The metallurgical behaviour during brazing of Ni-base alloy Inconel 600 to Si_3N_4 with Ag71Cu27Ti2 filler metal

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Detailed observations were carried out on the metallurgical behaviour of joint-brazing of nickel based alloy Inconel 600 to Si_3N_4 with Ag71Cu27Ti2 filler metal, with emphasis on the interface between the filler metal and the Inconel 600 and the effects of nickel which was the predominant element in the base metal. Based on the experimental results, the mechanism of bonding Inconel 600 to the filler metal is attributed to the diffusion of silver and copper along the grain boundaries of the Inconel 600, which results in mechanical anchoring. The effects of nickel on the metallurgical behaviour of filler metal are summed up as enhancing the separation of silver- and copper-rich liquid phases from the molten filler metal; combining titanium and decreasing its activity in the reaction with Si_3N_4 at the interface with ceramics; promoting the diffusion of silver and copper into Inconel 600; and facilitating the flow of filler metal over the surface of Inconel 600.

1. Introduction
Owing to the desire to incorporate silicon nitride components into engines and the remarkable performance of titanium-activated Ag–Cu filler metal, considerable effort has been devoted to joining Si_3N_4 with a filler metal of this type [1–5]. However, the majority of work has focused on the wetting of the filler metal and the formation of strong bonding at the interface of ceramics. Little work has been devoted to the joining of Inconel 600 [6]; however, in the work that has been reported, little attention was given to the behaviour of the interface between Inconel and the filler metal. It has been revealed that a difference in reaction kinetics between the braze–structural alloy and braze–ceramics is readily apparent.

The present work investigated the joining of Inconel 600 to Si_3N_4 with Ag71Cu27Ti2 filler metal, with emphasis on the metallurgical behaviour of the interface between the filler metal and the base metal, and the effects of nickel which was the predominant element in Inconel.

2. Experimental procedure
2.1. Materials
The composition of the materials is shown in Table I.

Cubic specimens 10 mm × 10 mm × 10 mm were used for investigation of metallurgical behaviour. Specimens 10 mm × 10 mm × 20 mm were brazed to make four-point bending test bars of 3 mm × 4 mm × 40 mm. Specimens were polished with a series of sandpapers and then Al_2O_3 powder. Filler metal was melted in vacuum and rolled to 100 μm sheet, then polished with sandpapers. All materials were cleaned with acetone just before joining.

2.2. Brazing procedure
Specimens were positioned to form a butt joint, consisting of one metal cube and one ceramic cube with a braze sheet between them. A weight of 65 g was placed on top of the metal.

The heating rate below 600 °C was 20–30 °C min^{-1}, then 10 °C min^{-1} to the brazing temperature. The brazing temperatures were set at 800°, 830°, 860° and 900°C; holding times were 5 min for 830°, 860° and 900 °C and 10 min for 800 °C brazing. An additional experiment with a 20 min holding time at 900 °C was set, with a cooling rate of 20 °C min^{-1} above 500 °C and then 2 °C min^{-1} to room temperature. For four-point bending test specimens, the cooling rate was only 1 °C min^{-1}, and in an additional experiment, the specimen was put under pressure, increasing from 3 MPa at 700 °C to 13 MPa below 550 °C.

2.3. Mechanical tests and micro-metallography
The joining strength of a butt joint was determined by four-point bending test, with a crosshead speed of 0.2 mm min^{-1} at room temperature.

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TABLE I Composition (wt %) of the materials

	C	Mn	Ni	Fe	Co	Cr	Ag	Cu	Ti	Zr
Inconel 600	< 0.15	> 1	> 72	6–10		14–17				
Covar	0.06	0.5	29	Bal.	17					
Ag–Cu braze							72	28		
Ag–Cu–Ti braze							71	27	2	
Ag–Cu–Ti–Zr braze							68	27	1	4
Ceramic Si_3N_4 Sintered with additives of Al_2O_3 and Y_2O_3										

The cross-sections were examined by area analyses of electron probe for micro-analysis (EPMA) and linear analysis of energy dispersion of X-rays (EDX).

3. Results and discussion

3.1. Bonding mechanism at the interface between Inconel 600 and Ag71Cu27Ti2 filler metal

Fig. 1 shows the secondary electron image (SEI) and area distribution of elements of a specimen brazed at 900 °C (holding 20 min). From Fig. 1 it is found that appreciable diffusion of silver and copper along boundaries of grains induces these elements to penetrate into Inconel to a depth of 20 μm and results in mechanical anchoring. This forms a strong bonding between Ag–Cu–Ti filler metal and Inconel base metal.

The band-pattern island, rich in nickel, in the joint (shown by the dark-grey band in the middle of Fig. 1a) is considered to be separated from the base metal by Ag–Cu liquid phase, rather than solidified from a nickel-rich liquid phase, based on the following observations.

1. The nickel-rich island has almost the same composition as that of the base metal. Fig. 2 shows the compositions analysed at two points, one in the base metal and the other in the nickel-rich island. It is apparent that in the nickel-rich island, the contents of the main constituents nickel, chromium and iron are the same as in the base metal. The small amounts of titanium and copper in the nickel-rich island are obviously obtained by diffusion from the filler metal. If the nickel-rich island had been solidified from the liquid, owing to the high solubility of copper and nickel in each other, its copper content should have been greater than has been found in Fig. 2b.

This argument could be strengthened by the linear distribution of nickel, chromium and iron shown in Fig. 3b, which shows that the linear distribution of chromium and iron follow the same trend as nickel in the nickel-rich island.

2. The nickel-rich island always forms a continuous band pattern and at some part it is still connected to the base Inconel grain, as shown in Fig. 4. It is reasonable to consider that when the brazing time is not long enough, the silver and copper liquids diffuse along the grain boundaries and forms mechanical anchoring. When the brazing time is long enough, silver and copper liquids penetrate through the grain boundaries and separate the grains from the base metal.

3.2. Effects of nickel on the metallurgical behaviour of filler metal

3.2.1. *The separation of silver- and copper-rich liquid phases from molten filler metal*

A high nickel content in Inconel enhances the separation of silver- and copper-rich liquid phases from molten filler metal.

