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Joining of Si–Ti–C–O fibre-assembled ceramic composites with 72Ag–26Cu–2Ti filler metal

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Si–Ti–C–O fibre-assembled ceramic composites were joined with 72Ag–26Cu–2Ti filler metal at 1123 K and 1223 K in vacuum. The composites consisted of Si–Ti–C–O fibres, which were assembled unidirectionally, and oxide material filling the spaces between the fibres. During the joining process, frothing occurred at the joining interfaces. Joining interfaces were observed by SEM and analysed by electron probe microanalysis and X-ray diffraction. The strength of the joints was evaluated by four-point bending tests. Most of Si–Ti–C–O fibre/filler metal interfaces and the oxide material/filler metal interfaces were firm without cracking and separation. At the fibre/metal interfaces, a high concentration of titanium was confirmed. Among the specimens joined at 1123 K, the average strength, measured by the bending test, was 96 MPa. It was inferred that the defects at the joining interfaces formed by frothing had decreased the strength of the joints. Metallizing of the surfaces to be joined with the same filler metal as a pretreatment before joining, was effective in preventing frothing during joining and improving the joining strength. The average strength of the joints with pretreatment was 211 MPa.

1. Introduction

A Si–Ti–C–O fibre-assembled ceramic composite is considered to be one of the most promising structural materials for high-temperature industrial applications, owing to its high strength, excellent fracture toughness and good oxidation resistance [1–3]. In order to use that material in industry, joining techniques are essential.

Many joining techniques of structural ceramics, such as Si_3N_4 and SiC, have been developed. In particular, convenient joining methods using filler metal have been widely applied for industrial applications. However, the number of reports on joining of ceramic composites is limited [4, 5].

In the present work, joining of Si–Ti–C–O fibre-assembled ceramic composites with Ag–Cu–Ti filler metal was studied experimentally. A similar filler metal has been used for joining of monolithic SiC ceramics [6–8]. For industrial applications, ceramic composites often have to be joined with some other material. However, in order to avoid a complicated residual stress problem due to thermal expansion mismatch, joining of composite specimens was carried out in this study.

2. Experimental procedure

2.1. Materials and joining procedures

Si–Ti–C–O fibre (Tyranno fibre)-assembled ceramic composites (Ube Industries Ltd) were used for the experiments. The composition and some properties of the Si–Ti–C–O fibre are shown in Table I [2]. Considering that the oxygen contents of most of the commercially available monolithic SiC ceramics are lower than 2 wt %, the Si–Ti–C–O fibre contained significant quantities of oxygen. The composites were manufactured by hot pressing of previously oxidized fibres, which were assembled unidirectionally. In the sintered body, amorphous oxide material completely filled the spaces between the assembled fibres. In the microstructure of fibres in the composite, TiC, β-SiC and graphite nanocrystals dispersed in an amorphous phase containing a large amount of oxygen, were reported [3]. The flexural strength of the composites, measured by the three-point bending test (Specimen size 3 mm × 4 mm × 40 mm, span 30 mm), was about 690 MPa on average.

As-received composite (10 mm × 76 mm × 76 mm) was cut and ground into pieces of size about 10 mm × 10 mm × 20 mm. The surfaces to be joined (10 mm × 10 mm) were prepared to be perpendicular to the fibres in the specimens. Therefore joining interfaces were formed to be perpendicular to the direction in which the composites showed the maximum tensile strength. The surfaces to be joined were mirror polished with 1 μm diamond powder after grinding with a 3000 grit diamond disc.

As filler metal, Ag (72 wt %)–Cu (26 wt %)–Ti (2 wt %) alloy foil with a thickness of 0.1 mm was inserted between two specimens to be joined. Joining conditions are shown in Table II. By referring to the above-mentioned reports on the joining of monolithic SiC ceramics [6–8], the joining temperatures were determined.

