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Rapidly solidified low-silver brazing filler alloy foils

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A rapidly solidified (RS) low-silver brazing alloy with 50% saving in silver has been developed as a potential substitute for the conventional Ag 72% – Cu 28% eutectic alloy. Major applications are envisioned in the electronics and vacuum tube industries. The RS alloy possesses brazing characteristics better than its conventionally cast counterpart, and superior to the traditional silver–copper eutectic alloy.

1. Introduction

Rapid solidification processing (RSP) involves high cooling rates [1]. This can produce several phenomena, such as extension of primary solid solubility, bulk micro-crystallinity, new metastable phases or amorphous phases [2, 3]. Rapidly solidified (RS) materials, in the form of ribbons can offer superior chemical and microstructural homogeneity during direct use in joining. The literature shows [4] that a more uniform joint microstructure, free of voids and macroscopic segregation, can be produced in this case.

Additionally, rapid solidification can induce improved ductility in foils of filler metal systems. These foils may be used as preforms and can eliminate the need for large joint clearances to achieve complete filling of the brazed cross-section, thus providing stronger brazements. The absence of contaminating organic solvents eliminates soot formation and furnace fouling, apart from affecting the joint properties. The low level of gaseous impurities in the RS foil is another attractive feature for vacuum furnace brazing of critical aircraft engine parts [5].

Many of the standard compositions of nickel-base brazing filler metals (conforming to AWS BNi classification) used for high-temperature brazing, have been cast into wide strips with full or partial amorphous structure obtained by the RS technique [6, 7]. The RS foil here is sufficiently ductile to cope with complex joint geometries and can be cut or stamped to an exact joint shape. Silver brazing alloys (BAg AWS classification) are also widely used for low-temperature brazing of ferrous and non-ferrous metals. These alloys are inherently ductile and, therefore, available in a variety of shapes and forms. Nonetheless, RSP [4] allows the production of foils free of oxide scales (generally formed during hot rolling) and the organic contaminants (inherited from the lubricant of the rolling mill).

Copper-base brazing filler alloys such as BCuP-1, BCuP-2 and BCuP-5 (of the AWS) in RS microcrystalline form, are reported in the literature to be sufficiently ductile for serving as filler metals in electrical contact brazing [4].

In view of the rapid growth of the electrical and electronics industries today, there is an increased demand for developing brazing filler alloys, more particularly of the reduced-silver types for cost-effectiveness. Such an alloy has been developed recently by the authors at the National Metallurgical Laboratory (NML) [8, 9]. This has been promoted as a substitute for the conventional 72% Ag–28% Cu eutectic alloy which is widely used in the electronic and vacuum tube industries [10–13]. The present work has been aimed at investigating the brazing performance of the new NML alloy in the rapidly solidified form.

2. Experimental procedure

2.1. Materials and conventional melting

Silver, copper and tin of 99.99% purity were used to prepare the alloys. The initial melting was done in an electric pot-type furnace using a graphite crucible and the alloys were conventionally cast. The compositions of the new NML alloy, and those used for comparison, are given in Table I.

2.2. Ribbon casting

Rapidly solidified foils of the low-silver alloy were made in a commercial melt-spinner (Marco-Materials, USA). Here, induction melting of a rod of the given alloy was carried out in a quartz crucible with a circular nozzle at the bottom. The molten mass was

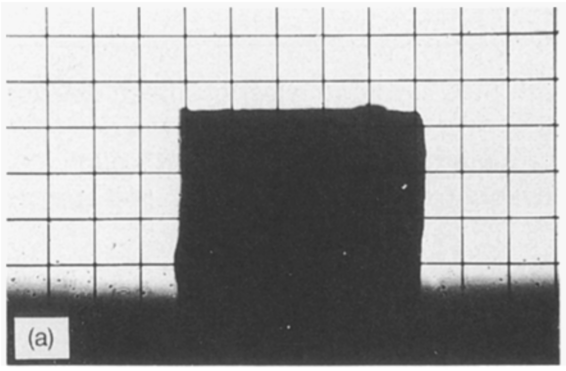
TABLE I Chemical composition of the alloys (wt %)

Alloy designation	Alloy description	Ag	Si	Sn	Cu
AR	Low-silver alloy (RSP)	36.30	3.00	0.10	Bal.
AC	Low-silver alloy (conventionally cast)				
EC	Ag–Cu eutectic alloy (conventionally cast)	72.00	–	–	28

then ejected by argon gas pressure and allowed to impinge on a rotating copper wheel. A cooling rate of the order of 10^6 °C s^{-1} was obtained for the operational conditions used.

2.3. Differential thermal analysis (DTA)

Solidus and liquidus temperatures of the alloy were determined with a DTA (Netz-type) using a heating rate of 10 °C min^{-1} in an inert atmosphere.



