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Joining of carbon fibre-reinforced silicon nitride composites with 72Ag–26Cu–2Ti filler metal

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Unidirectionally reinforced carbon fibre/Si_3N_4 matrix composites were joined with 72Ag–26Cu–2Ti filler metal. Joining interfaces were observed by SEM and analysed by energy dispersive spectroscopy. The strength of the joints was evaluated by four-point bending tests. Most of the interfaces of Si_4N_4 matrix/filler metal were firm without cracking and separation. At the interfaces, reaction between the composites and filler metal was limited. Only a concentration of titanium at Si_3N_4 matrix/filler metal interface was confirmed. On the fracture surfaces, many holes left as traces of pull-out of carbon fibres and pulled out fibres could be observed. The maximum joining strength and the average strength, measured by the bending test, were 159 MPa and 107 MPa, respectively. The pull-out process of fibres from the matrix and the reasons for the large scatter in the strength of joints, were discussed. The fibre pull-out behaviour could be related to fibre distribution density at the joining interface.

1. Introduction

Many joining techniques of structural monolithic ceramics, such as Al_2O_3, Si_3N_4 and SiC ceramics, have been developed. In particular, convenient methods using a filler metal have been widely used for joining of some kinds of ceramics. However, the joining of fibre-reinforced ceramic composites, which might be more important than monolithic ones for industrial applications due to their excellent fracture toughness, has not yet been reported [1].

In the case of a joint of fibre-reinforced composites with filler metal, the structure of the joining interface, consisting of three kinds of interfaces (fibre/filler metal, matrix/filler metal and fibre/matrix) would be complicated, compared with that of a joint of monolithic ceramics.

In this report, the joining of unidirectionally reinforced carbon fibre/Si_3N_4 matrix composites with Ag–Cu–Ti filler metal was studied experimentally. Similar filler metal has been widely used for the joining of monolithic Si_3N_4 ceramics [2, 3], and also for the joining of bulk carbon to Inconel 625 [4] and molybdenum [5].

For industrial applications, composite ceramics often have to be joined with some metal or some other ceramic. When a composite ceramic is joined to some other material at high temperatures, a complicated residual thermal stress field appears near the joining interface, due to the thermal expansion mismatch of the materials to be joined. Therefore, in order to avoid such a residual stress problem, joining of a composite specimen to the same composite was carried out in this study.

2. Experimental procedure

2.1. Materials and joining procedures

Unidirectionally reinforced carbon fibre/β-Si_3N_4 matrix composites (Noritake Co. Ltd) were used for the experiments [6, 7]. Some properties of the composites are shown in Table I. The volume content of mesophase-pitch-based carbon fibres (fibre radius about 3.8 μm, fibre strength 2 GPa, Young's modulus 500 GPa) was about 35%.

Scanning electron micrographs of mirror-polished specimens are shown in Fig. 1. Inhomogeneously distributed carbon fibres and large-scale cracks, which were perpendicular to the fibres, were observed in the Si_3N_4 matrix. The inhomogeneous distribution of fibres in a cross-section of a plate is supposed to have been formed before burning. The distribution could be formed by preparation of a pile of sheets containing fibres before burning in order to form a thick plate of composite, while cracks perpendicular to the fibres are supposed to have been generated by burning. During that process to form a dense ceramic matrix, inevitable shrinkage of the matrix would have occurred. On the other hand, the dimensions of the fibres would have

TABLE I Some properties of the composites used for experiments

Bulk density (10^3 kg m^{-3})	2.41
Flexural strength (MPa)	690 (at room temp.)
Fracture toughness (MPa m$^{1/2}$)	28.1 (at room temp.)
Young's modulus (GPa)	220 (at room temp.)
Thermal expansion coefficient (10^6 K^{-1})	0.5 (0°) 4.3 (90°)