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TABLE I Composition and some properties of Si–Ti–C–O fibre [2]

Chemical composition (wt%)					Density at 298 K ($g\,cm^{-3}$)	Diameter of fibre (μm)	Tensile strength (GPa)
Si	C	O	Ti	B			
48–57	30–32	13–18	2	< 0.1	2.3–2.4	8.5	3.0–3.6

TABLE II Joining conditions

Joining temperature (K)	1123, 1223
Joining pressure (kPa)	44
Holding time (s)	600
Atmosphere	Vacuum (below 6×10^{-3} Pa)

2.2. Pretreatment

As a pretreatment before joining, oxidation and metallizing of some of the specimens to be joined were also carried out.

Oxidation of some specimens at 1423 K for 3.6×10^4 s in air was carried out as a pretreatment. These conditions were determined on the basis of the oxidation conditions for Si–Ti–C–O fibres before sintering during the manufacturing processes [1]. The surfaces to be joined were completely covered with glassy oxide material, containing silicon, titanium and oxygen. It could be regarded as a similar material to the amorphous material filling the spaces between the fibres in the composite.

Metallizing of the surfaces to be joined as a pretreatment before joining, was also carried out. After putting the Ag–Cu–Ti foil (thickness 0.1 mm) on the surfaces to be joined, the specimens were heated to 1123 K in a vacuum and held for 600 s. After the pretreatment, two specimens were attached together as a joining couple. The joining conditions were the same as the conditions shown in Table II. No other foil was inserted between the metallized specimens.

In the following sections, when mention of the oxidation or metallizing as a pretreatment is not made, joining was carried out without pretreatment.

2.3. Methods for analysis of joining interfaces and evaluation of joining strength

The SEM observation and electron probe microanalysis (EPMA) of a joining interface, which was mirror polished with 1 μm diamond powder, were carried out.

For the evaluation of joining strength at room temperature, bending specimens for four-point bending tests, of size 4 mm × 4 mm × 40 mm, were prepared from the joined specimens. The surfaces of the specimens were finished by grinding with a 400 grit diamond wheel. Then the specimens were chamfered with a 600 grit diamond disc. Crosshead speed, upper span and lower span for the bending test were 0.5 mm min^{-1}, 10 and 30 mm, respectively.

The SEM observation and X-ray diffraction (XRD) analysis on fracture surfaces of bending specimens were also carried out. Etched fracture surfaces were also analysed. Filler metal layers adhered to the fracture surfaces were removed by etching with nitric acid.

3. Results and discussion

3.1. Observation and analysis of joining interfaces

Fig. 1 shows the joining zone of a joined specimen. Filler metal drops as apparent traces of frothing could be observed on the surface. Some reaction which formed a gaseous material had occurred at the molten filler metal/composite interface. Frothing has not been reported in the joining processes of monolithic SiC ceramics sintered with any additives using a similar filler metal [6–8].

The thicknesses of the filler metal interlayers of specimens joined at 1123 K and 1223 K, were about 29 and 24 μm, respectively. At high joining temperatures, the viscosity of the molten filler metal was so low that a large amount of filler metal was pushed out of the joining zone by a small joining pressure of 44 kPa.