2.4. Wettability test

The brazing alloy test samples of size 3 mm × 3 mm × 3 mm, and the base plates (copper, nickel) of size 24 mm × 12 mm × 1 mm, used for this test, were polished and degreased. The test sample was placed at the centre of the polished surface of the base metal platelet (Fig. 1). A thermocouple was placed below the base plate and the assembly was inserted into a tube furnace. A Leitz microscope, attached to the tube furnace, was used to monitor the softening process *in situ* under an argon atmosphere.

Direct photographs of different softening stages of the test sample were taken. Finally, a photograph of the contact angle of the alloy on the base metal at the brazing temperature (50 °C above liquidus) [14] was taken and the angle, θ, as well as the wetted area, A, measured (Fig. 1). On this basis, the wetting index (WI = $A \cos\theta$) was evaluated.

2.5. Brazing technique

The torch brazing technique was employed for joining copper-to-copper and nickel-to-nickel strips with the

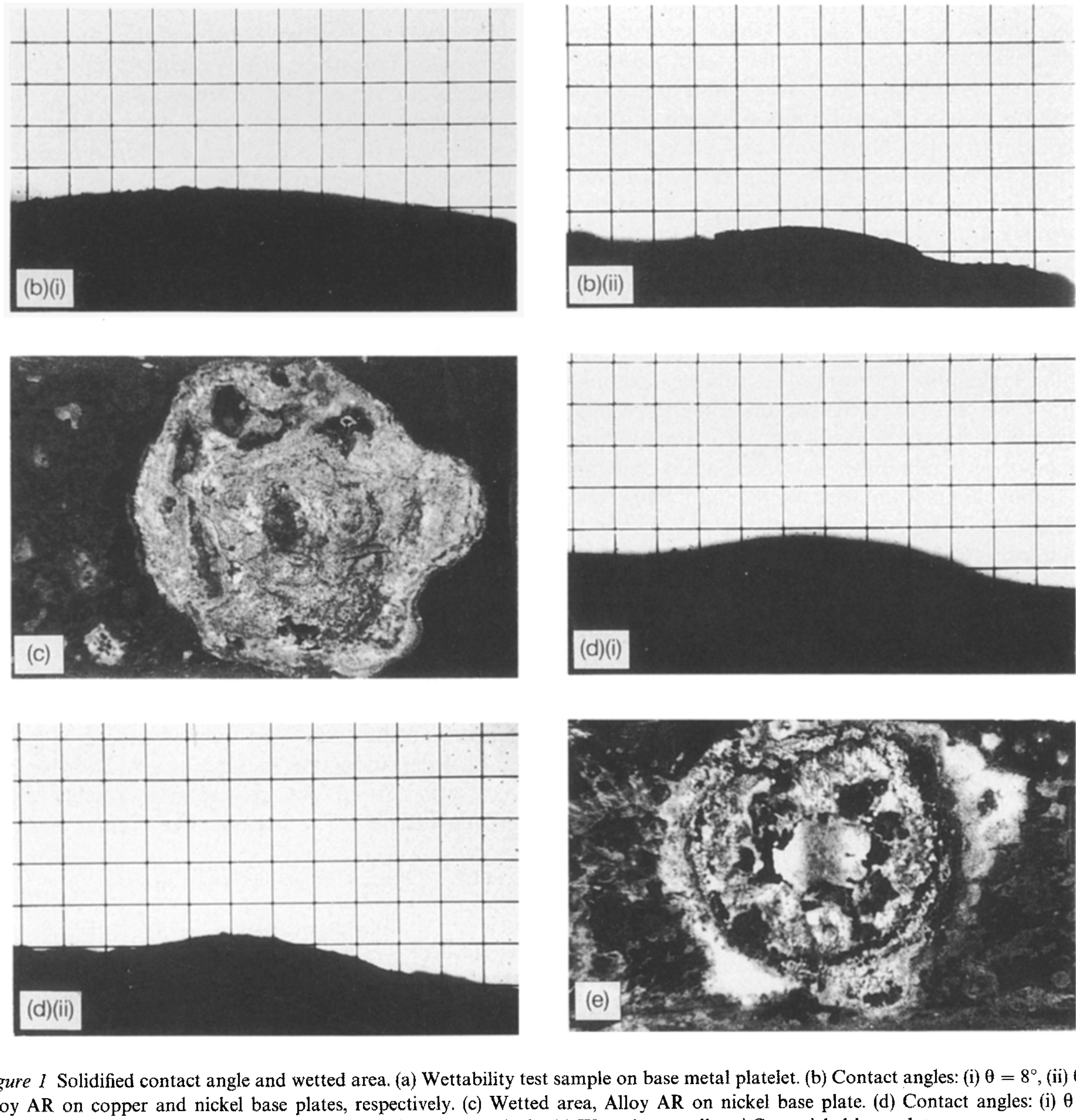


Figure 1 Solidified contact angle and wetted area. (a) Wettability test sample on base metal platelet. (b) Contact angles: (i) θ = 8°, (ii) θ = 7°, alloy AR on copper and nickel base plates, respectively. (c) Wetted area, Alloy AR on nickel base plate. (d) Contact angles: (i) θ = 12°, (ii) θ = 10°, alloy AC on copper and nickel base plates, respectively. (e) Wetted area, alloy AC on nickel base plate.