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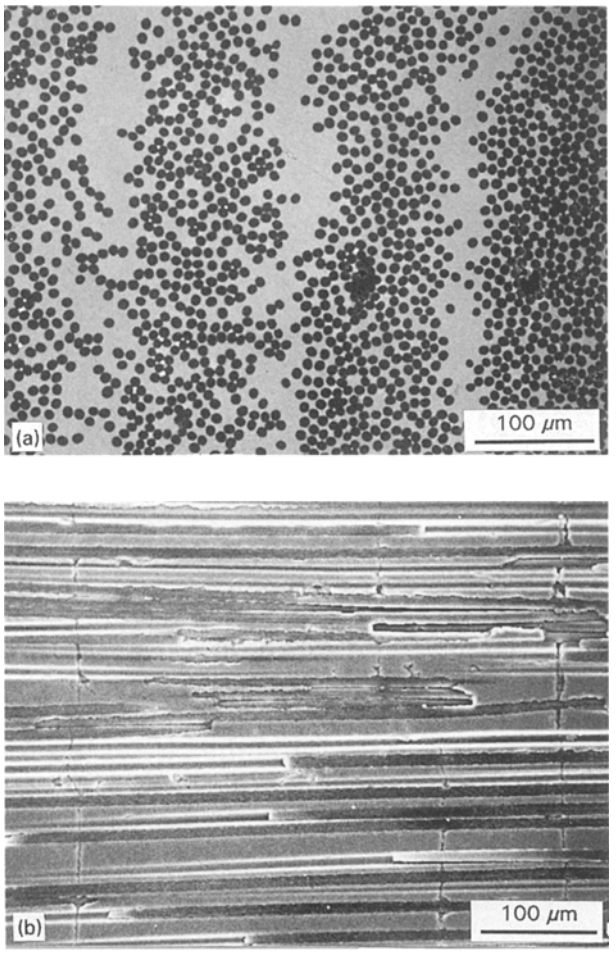

Figure 1 Scanning electron micrographs for mirror-polished surfaces of a specimen. (a) Cross-section perpendicular to carbon fibres. (b) Cross-section parallel to carbon fibres.

hardly changed. The initial cracks, therefore, would have been generated in the ceramic matrix.

The as-received composite (5 mm × 76 mm × 76 mm) was cut and ground into pieces of size about 4.7 mm × 4.7 mm × 18 mm. The surfaces to be joined (4.7 mm × 4.7 mm) were prepared to be perpendicular to the fibres in the specimens. Those surfaces were mirror polished with a 3000 grit diamond disc after grinding. Therefore, joining interfaces were formed to be perpendicular to the direction in which fibre-reinforced composites show the maximum tensile strength.

As filler metal, an 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. The joining conditions are shown in Table II. The joining

TABLE II Joining conditions

Joining temperature	1123 K
Holding time	600 s
Joining pressure	44 kPa
Atmosphere	Vacuum (below 7×10^{-3} Pa)

TABLE III Bending test conditions

Upper span	10 mm
Lower span	30 mm
Cross head speed	0.5 mm min^{-1}
Radius of span edge	2.5 mm
Temperature	Room temp.

temperature was determined by reference previous reports. [2–5].

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

The SEM observation and energy dispersive spectroscopic (EDS) analyses of joining interfaces, which were mirror polished with 1 μm diamond powder, were carried out. For the evaluation of joining strength, specimens for four-point bending tests, of size 4 mm × 4 mm × 36 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. Conditions for the bending test are shown in Table III. The SEM observation of fracture surfaces was also carried out. In order to compare the joining strength of the composites with that of monolithic Si_3N_4 ceramics, the evaluation of the strength of Si_3N_4 ceramics (hot-pressed ceramics with Al_2O_3 (2.9 wt %) and Y_2O_3 (5 wt %) as sintering aids, average flexural strength 1056 MPa) joined under the same conditions, was also conducted.

3. Results and discussion

3.1. Observation and analyses of joining interfaces

Fig. 2 shows a scanning electron micrograph and results of EDS microanalyses of a joining interface. The thickness of the Ag–Cu–Ti filler metal interlayer was about 31 μm. It is inferred that, at high joining temperatures, the viscosity of the molten filler metal was so low that a large amount of filler metal was removed from the joining interface by a small joining pressure of 44 kPa.