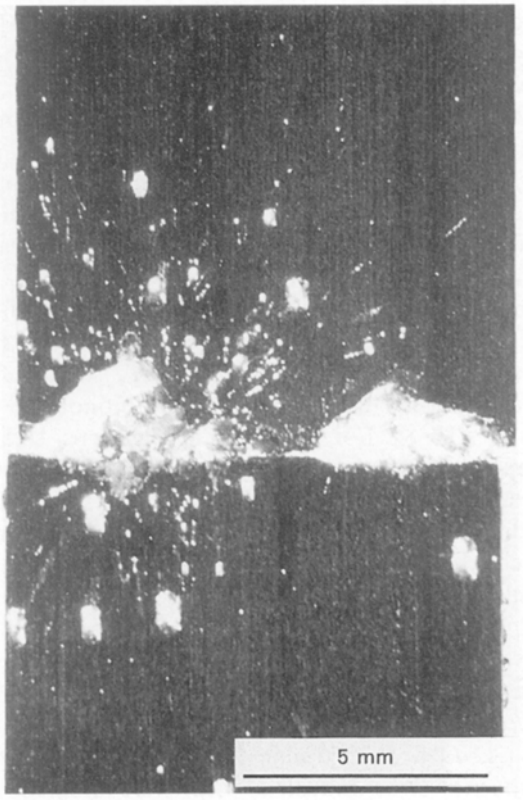

Figure 1 Joining zone of the composites (joining temperature 1123 K).

In the case of joining of previously oxidized specimens, frothing did not occur at all. By considering that surface to be joined was covered with an oxide material similar to the material filling the spaces between the fibres, it was inferred that some reaction, which formed a gaseous material, occurred at the Si–Ti–C–O fibre/Ag–Cu–Ti filler metal interfaces.

A scanning electron micrograph and results of EPMA analysis of a joining interface are shown in Fig. 2. Most of the fibre/filler metal interfaces and oxide material/filler metal interfaces were firm without cracking. At the joining interfaces, titanium was present in high concentrations. In particular, at the fibre/metal interface, the concentration of titanium was extremely high. The thickness of the titanium-rich layer was about 2 μm.

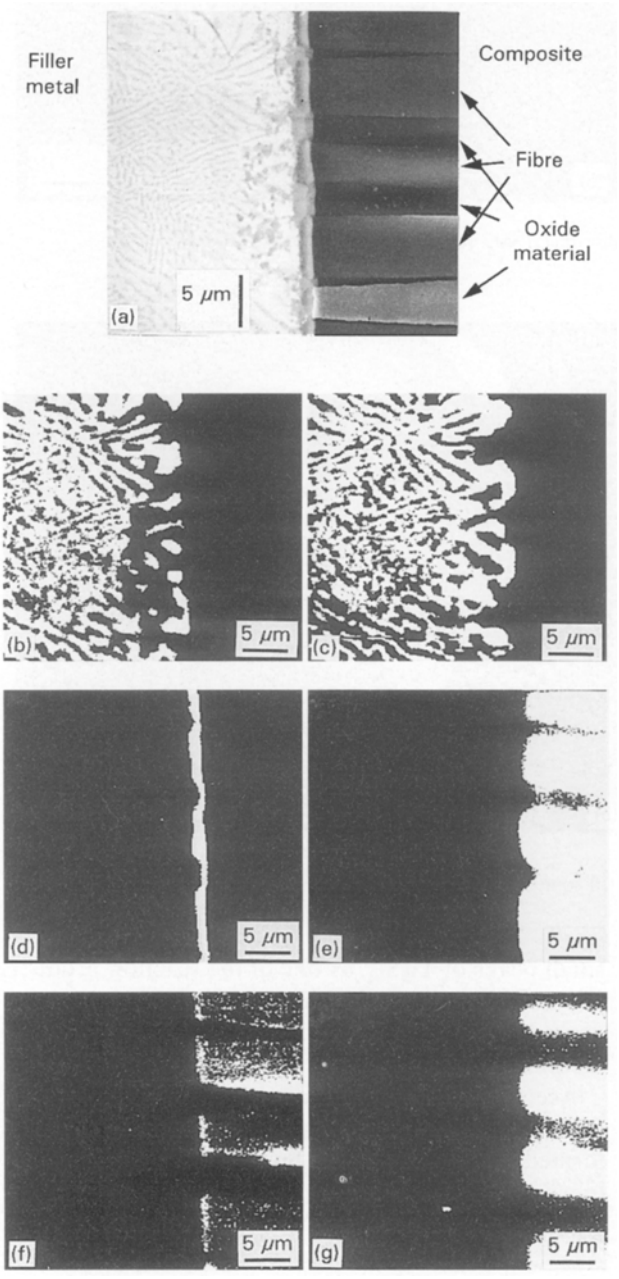

Figure 2 (a) Scanning electron micrograph and (b–g) results of EPMA analysis for the joining interface (joining temperature 1123 K). (b) silver, (c) copper, (d) titanium, (e) silicon, (f) carbon, (g) oxygen.