Fig. 5 shows secondary electron images of Si_3N_4 joint-brazed to various base metals with various filler metals.

The effect of titanium on the microstructure of Ag–Cu filler metal is demonstrated by the coarse silver-rich phase (white area) and the copper-rich phase (dark-grey area) in Fig. 5b, compared with that in Fig. 5a. In Fig. 5b the larger dark-grey blocks of copper-rich phase on the left-hand side are considered to be solidified from separated liquid. This implies that titanium has the effect of separating the Ag–Cu filler metal into silver-rich and copper-rich liquid phases. This effect has been demonstrated by Chang *et al.* [7], who revealed a region of liquid immiscibility in the phase diagram for the silver–copper–titanium system shown in Fig. 6. It can be seen that the liquid separates to silver- and copper-rich liquid phases with additions of titanium even as low as 1%.

Further coarsened silver- and copper-rich phases are observed when joint brazing Si_3N_4 to Inconel 600 with a nickel content of > 72% (shown in Fig. 5c) compared with Covar with a nickel content of 29% (shown in Fig. 5b). In Fig. 5c the large silver- and copper-rich grains (see Fig. 8) are apparently solidified independently from the corresponding separated liquids. This phenomenon indicates the effect of nickel on the separation of Ag–Cu filler metal. The seriousness of the immiscibility of silver- and nickel-rich liquid phases in the binary diagram of the Ag–Ni system (Fig. 7) has been reported [8]. The immiscibility of nickel and silver possibly causes further separation of silver- and copper-rich liquid phases in Ag–Cu–Ti filler metal, because in copper-rich phase, an appreciable amount of nickel always exists, which diffuses from the base metal.

3.2.2. *The diffusion of silver and copper along grain boundaries of the base metal*

Fig. 8 shows the area distribution of silver and copper in the joint of Si_3N_4 to Inconel 600 shown in Fig. 5c. The white phases distributed at grain boundaries on the left-hand side of Fig. 5c are revealed to be silver- and copper-rich phases.

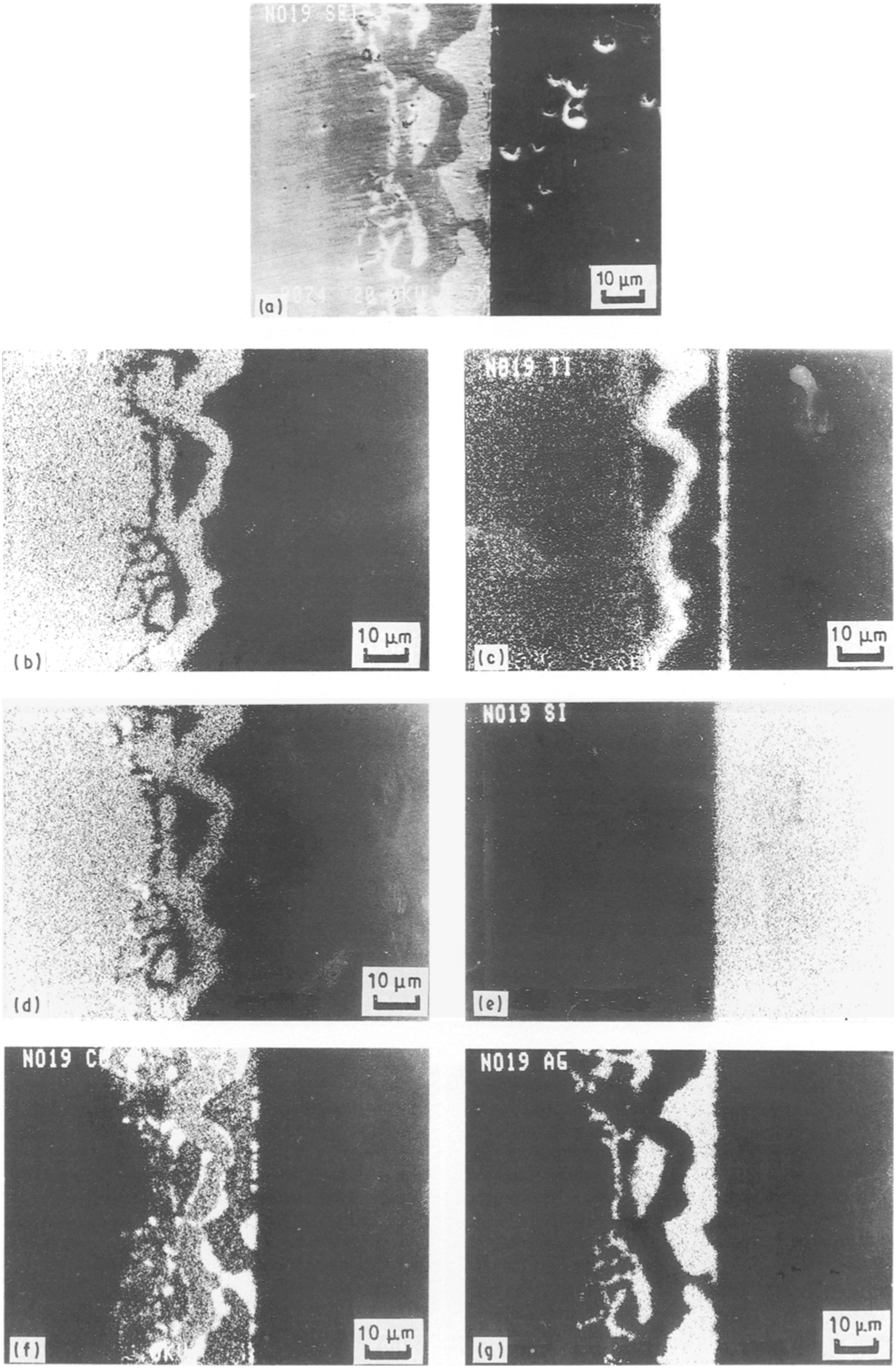


Figure 1 Secondary electron image (SEI) and area elemental distribution of a joint brazing Inconel 600 to Si_3N_4 with Ag71Cu27Ti2 filler metal at 900 °C (holding time 20 min) (a) SEI, (b) Ni, (c) Ti, (d) Cr, (e) Si, (f) Cu, (g) Ag.

