material and the alumina plate. For both bare and coated carbon fibers, the highest joint strength was obtained at an intermediate carbon fiber content of 20 vol-%. Comparison of Tables 2 and 3 shows that the strengths were much higher for joints using Ni-coated fibers than the corresponding joints using bare fibers.

Fractography

Figures 2 and 3 show scanning electron microscope (SEM) photographs of debonding surfaces on the Kovar side obtained after shear strength measurement for joints using bare fibers and those using Ni-coated fibers, respectively. They reveal the structure of the brazing material. Figure 2 clearly shows the poor wetting of the bare carbon fibers by the alloy; gaps were present at the interface between each fiber and the alloy matrix. Figure 2C shows that, for 28 vol-% fibers, there was not enough alloy to surround each fiber or to coalesce the materials being joined, thus causing the low shear strength for joints of this composition (Table 2). Figure 3 shows that the wetting is much improved by the Ni coating on the fibers, thus causing the higher shear strengths for joints using Ni-coated fibers.

Coefficient of Thermal Expansion

The coefficient of thermal expansion (CTE) of composite brazing materials was measured using a DuPont Instruments TMA2940 thermomechanical analyzer operated at a heating rate of 5°C/min (41°F/min). Prior to the measurement, the samples had been annealed in air at 400°C (752°F) for 3 h. The mean CTE at 240° to 300°C was 20.5×10^{-6}, 18.3×10^{-6} and 15.2×10^{-6} °C^{-1} for samples containing 0, 16 and 20 vol-% Ni-coated carbon fibers, respectively. Hence, the fibers indeed decreased the CTE of the composites.

Discussion

The carbon fiber composite brazing material can be sprinkled in the same way as conventional brazing materials, since it is a mixture of short carbon fibers and the brazing alloy powder. However, the hot pressing requirement of the composite brazing material complicates processing, compared to a conventional brazing alloy.

Although Ag-Cu was used in this work as the alloy, any other brazing alloy may be used provided that the alloy melt does not react with the carbon fibers. Better results than those reported here are expected if Ag-Cu-Ti or Ag-Ti are used instead of Ag-Cu because Ti improves the wetting of the ceramics by the alloy (Ref. 3). The need for hot pressing during brazing and the need for the metal coating on the carbon fibers may be lessened by the use of Ag-Cu-Ti or Ag-Ti instead of Ag-Cu. The lessening of these needs will greatly decrease costs.

The use of metal-coated carbon fibers instead of bare carbon fibers is necessary for the composite brazing material to be a sound composite, at least in the case of Ag-Cu. Although this work used Ni coating for the carbon fibers, Cu coating may be used instead. Copper-coated carbon fibers were used in carbon fiber composite solders (Ref. 2).

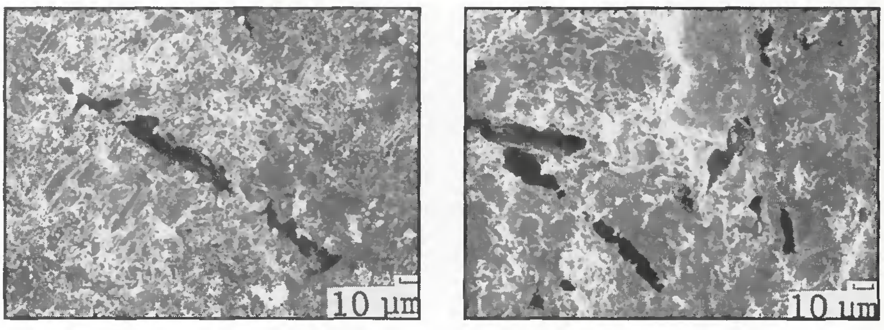

Fig. 3 — SEM photographs of shear surfaces on the Kovar side for joints brazed by using Ag-Cu with 20 vol-% Ni-coated carbon fibers (left), and 30 vol-% Ni-coated carbon fibers (right).

The thermal expansion of carbon fibers is anisotropic. This anisotropy cannot be neglected if one has a filler material containing carbon fibers that are aligned in essentially one direction. This paper, however, discusses carbon fibers that are three-dimensional and random in orientation. Thus, the filler material is isotropic, even though individual fibers are anisotropic.

Since the alumina-to-Kovar joints sheared at the alumina/filler material interface, the strengths shown in Table 3 correspond to the shear strengths between alumina and the filler material. Hence, the composite filler material is valuable for ceramic joints. In general, the composite brazing material described here is valuable for the joining of not just alumina and Kovar, but any material with a low thermal expansion. The coefficient of thermal expansion of the composite brazing material decreases with increasing fiber content, so the optimum fiber content may vary from one pair of materials being joined to another. For the joining of alumina, the optimum fiber content is 20 vol-%. The optimum fiber content is expected to decrease with increasing fiber length, but this dependence was not investigated in this paper.

An upper limit on the fiber content results from the need for a sufficient amount of alloy for coalescence. This upper limit is beyond 30 vol-% for Ni-coated carbon fibers in Ag-Cu and is between 24 and 28 vol-% for bare carbon fibers in Ag-Cu.

It is possible to use continuous carbon fibers instead of short carbon fibers for the composite brazing material. The continuous fibers would be more effective than the short fibers in reducing the coefficient of thermal expansion and in strengthening the brazing material. However, they make the shaping of the composite brazing material less convenient, and the composite brazing material cannot be applied in the form of a powder mixture. Nevertheless, the continuous fiber composite brazing materials may be made into a metal-matrix composite sheet, which can then be sandwiched by the materials being joined for the purpose of brazing. The metal-matrix composite may be prepared by hot pressing or liquid metal infiltration.

Conclusions

A new composite filler metal containing silver-copper alloy and 20 vol-% short Ni-coated carbon fibers has been developed. It can increase the joint strength by up to 300%. This new filler material alloy composite will make stronger joints a reality when joining ceramics. Moreover, it has demonstrated a new concept for filler metal improvement, *i.e.*, the concept of using a composite filler metal of low thermal expansion.

The brazing material was applied in the form of a mixture of short carbon fibers and silver-copper alloy powder. The strength for alumina-to-kovar brazed joints tested under shear was increased by 65% when 20 vol-% bare carbon fibers were used, relative to the joint strength when no fiber was used. The joint strength was increased by ~300% when 20 vol-% Ni-coated carbon fibers were used, relative to the joint strength when no fiber was used. The Ni coating was needed to enhance the wetting of the fibers by the alloy. The optimum fiber content was 20 vol-% for alumina-to-Kovar brazed joints.

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