The concentration of carbon was also increased at the titanium-rich fibre/metal interfaces. Carbon could not be confirmed in the oxide material. On the other hand, the concentration of oxygen was lowered near the fibre/filler metal interfaces.

3.2. Joining strength and fracture surfaces

The results of evaluation of joining strength are shown in Fig. 3. The average and the maximum strengths were 96 and 175 MPa for specimens joined at 1123 K, respectively. In spite of the relatively high maximum strength, the average strength value was low due to large scattering of the measured strength values (Weibull modulus, $m = 3.2$). The average strength of specimens joined at 1223 K was 69 MPa, which was lower than that of the specimens joined at 1123 K.

The fracture surfaces of a bending specimen (bending strength 108 MPa), are shown in Fig. 4. The shapes of fibres were transcribed on the filler metal layer. Cracks propagated along the fibre/filler metal interfaces. At the oxide material/filler metal interfaces, cracks could propagate either along the interfaces or inside the oxide material. No traces of pullout of fibres were observed at all. Therefore, the fracture toughness of the joining interfaces ought to have been low.

On the fracture surfaces, some traces of large defects, which looked like the traces of bubbles formed at the joining interfaces, were clearly observed, as shown in Fig. 5. It was inferred that the molten metal layer had been so thin that part of the formed gaseous material had been caught in the metal layer.

It was clear that those defects had caused serious degradation of the joints and large scattering of the joining strength. The location and the size of the defects ought to have influenced the strength of the joints. It can also be inferred that frothing at 1223 K,

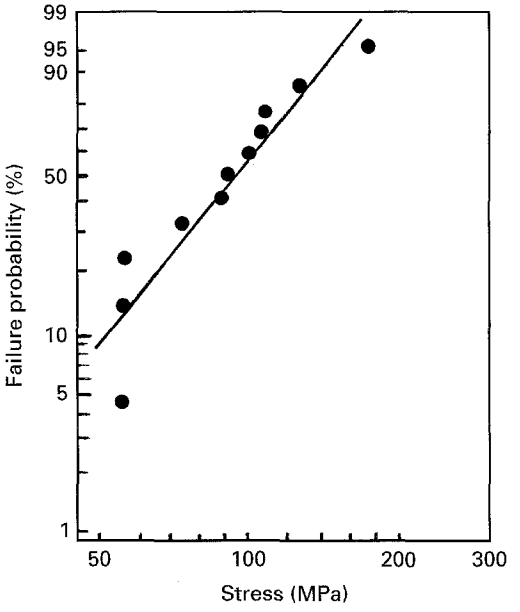

Figure 3 Joining strength evaluated by the bending test (joining temperature 1123 K, mean strength, $\sigma_m = 96$ MPa, Weibull modulus, $m = 3.2$).