RS filler alloy ribbon samples. Parts to be brazed, with brazing foil placed in between, were held together by appropriate fixturing. Filler alloy foils of 50 μm thick were placed at the joint to provide an adequate supply of filler metal during brazing. An oxyacetylene torch was used for brazing. Acetylene flow was adjusted to make the flow slightly reducing until the filler metal began to melt and flow. Following the brazing, oxides, residues, etc. (if any), were removed from the brazed joint by wire brushing and then washing with running water.

2.6. Evaluation of the mechanical properties of the brazed joint

The mechanical properties of the brazed joint, such as tensile, impact and shear strengths of copper-to-copper and nickel-to-nickel joint samples with RS filler foils, were determined. For the tensile strength, an Instron tensile testing machine was employed making use of butt-joint specimens (Fig. 2a). The impact and shear strengths of the butt/lap joint specimens (Fig. 2b and c) were also determined. For the shear test, the specimen was placed in a device providing a strong lateral support (Fig. 3) and compressive load was applied through tungsten carbide pushers.

2.7. Structural characterization

Optical, X-ray diffraction (XRD) and SEM studies were performed on RSP foils and copper-to-copper and nickel-to-nickel brazed joint samples with the alloy AR. For XRD, the radiation used was CrK_α.

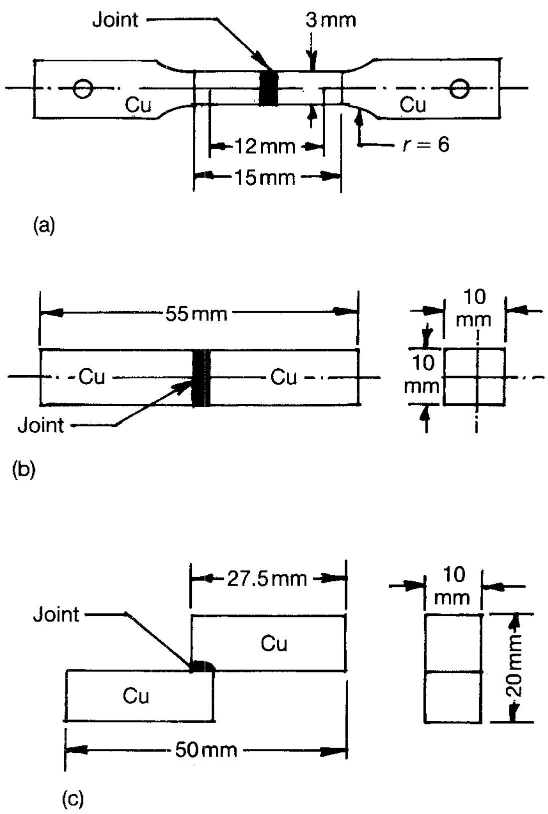


Figure 2 Test pieces for brazed joint mechanical properties. (a) Tensile, (b) impact, and (c) shear test pieces.

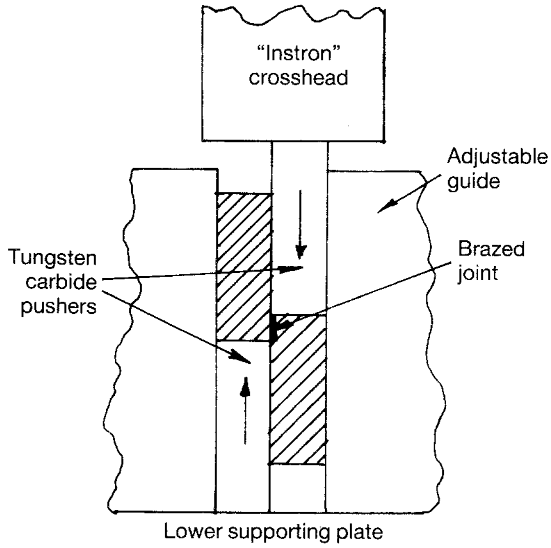


Figure 3 Schematic arrangement of shear test.

3. Results and discussion

It may be observed that the NML alloy (AR/AC) has nearly the same composition in the conventionally cast (AC) and under the RS conditions (AR). Because the latter was conducted in an argon atmosphere, there was no difficulty in maintaining the composition. The solidus and liquidus temperatures of the low-silver alloy are 765 and 785 °C, respectively, for AR and for AC conditions. These data match very well with those by Yoshida and Morikawa [15].