Si_3N_4 matrix/filler metal interfaces were firm without cracking, while about one-third of the carbon fibres on the observed surface had fallen off during preparation of the specimen for observation. From these results and data on the joining strength given elsewhere [3–5], it is inferred that the joining strength of the carbon fibre and the filler metal was low, compared with that of the Si_3N_4 matrix and the filler metal. Furthermore, no traces of eutectic melting at triple points of Si_3N_4, carbon and Ag–Cu–Ti filler metal could be observed.

As the result of EDS analyses, the concentration of titanium at the Si_3N_4/filler metal interfaces was confirmed. The formation of TiN can be expected [2, 3]. The concentration and absence of other elements were not confirmed near the interfaces.

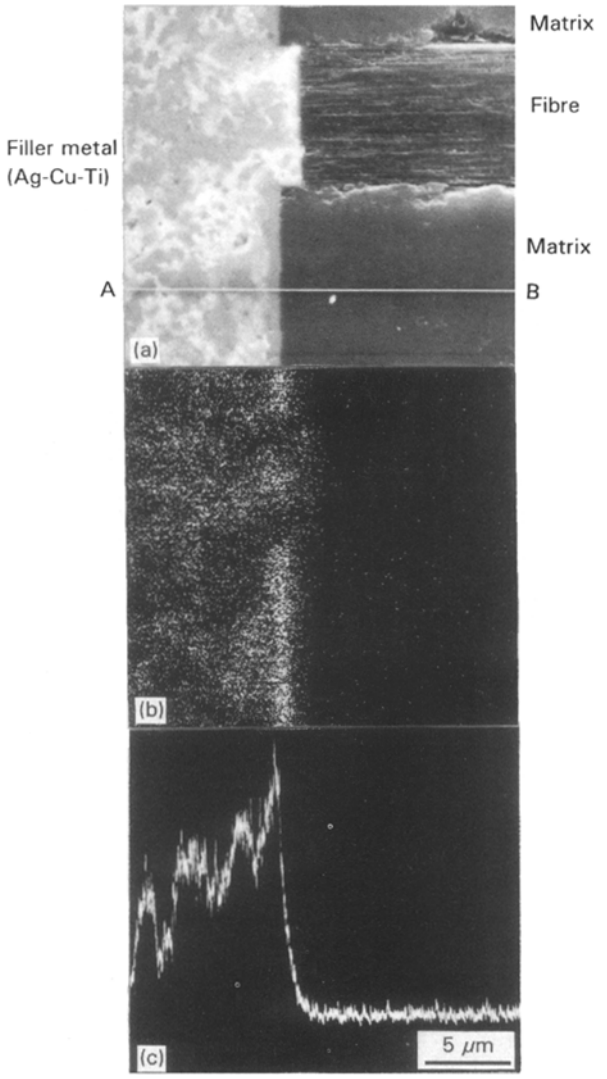

Figure 2 Scanning electron micrograph and results of EDS micro-analyses for the joining interface. (a) Micrograph, (b) dot map for titanium, (c) line profile for titanium on line A–B.

3.2. Fracturing processes

A typical load–displacement curve during the bending test of the joint is shown in Fig. 3. After elastic deformation (period A–B), brittle fracture (B) and sudden falling of the load (B–C), a gradual decrease in the load (C–D) appeared.

Fracture surfaces of a bending specimen, are shown in Fig. 4. Many holes (traces of the pull-out of carbon fibres) on Si_3N_4 layers adhered to the filler metal (Fig. 4a), and naked fibres pulled out from the matrix (Fig. 4b), were observed. However, over about three-fifths of the area of the fracture surfaces, where the density of the fibre distribution was relatively high, the crack had propagated along the joining interface of the composite and the filler metal without pull-out occurring.

Fig. 5 shows a cross-section of the fracture surface, on which the holes could be observed. The thickness of the Si_3N_4 matrix layer adhered to the filler metal was about 32 μm on average. The traces of pull-out of fibres were confirmed there.