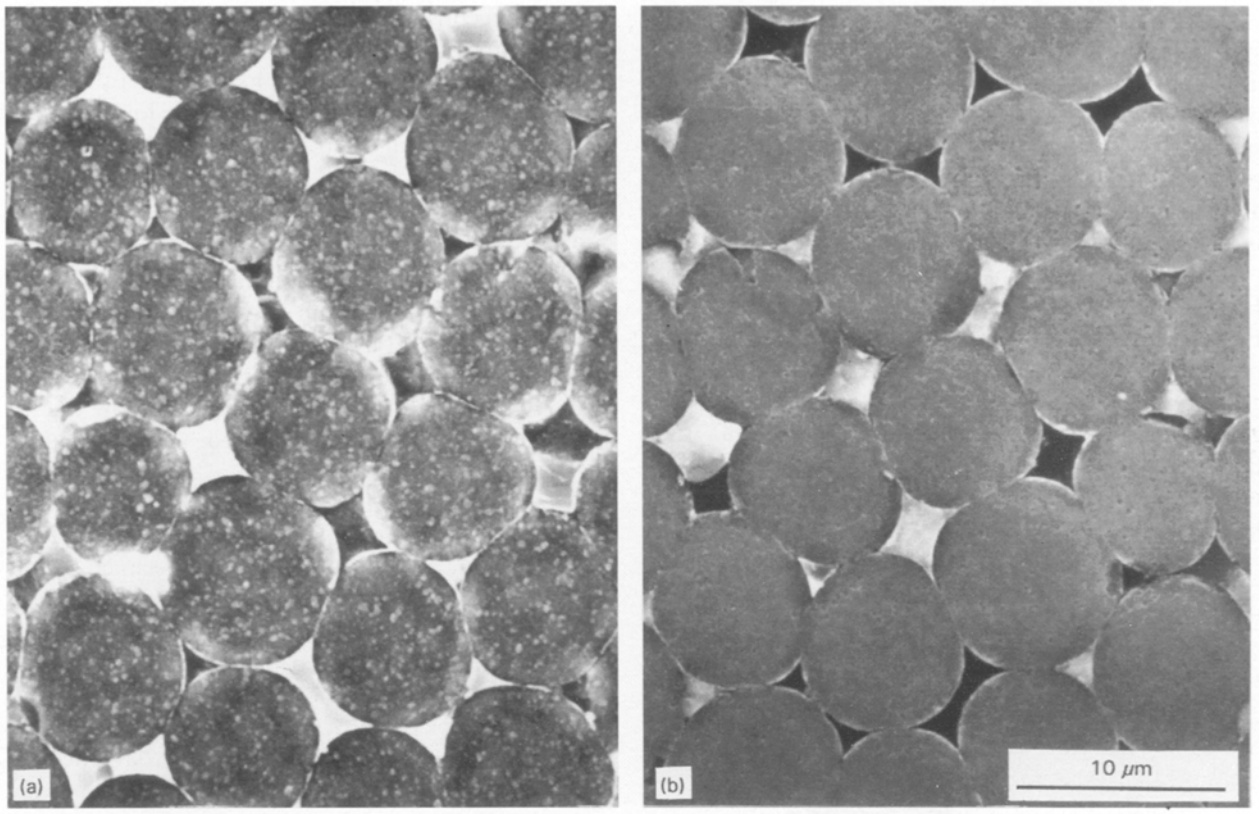

Figure 4 Fracture surfaces of a joint (joining strength 107 MPa) : (a) filler metal side, (b) composite side.