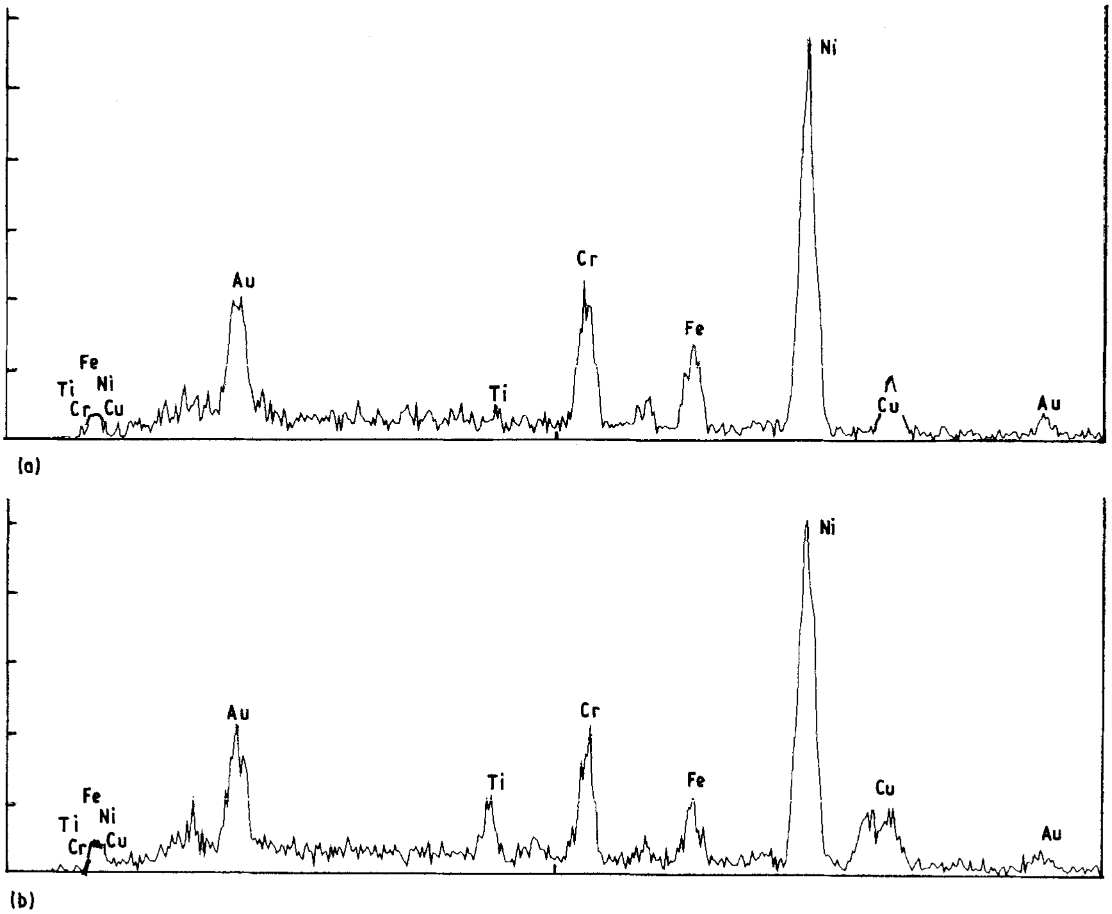


Figure 2 Compositions analysed at points (a) in base metal, and (b) in the nickel-rich island in the joint (same specimen as in Fig. 1).