The effect of pull-out of carbon fibres from the ceramic matrix on the work of fracture, which would prevent catastrophic failure of the joint, was expected.

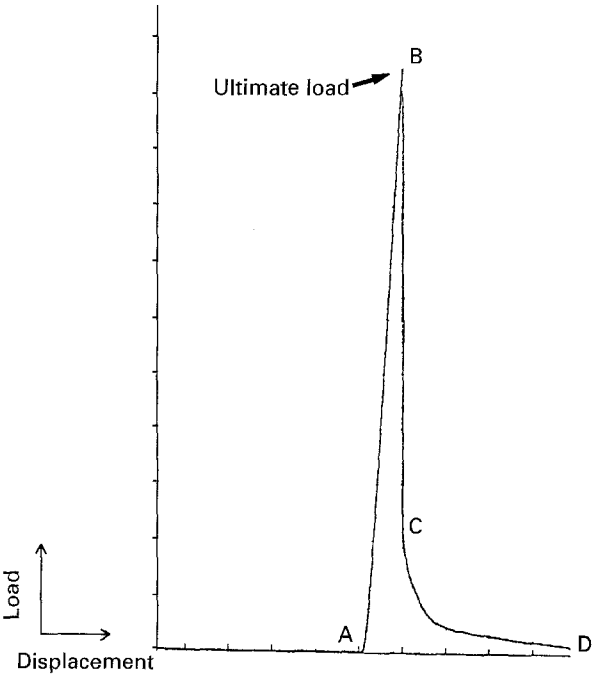

Figure 3 Load–displacement curve during the bending test.

However, it is not clear in the load–displacement curve during the bending test (Fig. 3). The effect of the pull-out on the fracture behaviour might be too small to be confirmed, because of the short pull-out fibre length of about 32 μm and a relatively small number of pulled out fibres in relation to the total numbered fibres adhered to the filler metal interlayer. The pull-out effect also might be mixed with that of the deformation of the filler metal interlayer peeled away from the composites during the last period of the fracturing process (C–D in Fig. 3).

Fig. 6 shows five schematic modes of fracture of a joint consisting of unidirectionally reinforced fibre/ceramic matrix composites and a joining interlayer. A crack propagates along a joining interface (modes a and b), or inside a ceramic matrix (modes c, d and e). In the case of a composite ceramic which is effectively reinforced by thin, long fibres, mode e can be neglected. As the result of SEM observation, it is clear that fracture with mixed mode of modes a and c occurred in this experiment. In the area where the density of the fibre distribution was high, the surfaces formed with mode a fracture were observed.

A schematic illustration of a fibre pull-out process with mode c fracture is shown in Fig. 7. It is assumed that the matrix has an initial crack (distance from the joining interface, L), and debonding has occurred at the fibre/matrix interface between the interlayer and the initial crack during preparation of specimens to be joined and during joining; the sliding stress, τ, which appeared in the debonding area, is uniform. The average area of the cross-section of the matrix per fibre, A_m, can be shown as follows

$$A_m = \pi D^2(1 - F)/4F \quad (1)$$

where F and D are the fibre volume fraction ($0 < F < 0.907$) and fibre diameter, respectively. The tensile stresses in the fibre and the matrix caused by

