Brazing of micrograin-filled quartz fiber reinforced silica composites and Invar using Ag-21Cu-4.5Ti alloy

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Brazing of quartz fiber reinforced silica composites (QFSC) to Invar alloy was carried out in a vacuum at 1173 K for 10 min using Ag-21Cu-4.5Ti metal filler. Experiments indicated that composites prefilled with CaCO_3 micrograins had good wettability. The CaCO_3 decomposed to CaO during brazing. After brazing, a joint of structure QFSC/ $3\text{CaO}\cdot 2\text{SiO}_2 + \text{Ti}_3\text{O}_5 + \text{Fe}_2\text{Ti} + \text{NiTi} + \text{Ag}(\text{s},\text{s}) + \text{Cu}(\text{s},\text{s})/\text{Invar}$ was established. The shear strength of the brazed joint reached 11.6 MPa at room temperature, which is about five times the shear strength of that obtained without surface filling.

composites, wettability, filler reinforcement, brazing, microstructure, strength

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In the field of advanced composites, fiber braided composites are increasingly receiving attention because they are lightweight, and have excellent mechanical strength and high temperature resistance [1–4]. Quartz fiber reinforced silica composites (QFSCs) also have special electrical properties. Because they have poor machining properties, one focus of research into applications of these composites is on joining them with dissimilar materials.

Recently, research into joining of fiber braided composites has focused mainly on brazing [5–8]. It has been suggested that fiber braided composites have low interlaminar contact strengths because their loose texture results in poor dynamic properties [9,10]; this could make it difficult to form perfect joints at the interfaces. Several techniques have been considered for reinforcement of composites, such as resin transfer molding and vacuum assisted resin transfer molding for different textile performs (2D or 3D textile architectures) [11]. Filler reinforcement using micrograins is an effective modification for reinforcing incompact structures [12,13]. We may infer that good joints could be

achieved by reinforcing fiber braided composites with fillers. The aim of our investigation was to study the brazing of Invar alloy to QFSC through experiments examining the effects of micrograin fillers on the composite surface, using Ag-21Cu-4.5Ti as the braze filler metal. The microstructure and joining mechanism were also investigated.

1 Experimental

The QFSC was synthesized by immersion sintering of quartz fibers and silica sol. The composite had different strengths in different directions (the shear strength in the vertical direction reached 160 MPa, but in the parallel direction was only 10.6 MPa). In the present study, the surface parallel to the orientation of the fibers was used for brazing. Commercial Invar alloy (see Table 1 for the chemical composition) was used as the substrate, and the filler metal used in the vacuum brazing was commercial Ag-21Cu-4.5Ti foil.

The QFSC samples (thickness 5 mm), Invar alloy (thickness 5 mm), and filler metal (thickness 50 μm) were cut into slices of dimensions 5 mm $\times$ 5 mm, and cleaned ultrasonically in

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Table 1 Chemical composition of Invar alloy (wt.%)

Fe	Ni	Mn	Si	S	C	P
Remaining	35.0–37.0	0.2–0.6	0.2	0.02	0.02	0.05

acetone for 15 min.

After cleaning and air-drying, the QFSC was dipped into $\text{Ca}(\text{OH})_2$ solution, followed by CO_2 gas insufflation (gas velocity 0.008 m s^{-1}) for 15 min. The QFSC surface was then wiped using a pledget dipped in acetone. The micrograin-filled QFSC was prepared by this step. The Invar substrates were polished using metallographic abrasive papers.

The assemblages of QFSC/Ag-21Cu-4.5Ti/Invar were brazed in a vacuum at 1173 K for 10 min, with a normal load of 0.02 MPa, using micrograin-filled QFSC. The heating and cooling rates were 10 K min^{-1} . To compare the strengths of the joints, the original QFSC was also brazed to Invar using Ag-21Cu-4.5Ti foil under the same conditions.

The shear strengths of the joints were tested using a materials testing machine (Instron-5569, Instron, Norwood, MA, USA) with a loading rate of 1 mm min^{-1} . The cross-sectional microstructures of the brazed joints were examined using a scanning electron microscope (SEM S-4700, Hitachi, Tokyo, Japan) equipped with an energy-dispersive spectrometer (EDS) and an electron probe X-ray microana-

lyzer (EPMA). The reaction products were identified by X-ray diffraction (XRD; JDX-3530M, JEOL, Tokyo, Japan).