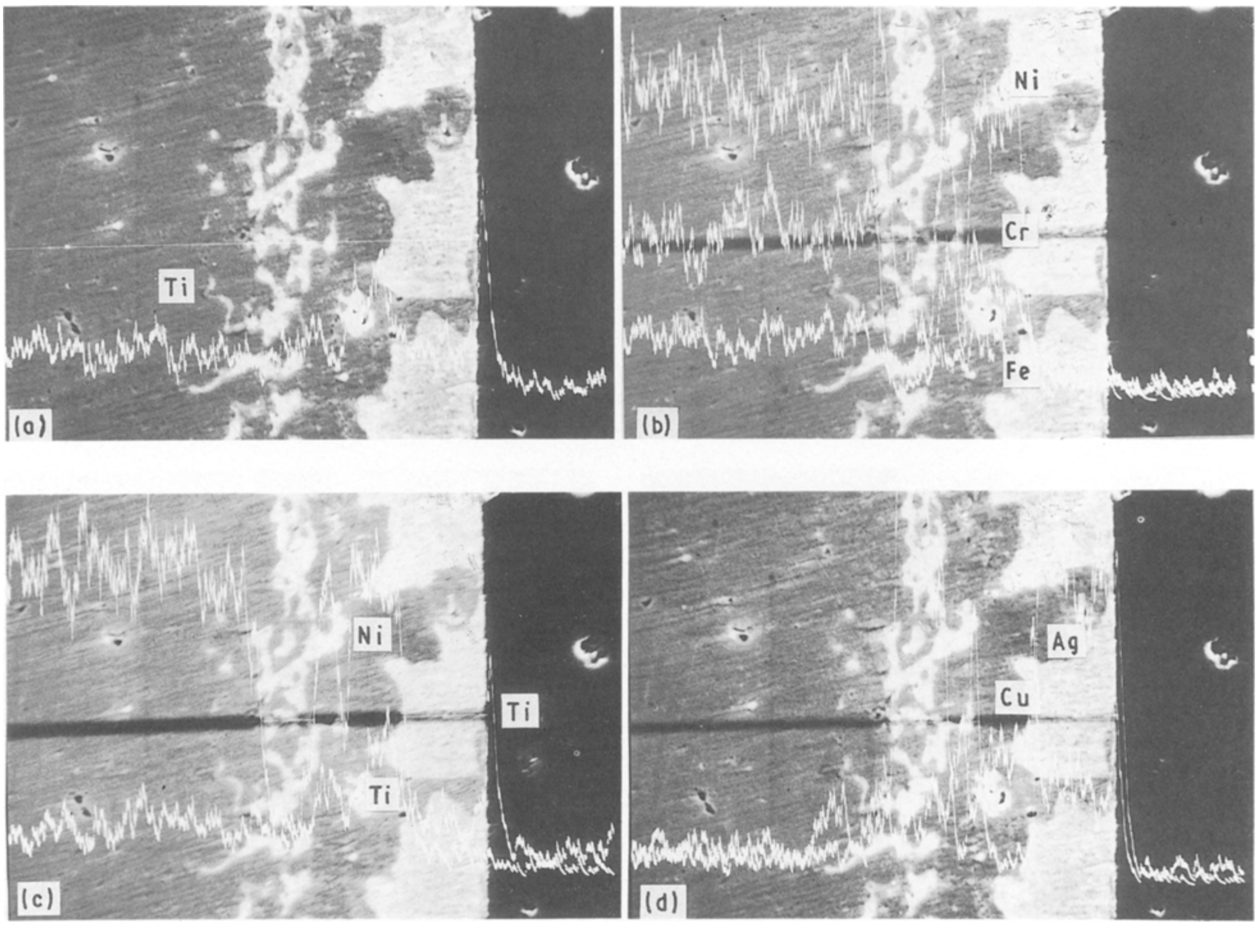


Figure 3 Linear distribution of elements in the brazing joint (same specimen as in Fig. 1) (a) Ti, (b) Ni, Cr, and Fe, (c) Ni and Ti, (d) Ag and Cu, X1500.

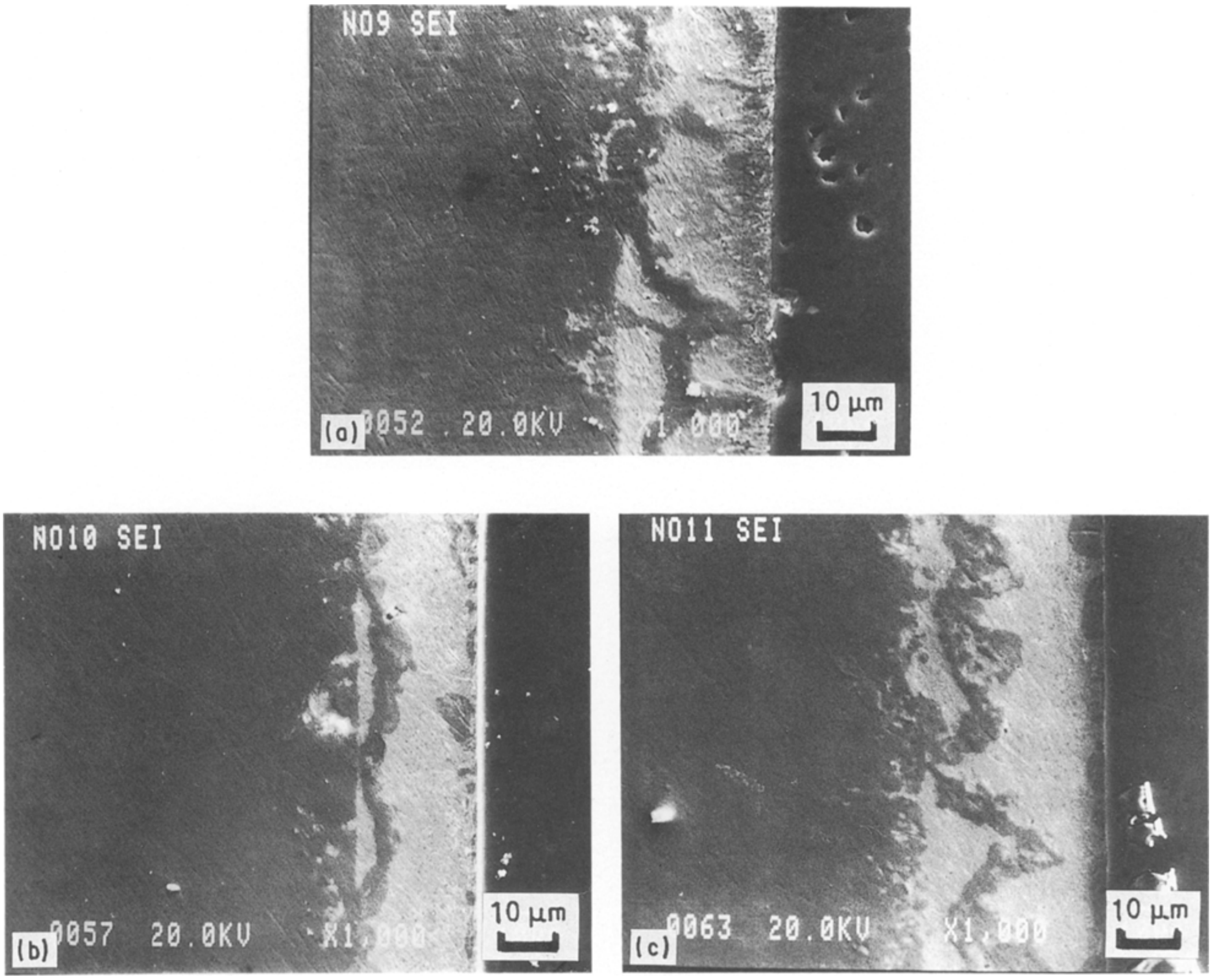


Figure 4 The patterns of the separated nickel-rich island in the brazing joint (grey area: mainly of nickel-rich phase). (a) Brazed at 860 °C, (b) brazed at 830 °C, (c) brazed at 800 °C.

As shown in Figs 5c and 8, copper and silver could penetrate through the grain boundaries into the Inconel 600 base metal to a depth of 30 μm. However, in Fig. 5b, which shows the joint-brazed Covar and Si_3N_4 with the same filler metal, no trace of diffusing silver- or copper-rich phase could be found in the base metal and no base metal band was separated by these phases. Comparing the different behaviour of the diffusion of silver and copper in these two joints, brazing alloys with different nickel contents, and taking into account the affinity of nickel for copper, it is reasonable to attribute the intensive diffusion of silver and copper into Inconel 600 to its high nickel content. The appropriate diffusion of silver and copper could strengthen the bonding between filler metal and base metal, but excessive diffusion of these low melting-point elements may deteriorate the high-temperature resistance of the matrix. By decreasing the brazing temperature to 800–830 °C the depth of diffusion of silver and copper could be reduced to only 10 μm as shown in Fig. 4c.