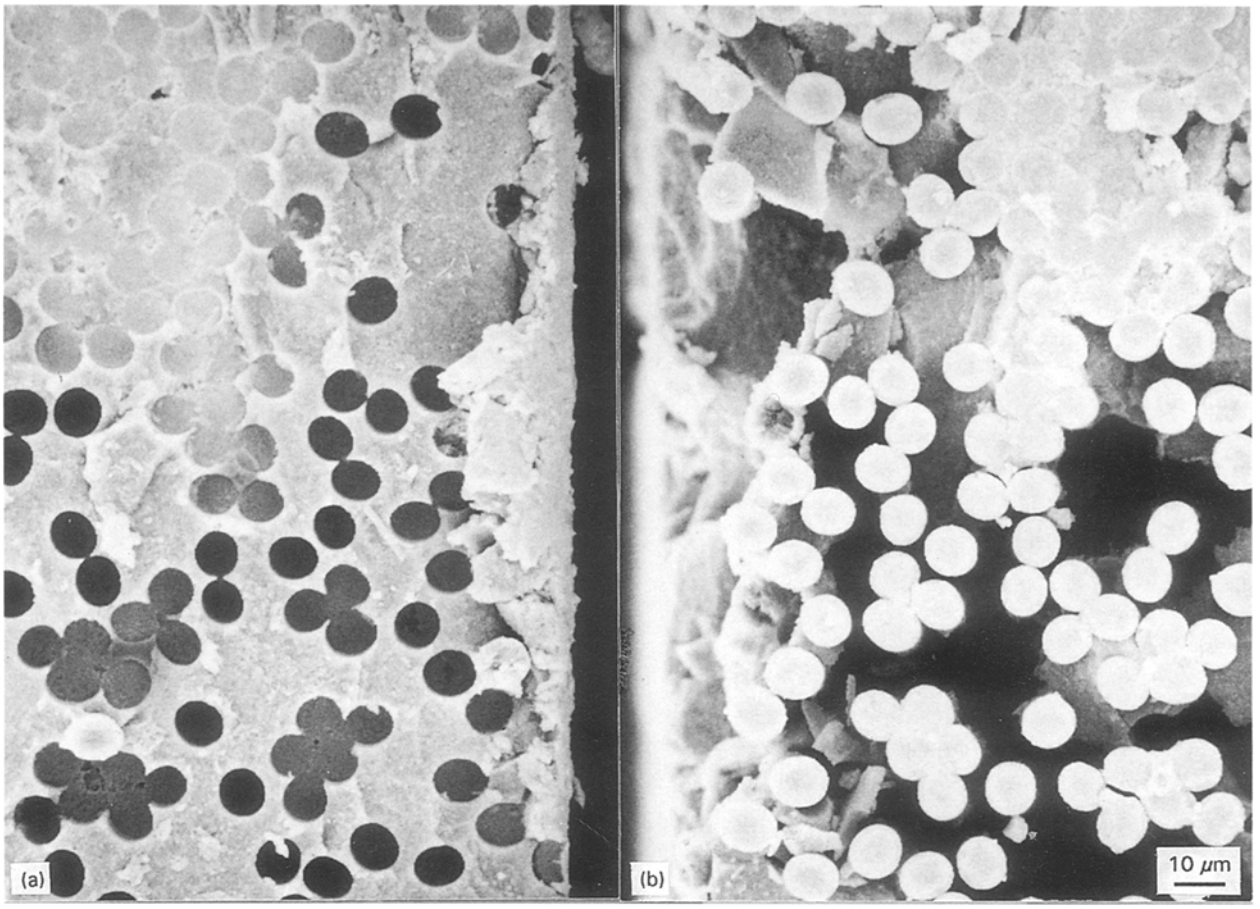

Figure 4 Fracture surfaces of a joint (joining strength 107 MPa). (a) Filler metal side (partially covered with Si_3N_4 layers adhered to the filler metal interlayer). (b) Composite side.

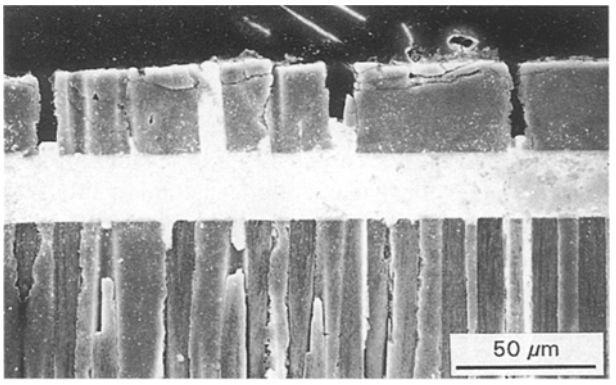

Figure 5 Cross-section of the fracture surface.