2 Results and discussion

2.1 Microstructure and joint strength

As shown in Figure 1(a), the joint obtained with QFSC/Invar brazed directly using a AgCuTi alloy has an imperfect junction, and the interface near the QFSC has been fragmented into small pieces. The joint obtained with Invar and QFSC predeposited with micrograins had good wetting properties and a strong connection (Figure 1(b)). The results of the EDS line scan across the joining interface are shown in Figure 1(c). It can be seen from Figure 1(c) that Fe and Ni diffuse into the brazing seam. The distribution of Ni is 15–20 at.% and that of Fe is greater than 40 at.%. However, the distribution is not uniform in the brazing zone. In contrast, the Cu and Ag contents of the joint are both in the range 60–80 at.%. Ti is found mainly in two parts: 15–20 at.% aggregated with Fe and Ni at the center of the junction, and almost 45 at.% diffused into the interface of the composite. The total Ca content is so low that it can be dismissed as simple deposition.

To examine the joint properly, it is necessary to look at the microstructures of the Invar/AgCuTi and AgCuTi/QFSC

Figure 1 Microstructure of (a) QFSC/Invar, (b) micrograin-filled QFSC/Invar and (c) EDS line scan results of junction in (b), brazed with AgCuTi alloy at 1173 K for 10 min.

interfaces (see Figure 2). The results of spot EDS analyses across the joining interfaces are shown in Table 2, with each position referred to in Figure 2. The gray blocks near the Invar are Cu-rich phases containing little Fe and Ni, so they are Cu-based solid solutions (Cu(s,s)) in terms of the Cu-Fe phase diagram. At the joint center, some Ti and a little Ni are found in the layer of Fe-rich phase (black strip in Figure 2). Some intermetallic compounds may be formed between Ti and Fe, and Ti and Ni. The elements in the white matrix of the joint seam are Ag, Cu, and O; the amount of Ag is higher than the amounts of Cu and O, from which it can be inferred that a Ag-based solid solution is formed in this white region. On the composites side, a gray layer of composition 19.60 at.% O/38.05 at.% Ti/18.19 at.% Fe/15.61 at.% Ni is found adjacent to the QFSC border, which may also be composed of intermetallic compounds and oxides. It is clear that reaction occurs between the quartz fiber surface and the filler metal.

To identify the reaction phases of the joint further, the specimens brazed at 1173 K for 10 min were ground to expose the reaction layer at the interface. XRD analysis was then performed on the interface reaction layer; the results are shown in Figure 3. From previously reported results [14, 15], it can be inferred from Figure 3 that the reaction products in the gray layer are mainly Ti_3O_5 , Fe_2Ti , and NiTi . Because the gray layer is only about 3 μm thick and near the QFSC quartz fibers and the filler metal, some of the phases in the XRD pattern can easily be identified as SiO_2 , Ag(s,s) , and Cu(s,s) .

Combining the results discussed above, the reaction

phases can be identified as follows: the gray blocks near the Invar are a Cu-based solid solution; the black strips at the center of the junction are composed of Fe_2Ti and NiTi ; the white phase is a Ag-based solid solution; and the reaction layer adjacent to the QFSC is composed of Fe_2Ti , Ti_3O_5 , and NiTi .

In the brazing process, quartz fibers reacted with CaO, formed by decomposition of CaCO_3 predeposited at the surface of QFSC (eq. (1)) at high temperature, to form silicate (eqs. (2)–(5)). As reported in [15], silicate is a type of ionic compound. Silicate formation would generate free O ions. The d-orbitals of Ti atoms have vacant electron sites, which could easily form pairs of electrons or covalent bonds with O ions. As a consequence, the reaction between CaO and silica provided an important support for interaction of the braze alloy.

The joint shearing test showed that the joint shear strength can reach 11 MPa at room temperature, which is equal to the composite strength paralleled with fibers. For comparison, the shear strength of a brazed joint without micrograin filling was tested; the results are shown in Table 3. It is evident that surface filling plays an active role in joining, and the joint strength is improved by more than five times.

2.2 Thermodynamic analyses

In the joining process, three main reactions occur at different periods. The relevant thermodynamic processes are discussed in the following.

As a result of reaction (1) in Ca(OH)_2 solution at room

Figure 2 SEM micrographs of the interfaces of (a) Invar/AgCuTi, and (b) AgCuTi/QFSC, marked on the joint in Figure 1(b).