3.2.3. Consumption of titanium in filler metal and decrease of its activity in the reaction with Si_3N_4

Fig. 1c shows that titanium segregates in the nickel-rich island, especially at its front, and at the interface between filler metal and ceramic. In the massive filler metal, in phases rich in silver or copper, the titanium content is very low. Taking into account the small titanium content in the filler metal, and that a large part of it has been consumed by the nickel-rich island, the remaining titanium at the interface between filler metal and ceramic is less than 1% of the filler metal. The reaction between titanium and Si_3N_4, therefore, must weaken the strength between filler metal and ceramic. One specimen brazed at 800 °C fractured at that interface in the four-point bending test. For this specimen, the titanium peak in linear analysis at the interface of the ceramics is much lower than that at the front side of the nickel-rich island, as shown in Fig. 9. However, in the case of brazing at 900 °C as shown in Fig. 3a, the titanium peak in linear analysis at the interface between the ceramic and the filler metal is still higher than that at the front of the nickel-rich island, although the total amount of titanium is higher in the latter. This indicates that high-temperature brazing could improve the reaction of titanium with Si_3N_4, even with a high nickel content in the base metal.

3.2.4. The overflow of copper-rich liquid phase of filler metal over the metal surface

Because nickel enhances the separation of silver- and

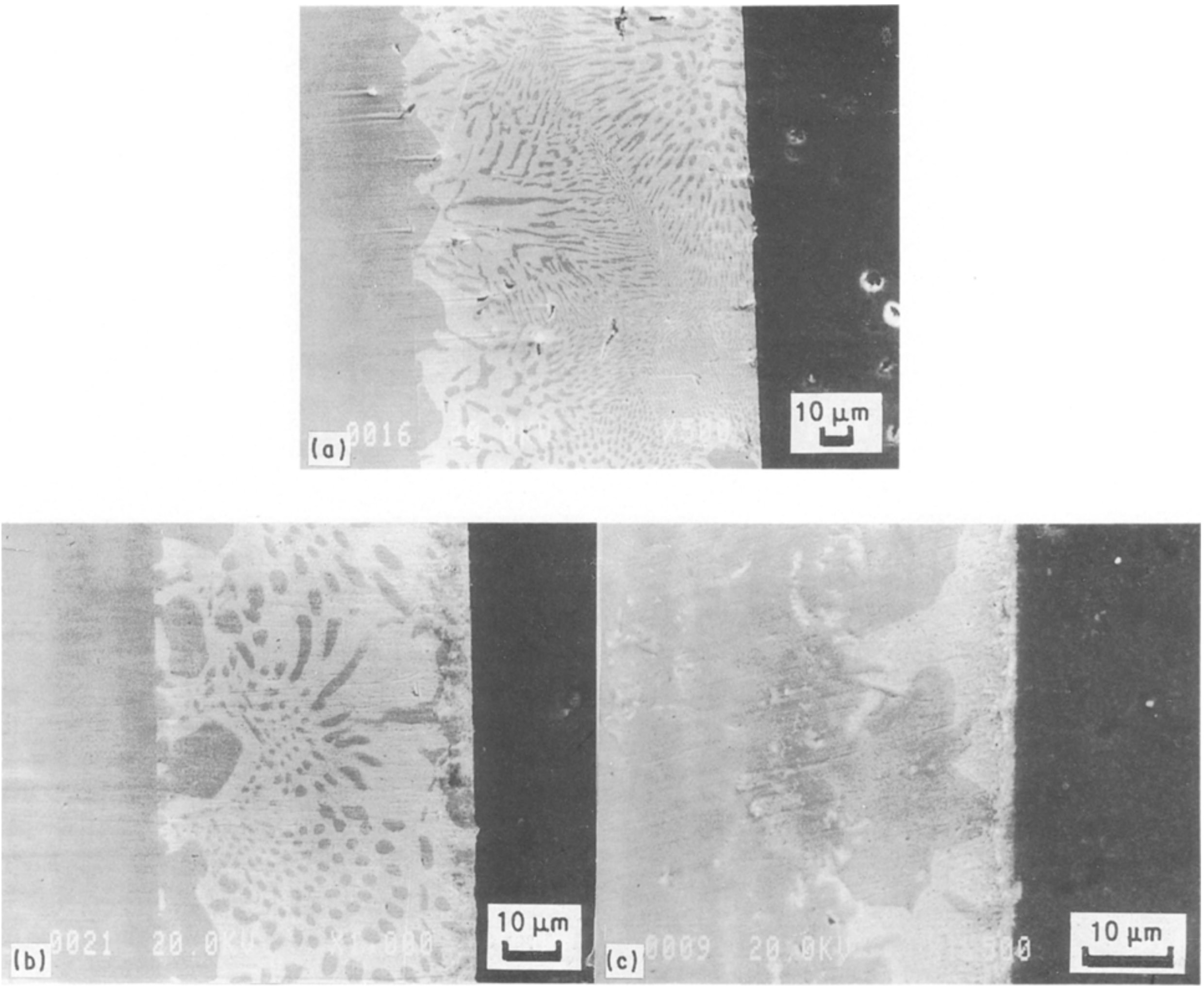


Figure 5 Secondary electron image of a joint brazed with similar parameters: (a) Si_3N_4–Covar with Ag72Cu28 filler metal; (b) Si_3N_4–Covar with Ag71Cu27Ti2 filler metal; (c) Si_3N_4–Inconel with Ag71Cu27Ti2 filler metal.

copper-rich liquid and the high affinity of copper for nickel facilities wetting by the copper-rich liquid of the nickel-base alloy, the overflow occurred when the heating rate was higher. In the case of a fixed distance between the two pieces to be brazed, the remaining liquid filler metal was insufficient to form an integrated joint. This phenomenon has been revealed previously [9].

3.3. Effect of zirconium on the metallurgical behaviour of titanium-activated Ag–Cu brazing filler metal

Zirconium has a similar affinity for nickel as titanium, yet lower affinity for nickel. Therefore, zirconium was considered to be a possible substitute for titanium to decrease the reaction on the Inconel 600 side yet maintaining that on the ceramic side. In the present work, 1% Ti was substituted by 4% Zr additive in the filler metal.