the uniform tensile stress applied to the joint can be shown as follows:

$$\sigma_f = (\sigma/F) - 4(L - x)\tau/D \qquad \text{(in the fibre)} \quad (2)$$

$$\sigma_m = 4F(L - x)\tau/D(1 - F) \qquad \text{(in the matrix)} \quad (3)$$

Conditions of the pull-out without failure of the fibre and the matrix are as follows

$$\sigma_{f,x=0} = (\sigma/F) - 4L\tau/D > S_{if} \geqq 0 \quad (4)$$

where S_{if} is the strength of the fibre/interlayer interface

$$\sigma_{f,x=L} = \sigma/F < S_f \quad (5)$$

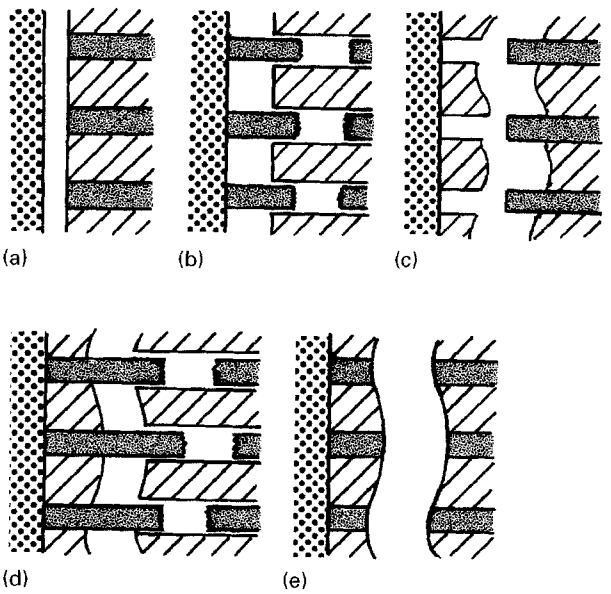

Figure 6(a–e) The various modes a–e of fracture of joints consisting of fibre-reinforced composites and a joining interlayer.

where S_f is the fibre strength

$$\sigma_{m,x=0} = 4FL\tau/D(1 - F) < S_{im} \quad (6)$$

where S_{im} is the strength of the matrix/interlayer interface

$$\sigma_{m,x=a} = 4F(L - a)\tau/D(1 - F) < S_m(a) \quad (7)$$

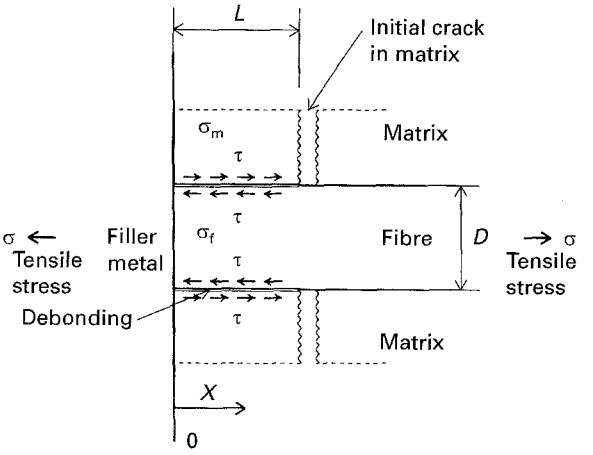

Figure 7 Schematic illustration of the fibre pull-out process.