Table 2 Chemical compositions of each region in different zones of Invar/QFSC joint brazed using AgCuTi filler metal at 1173 K for 10 min (at.%)

Sites	O	Si	Ag	Ca	Ti	Fe	Ni	Cu	Possible phases
1 (gray block)	04.02	01.52	03.28	01.05	00.80	04.06	03.21	82.06	Cu(s,s)
2 (black strip)	08.07	01.02	09.76	00.12	23.78	43.56	11.02	02.67	Fe_2Ti , NiTi
3 (white region)	17.16	00.00	59.95	00.00	00.99	05.81	05.88	10.21	Ag(s,s)
4 (gray layer)	19.60	05.24	00.83	00.42	38.05	18.19	15.61	02.06	Ti_3O_5 , NiTi , Fe_2Ti

Figure 3 XRD result for micrograin-filled QFSC/Invar joint brazed at 1173 K for 10 min using AgCuTi alloy filler.

Table 3 Shear strengths of QFSC/AgCuTi/Invar and micrograin-filled QFSC/AgCuTi/Invar brazed at 1173 K for 10 min

Type of sample assembled	Brazing technique	Shear strength of joint (MPa)	Remarks
QFSC/Ag-21Cu-4.5Ti/Invar	1173 K 10 min	0, 1.5, 1.8	Not joined and cracking at QFSC side
Micro-grains filled QFSC/ Ag-21Cu-4.5Ti/Invar	1173 K 10 min	11.6, 10.5, 12.1	Cracking at QFSC beside brazing seam for 0.5 mm, with some remains of fiber spalls

temperature, a large number of white grains are deposited at the surface of the quartz fibers:

The Gibbs free energy, calculated using the software package HSC Chemistry 5.0 (Outotec Oyj, Finland), is: $\Delta_r G_{(1)} = -72.623 \text{ kJ mol}^{-1}$.

In the heating process, the solid CaCO_3 deposited can be decomposed above 1118 K [16]:

After this step, micrograins of CaO are deposited on the surface of the quartz fibers in QFSC. CaO grains probably then react with the quartz fibers as shown in eqs. (3), (4), or (5).

In addition, reactions could occur between Ti and Fe, or Ti and Ni. The corresponding reaction equations are

In the brazing process, the Ti in the AgCuTi active foil could react with quartz fibers as in eq. (8).

The calculated Gibbs free energy values for eqs. (3) to (7) are shown in Figure 4. And the Gibbs free energy for eq. (8) is in the range of $-1959.802 \text{ kJ mol}^{-1}$ to $-1934.537 \text{ kJ mol}^{-1}$

Figure 4 Free energies of formation of possible reaction products formed during brazing.

from 1123 to 1183 K. It has been confirmed that all these reaction products can be produced in the joining process; the thermodynamic data suggest that $3\text{CaO}\cdot 2\text{SiO}_2$ is the most likely product of reaction between CaO and SiO_2 .

In summary, it can be that the reaction products at the interface are $3\text{CaO}\cdot 2\text{SiO}_2$, Ti_3O_5 , Fe_2Ti , and NiTi.

2.3 Process model

Based on the results discussed above, the vacuum brazing of Invar and a QFSC surface filled with micrograins is described in Figure 5. At room temperature, QFSC surface deposited by CaCO_3 micrograins, base material, and AgCuTi filler metal are assembled. In the heating period, CaCO_3 grains are gradually transformed into CaO micrograins above 1118 K; the micrograins can react with quartz fibers to form a solid solution. The filler alloy reacts with the quartz fibers and Invar simultaneously in the brazing period

to form a compact joint. After cooling, a joint interface consisting of $3\text{CaO}\cdot 2\text{SiO}_2$, Ti_3O_5 , Fe_2Ti , NiTi, Ag(s,s), and Cu(s,s) is formed. The joint structure can be described as: QFSC/ $3\text{CaO}\cdot 2\text{SiO}_2+\text{Ti}_3\text{O}_5+\text{Fe}_2\text{Ti}+\text{NiTi}+\text{Ag}(\text{s,s})+\text{Cu}(\text{s,s})/\text{Invar}$.

3 Conclusions

Deposition of CaCO_3 micrograins on QFSC was obtained by chemical reaction at room temperature; the micrograins improve the wettability of composites. The shearing strength of the brazed joint reached 11.6 MPa at room temperature, which is about five times the strength of joints of that obtained without surface filling.

Active braze reacted with QFSC fibers and formed a reaction layer about 5–8 μm thick. The structure of the brazed joint was: QFSC/ $3\text{CaO}\cdot 2\text{SiO}_2+\text{Ti}_3\text{O}_5+\text{Fe}_2\text{Ti}+\text{NiTi}+\text{Ag}(\text{s,s})+\text{Cu}(\text{s,s})/\text{Invar}$.

Figure 5 Model of micrograin-filled QFSC and Invar brazing using AgCuTi solder: (a) at room temperature, (b) solid solution reinforcement and interface reaction, and (c) cooling.

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