Fig. 10 shows the secondary electron image and the area elemental distribution of joint-brazed Si_3N_4 and Inconel 600 with filler metal Ag68Cu27Ti1Zr4. From Fig. 10 the following points can be made.

Both zirconium and titanium segregate at both interfaces between filler metal and base metal and filler metal and ceramics. Yet apparently titanium has a stronger tendency to segregate than zirconium at both interfaces. Quite the opposite to titanium, also at the interface, zirconium is distributed in the massive copper-rich phase.

Zirconium effectively alleviates the separation of silver- and copper-rich liquids in the filler metal and makes its microstructure more uniform.

Zirconium has the tendency to depress the diffusion of copper- and silver-rich liquids into Inconel 600 grain boundaries. Because there is a band (left-hand side of Fig. 10a) rich in nickel, titanium and zirconium, it is considered to be a layer of metallic compound, which possibly renders silver and copper diffusion more difficult.

Zirconium increases the brittleness of the interface between the filler metal and ceramic and causes cracking to occur in it (shown in Fig. 10a).

3.4. Effects of brazing parameters

In the region of the brazing temperatures used in present work, 900 °C gives the highest titanium segregation peak at the Si_3N_4–filler metal interface, and the widest region of diffusion of silver and copper into Inconel 600. The difference in the effects of various brazing temperatures and holding times on the

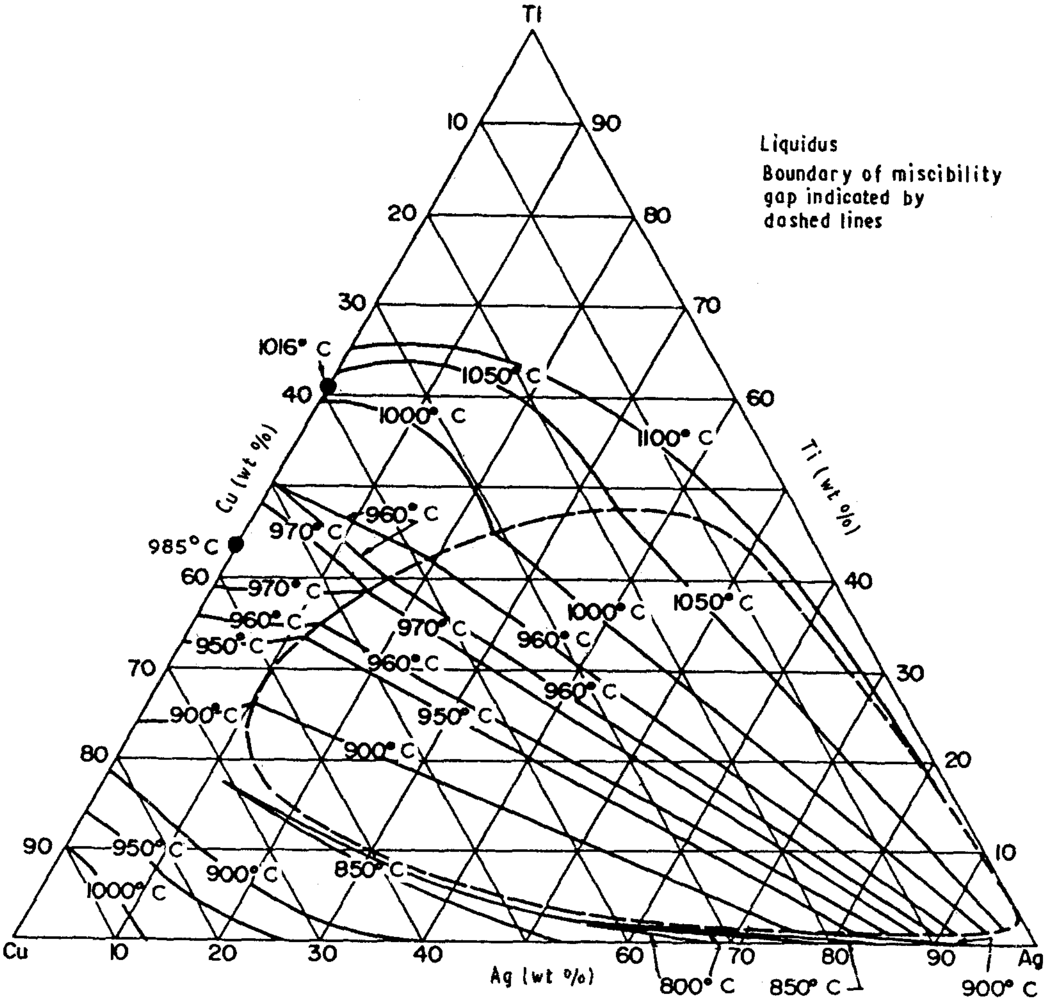


Figure 6 Phase diagram for the Ag–Cu–Ti system at various temperatures, showing the region of liquid immiscibility [7].