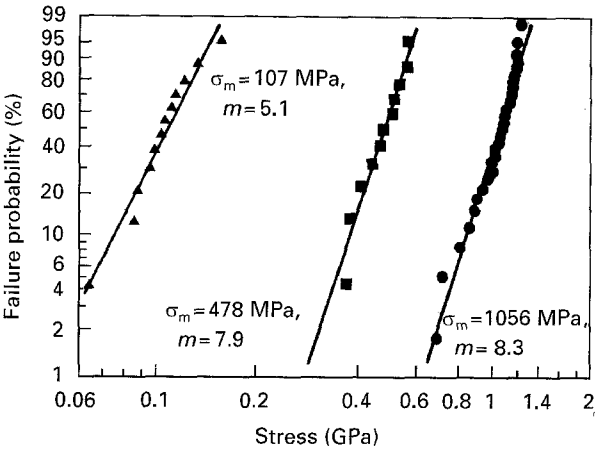

Figure 8 Joining strength evaluated by the bending test. Mean strength, σ_m, Weibull modulus, m. (●) Monolithic Si_3N_4 ceramics (not joints), (■) monolithic Si_3N_4 ceramics joined with Ag–Cu–Ti filler metal. (▲) carbon fibre/Si_3N_4 matrix composites joined with Ag–Cu–Ti filler metal.

where $S_m(a)$ is the strength of the matrix at $x = a$, $0 < a < L$.

When only Inequality 7 is not satisfied, cracking occurs in the matrix and makes the distance L short. Furthermore, when the strength of the matrix, $S_m(a)$, is constant, cracking occurs next to the joining interface. On the other hand, when only Inequality 6 is not satisfied, separation occurs at the matrix/interlayer interface.

It is clear that the large value of F makes it difficult to satisfy the four Inequalities 4–7 at the same time. Therefore, a high fibre distribution density would cause crack propagation next to the joining interface or separation at the joining interface, without the pull-out of fibres. This result almost coincides with the above-mentioned relationships between fibre pull-out behaviour and fibre distribution on the fracture surfaces.

3.3. Joining strength

Results of the evaluation of joining strength are shown in Fig. 8. The average and maximum strength of the joints of composites were 107 and 159 MPa, respectively. Compared with those of Si_3N_4 ceramic joints (478 and 569 MPa, respectively) and the average flexural strength of the composites (690 MPa), the strength of the joints was small. Considering the volume content of the fibres to be 35%, when the joining strength had depended on only the strength of Si_3N_4/filler metal interfaces, and the strength of the matrix had been as high as that of the monolithic Si_3N_4 ceramics, the average strength of the joints of the composites would have attained at about 310 MPa. It is inferred that the small joining strength was mainly induced by the low strength of the matrix due to the included large cracks and the low strength of the fibre/filler metal interface.

The scattering of the strength of the joints of composites was larger than that of the Si_3N_4 joints. For industrial applications, it is necessary to suppress the scattering. It can be deduced that the large scattering was caused by the following two factors. First, the distance between the initial cracks in the matrix and the joining interfaces (distance L in Fig. 7), was not constant. That distance would influence the pull-out fibre length and fracture behaviour of the joints. The second factor is the inhomogeneously distributed fibres in the matrix. When the area with high fibre distribution density in the joining interface (where the pull-out of fibres scarcely occurs and cracks propagate along the interface) is wide and located next to a tensile face of a bending specimen, the strength of a joint must be seriously affected by that area.

It is considered that the large scatter in the strength of unidirectionally reinforced fibre/ceramic matrix composite joints, is caused by their own inhomogeneous structure. Therefore, it would be difficult to suppress that scattering of joining strength.

4. Conclusion

On joints of unidirectionally reinforced carbon fibre/Si_3N_4 ceramic matrix composites with 72Ag–26Cu–2Ti filler metal, examination of their fracture behaviour and evaluation of their mechanical properties were conducted. Many holes, which were traces of pullout of carbon fibres on Si_3N_4 layers adhered to the filler metal, and fibres pulled out from the matrix Si_3N_4, were observed in some parts of the fracture surfaces. The density of fibre distribution on the surfaces to be joined had a great influence on the fracturing process. Joining strength values of the composite evaluated by bending tests were relatively small on average and were scattered widely, compared with those of the monolithic Si_3N_4 ceramics joined with the same procedures. It is considered that the large scattering of the joining strength is caused by the varying distance between the joining interface and the initial cracks in the matrix of the composite, and also the inhomogeneous distribution of fibres in the composite.

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