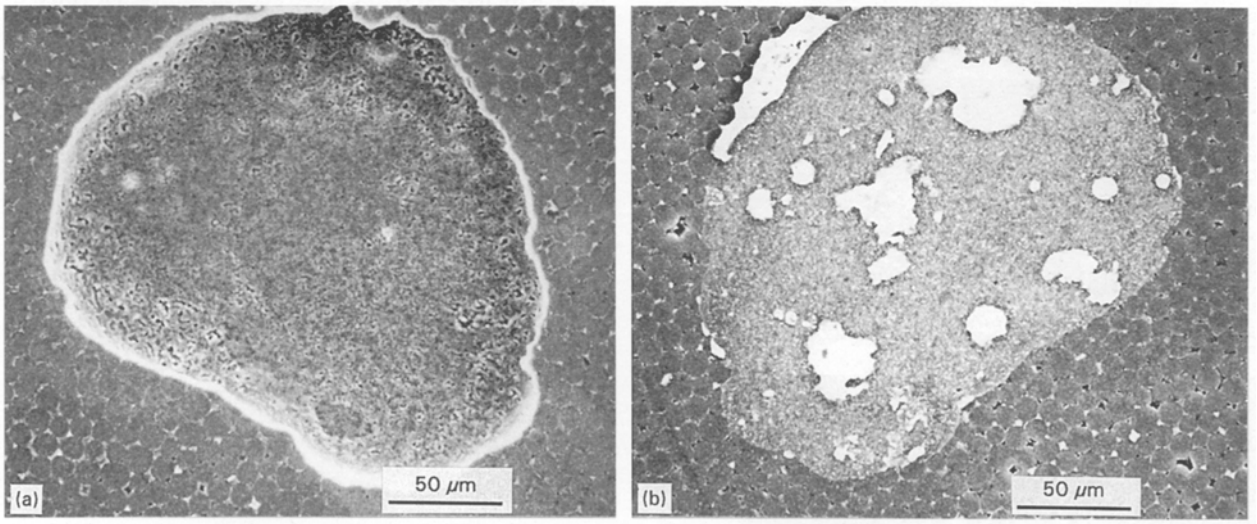

Figure 5 Traces of defects at the joining interface: (a) filler metal side, (b) composite side.

which should have been more severe than that at 1123 K, had caused the serious degradation of the strength. In order to improve the strength of the joints, it is necessary to suppress the formation of large bubbles at the joining interfaces.

X-ray diffraction patterns of the original body and fracture surfaces of a joint (joining temperature 1123 K) are shown in Fig. 6. Large peaks of β-SiC and peaks of TiC could be identified in all of the patterns. The β-SiC peaks in the pattern of the fracture surfaces without etching were obviously lower than those of the original body. The TiC peaks in the pattern of the fracture surfaces were higher than those of the original body. Only in the patterns of the fracture surfaces small peaks of Ti_5Si_3, as one of the reaction products could be identified. On the other hand, no peaks of any oxide crystals, including SiO_2 and TiO_2, could be identified.

According to the literature [6, 7], at Ag–Cu–Ti/monolithic SiC ceramic joining interfaces, products formed by the reaction of SiC and titanium, are TiC (next to the SiC ceramic) and Ti_5Si_3 (next to the titanium layer) crystals. The formation of Ti_5Si_4 and Ag_2Si crystals, as the other reaction products at the joining interfaces of the Ag–Cu–Ti/monolithic SiC ceramic containing 0.32 wt % free carbon, was also reported elsewhere [8]. Compared with the data from those references, it was considered that the reaction

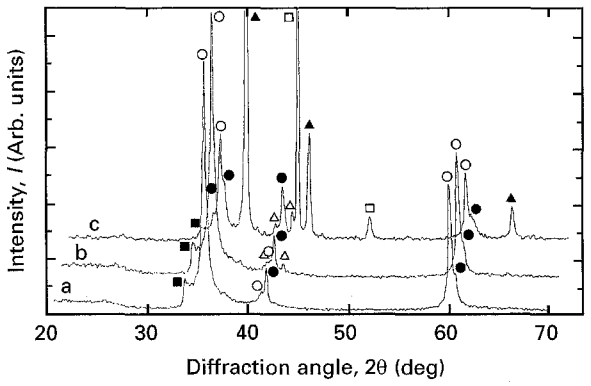

Figure 6 X-ray diffraction patterns of the original specimen and fracture surfaces of joints (CuK, 40 kV, 20 mA). (○) β-SiC (3C, cubic), (▲) Ag, (□) Cu,(■) SiC (2H, hexagonal), (●) TiC, (△) Ti_5Si_3. (a) Original specimen, (b) fracture surfaces after removing filler metal with etching, (c) fracture surfaces.

products formed at the joining interface in this study were similar to those at the Ag–Cu–Ti filler metal/monolithic SiC ceramic interfaces.

According to Ishikawa [1], a Si–Ti–C–O fibre heated above 1673 K in a noble gas atmosphere, forms SiO and CO as gases, with grain growth of β-SiC and TiC crystals in it. It was also reported that, when a SiC fibre containing significant quantities of oxygen is subjected to temperatures above 1473 K, evaporation of CO from the fibre and β-SiC grain growth in the fibre occur [9].