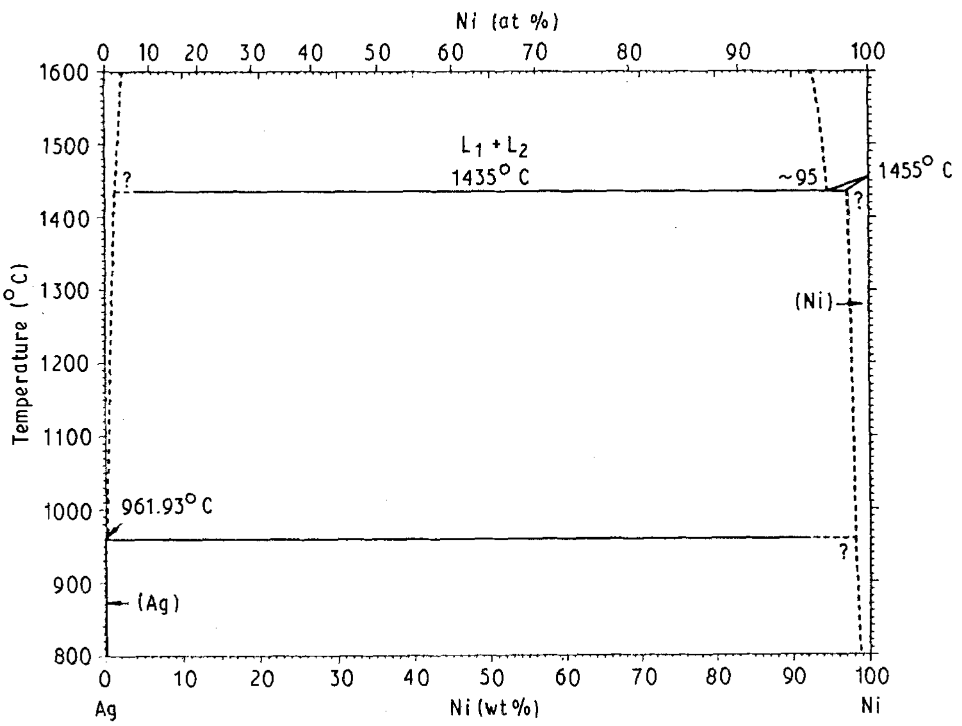
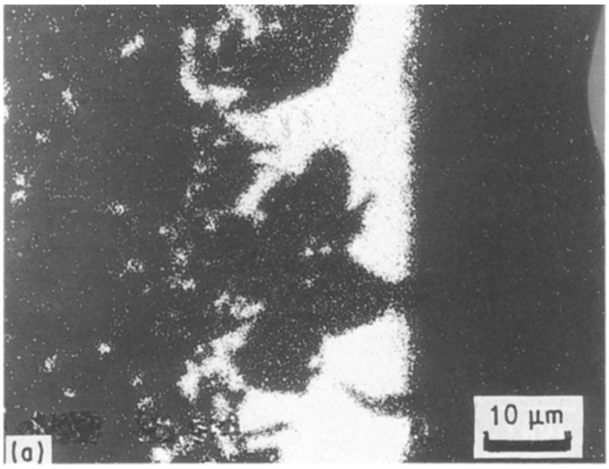


Figure 7 The phase diagram for the silver–nickel system showing the region of liquid immiscibility [8].

separation of silver- and copper-rich liquid phases is not appreciable (cf. Figs 1a and 4c). In all brazing regimes, the separation of liquids is serious.

Higher brazing temperatures and longer holding times could increase the thickness of the titanium segregation layer at the front of the nickel-rich island, yet the gradient of titanium concentration decreases and becomes more uniform in the nickel-rich island.



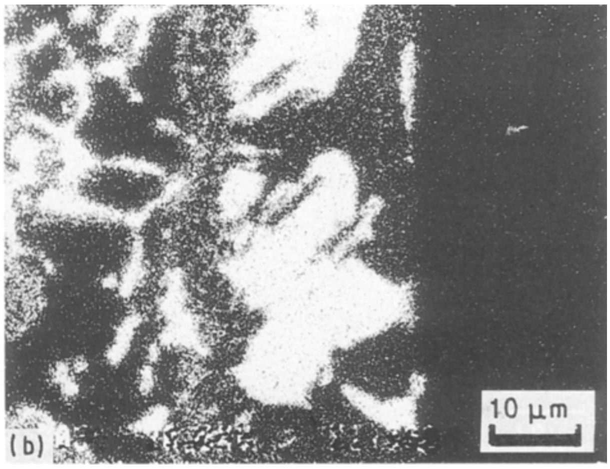


Figure 8 Area distribution of (a) silver and (b) copper in the joint shown in Fig. 5c.

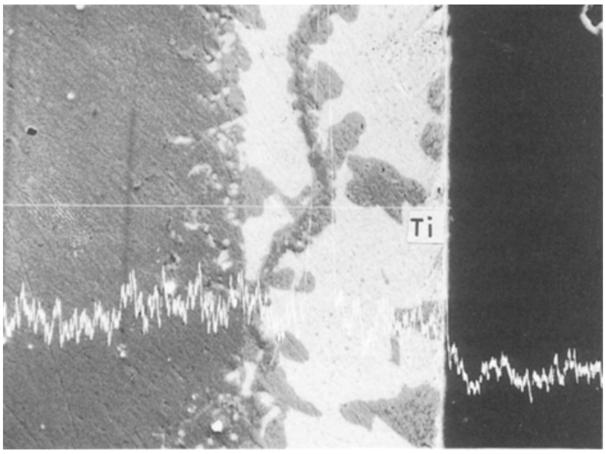


Figure 9 Linear distribution of titanium in the joint brazing Si_3N_4 to Inconel 600 at 800 °C, X1000.

If the heating rate is controlled at less than 15 °C min^{-1} and the titanium content in the filler metal is not too high, the overflow of filler metal could be prevented.

Because high brazing temperature causes a high residual stress and a wide diffusion zone of silver and copper, but low brazing temperature causes insufficient reaction at the ceramic interface, the optimum brazing temperature was selected as 830 °C. This is the lowest temperature at which all specimens fractured in the ceramic without problems occurring at the interface.

3.5. Residual stress causing cracking in ceramics

In order to prevent the joint from cracking, the cooling rate was decreased to only 1 °C min^{-1} from the brazing temperature to room temperature. One specimen used for the bending test was subjected to increasing pressure from 3 MPa at 750 °C to 13 MPa below 550 °C. However, owing to the great difference in the thermal expansion coefficient between Inconel 600 (around 13×10^{-6} °C^{-1}) and Si_3N_4 (around 3×10^{-6} °C^{-1}), in all brazed specimens cracking occurred before or after cutting the bending test specimens. In six bending specimens, where the crack had not extended inwards, the bending strengths measured were from 143–210 MPa. The average value was 174 MPa. Most specimens were cracked in the ceramic. Only one specimen, brazed at 800 °C, cracked at the interface between the filler metal and the ceramic in the four-point bending test.

From the metallurgical viewpoint, a sound joint, brazing Si_3N_4 to Inconel 600, could be obtained with appropriate brazing parameters (for example, brazing at 830 °C, holding time 10 min, heating rate 10 °C min^{-1}, cooling rate 5 °C min^{-1}). The bending strength could reach 200 MPa, but a special method has to be developed to prevent cracking occurring in the ceramic due to the residual stress.

4. Conclusions

From investigation of the metallurgical behaviour during brazing of nickel-based alloy Inconel 600 and Si_3N_4 with Ag71Cu27Ti2 filler metal, with emphasis on the interface between the filler metal and the Inconel 600 base metal and the effects of nickel, the conclusions could be drawn.

1. A sound metallurgical structured joint could be obtained with appropriate brazing parameters. The mechanism of bonding at the interface between the Inconel 600 and the filler metal is the diffusion of silver- and copper-rich liquid phases into the base metal along its grain boundaries, which results in a strong mechanical anchorage. In most cases, part of the grains of the base metal are separated from the matrix into the filler metal in the pattern of a nickel-rich band or island.

2. The effects of nickel in Inconel 600 on the metallurgical behaviour were found to be:

(a) an enhancement of the separation of silver- and copper-rich liquid phases in molten filler metal causing a coarse microstructure;

(b) promotion of the diffusion of silver and copper into Inconel 600 along its grain boundaries, and producing effects on the bonding between filler metal and base metal;

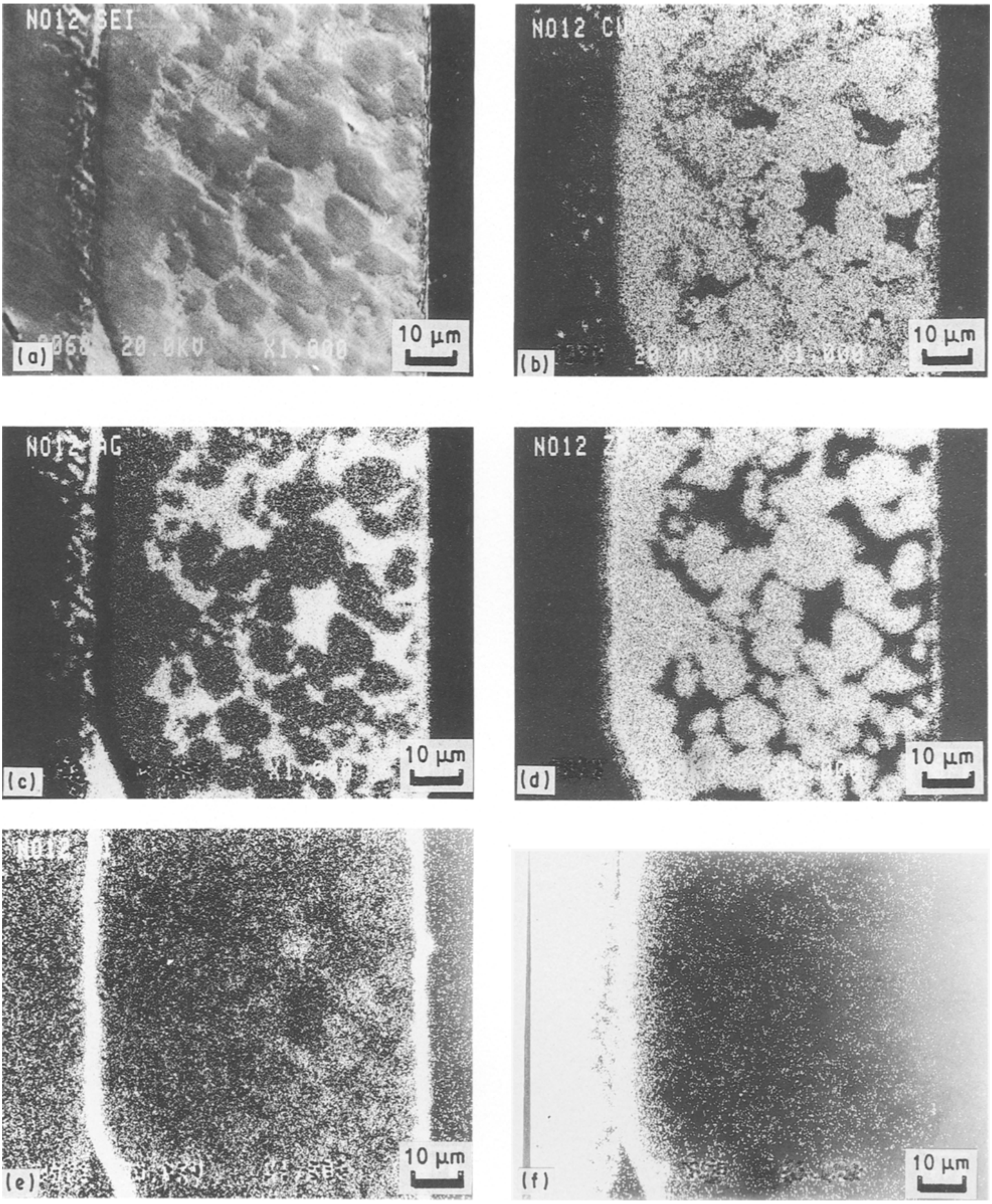


Figure 10 Secondary electron image and area distribution of elements in a joint brazing Si_3N_4 to Inconel 600 with Ag68Cu27Ti1Zr4 filler metal: (a) SEI, (b) Cu, (c) Ag, (d) Zr, (e) Ti, (f) Ni.

(c) combination of titanium and a decrease in its activity in the reaction with Si_3N_4 and producing effects on the bonding between filler metal and ceramic;

(d) facilitating the overflow of the liquid filler metal over the surface of the Inconel.

3. Zirconium could alleviate the separation of silver- and copper-rich liquid in the filler metal and make its microstructure finer. However, zirconium weakens the interface of the ceramic and causes cracking to occur at it.

4. In the region from 800–900 °C the difference in brazing temperature does not have any remarkable effect on the microstructure of the joint. Taking into account the decrease in residual stress in the ceramics, the brazing temperature is selected as 830 °C.

5. The residual stress-induced crack in the ceramics, produced by directly brazing the Inconel 600

to Si_3N_4 with filler metal Ag71Cu27Ti2 with a thickness less than 100 μm, remains to be solved.

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