In spite of the relatively low joining temperatures of 1123 K and 1223 K, it was inferred that the reaction of Si–Ti–C–O fibre and titanium at the joining interface, which had formed TiC and Ti_5Si_3 crystals, should have decreased the carbon and silicon contents and increased the oxygen contents in an amorphous phase of Si–Ti–C–O fibres in contact with the joining interface. It was supposed that the change of the composition had induced the formation of some oxide gas, which had caused the above-mentioned frothing.

3.3. Effects of metallizing as a pretreatment before joining

It might be concluded from the above-mentioned inference that, after reaction with the filler metal, Si–Ti–C–O fibre surfaces in contact with the metal had lost significant quantities of oxygen as a result of frothing. Therefore, it was expected that metallizing the surfaces to be joined with the filler metal to cause frothing and decrease the oxygen content before joining, would be effective in preventing frothing during joining.

It was confirmed by preliminary experiments, that bubbles formed at the interfaces during metallizing could easily escape through a thin molten filler metal layer of thickness 0.1 mm.

On the surfaces of the joints of specimens which had been previously metallized as a pretreatment, no traces of frothing could be observed. The strength of the joints is shown in Fig. 7. Compared with the joints without pretreatment, the average joining strength doubled, and the scattering of the joining strength was also improved (Weibull modulus, $m = 6.6$). The highest joining strength attained was 259 MPa. The effects of the metallizing as a pretreatment to prevent frothing during joining, on the joining strength, were obviously confirmed.

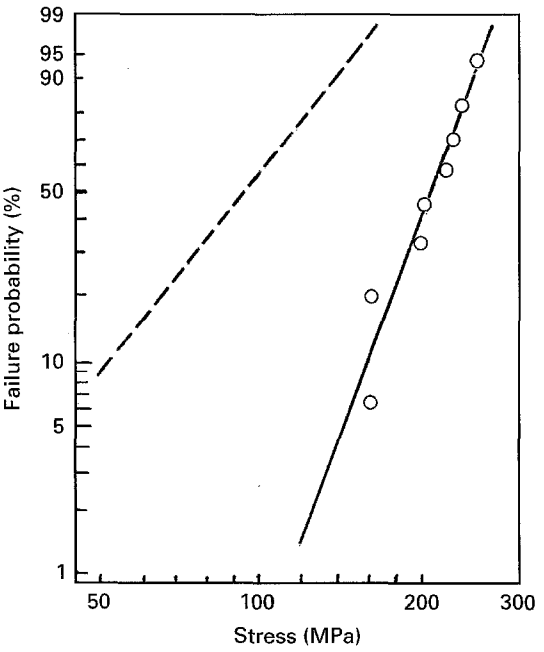

Figure 7 Effect of metallizing of the surfaces to be joined as a pretreatment before joining. (—) Joints with metallizing, joining and metallizing temperature 1123 K, mean strength, $\sigma_m = 211$ MPa, Weibull modulus $m = 6.6$. (- - -) Joints without metallizing (Fig. 3).

4. Conclusion

A study of joining of Si–Ti–C–O fibre-assembled ceramic composites with 72Ag–26Cu–2Ti filler metal was conducted experimentally. The joined interfaces were examined by SEM, XRD and EPMA. Joining strength was evaluated by a bending test of the joints. Reaction products formed at the joining interfaces were similar to those formed at monolithic SiC ceramic/Ag–Cu–Ti filler metal joining interfaces.

Without metallizing as a pretreatment, despite the relatively high maximum strength, the average value was low, owing to large scattering of the measured strength values. This ought to have been caused by the defects formed at the joining interfaces by frothing during joining. Metallizing of the surfaces to be joined as a pretreatment, was effective in improving the joining strength, both of the average strength and the scattering of the strength. The highest joining strength attained was 259 MPa.

In the fracture surfaces, no pullout of fibres was observed at all.

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