Table II shows the wetting properties for the alloys AR, AC and EC on copper and nickel bases. The contact angle in the case of the RSP foils (alloy AR) is only around 7°–8° and is lower than for both AC and EC alloys. The general wetting index (WI) for AR is superior to both AC and EC alloys (Table II). The improvement in wettability performance is indeed more pronounced for nickel-to-nickel joints. The presence of silicon in the low-silver alloy might be responsible for better properties than the alloy EC, as reported elsewhere [8, 9]. For the RSP alloy AR, the improvement is also believed to be due to better microstructural and chemical homogeneity.

The mechanical properties, such as tensile, impact and shear strengths of the brazed joints (Table III) for the AR alloy are observed to be superior to those for AC as well as EC alloys.

The microstructures of alloys AR and AC (Fig. 4a and b) reveal that grain size is extremely fine (0.5 μm) in the case of the RSP alloy ribbon. The conventionally cast alloy (AC) shows a slightly coarser (3 μm) grain size.

The X-ray data for the AC alloy are given in Fig. 5a. It would appear that apart from pure copper and pure silver lines, there are other lines corresponding to Cu_4Si/Cu_5Si complex phases. The X-ray data for the rapidly solidified (AR) alloy are given in Fig. 5b. Some important differences with the AC alloy should be noted. The intensity of lines exclusively corresponding to the intermetallics (more specifically Cu_4Si) has been appreciably reduced (in fact, of the two exclusive lines for Cu_4Si, only one is present at a reduced level). This

TABLE II Wettability test results

Alloy	Base metal used	Brazing temp. (°C)	Protective medium	Contact angle, θ (deg)	Wetted area, A [in^2 (mm^2)]	Wetting index[a] (WI = A cosθ)
AR	Copper	830	Argon	8	0.240(155)	0.24
	Nickel	830	Argon	7	0.270(174)	0.27
AC	Copper	830	Argon	12	0.225(145)	0.22
	Nickel	830	Argon	10	0.255(164)	0.25
EC	Copper	830	Argon	11	0.200(130)	0.20
	Nickel	830	Argon	10	0.230(148)	0.23

[a] WI = 0.2 or above, shows satisfactory wettability.

TABLE III Mechanical properties of brazed joints (a) copper-to-copper and (b) nickel-to-nickel

Alloy	Tensile strength (kg mm^{-2})	Impact strength		Shear strength (kg mm^{-2})
		(kg m)	(ft lb)	
AR (a)	19.40	1.54	11	12.50
(b)	20.25	1.50	10.75	13.00
AC (a)	17.00	1.40	10	10.00
(b)	18.76	1.33	9.5	11.75
EC (a)	15.76	1.30	9.3	9.75
(b)	16.00	1.33	9.5	10.00

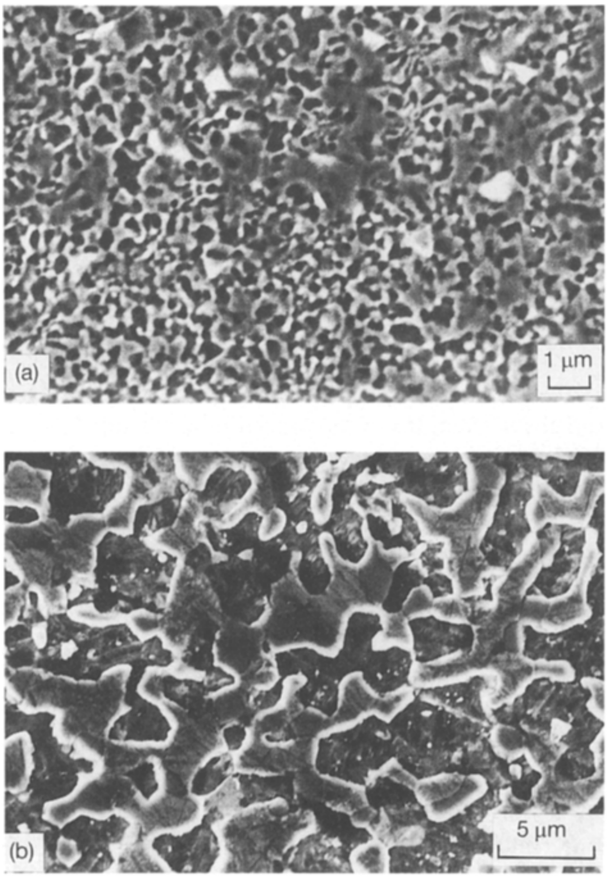


Figure 4 Scanning electron micrographs (a) for alloy AR, and (b) for alloy AC. The primary phase (initially equiaxed) is much finer the AR alloy.

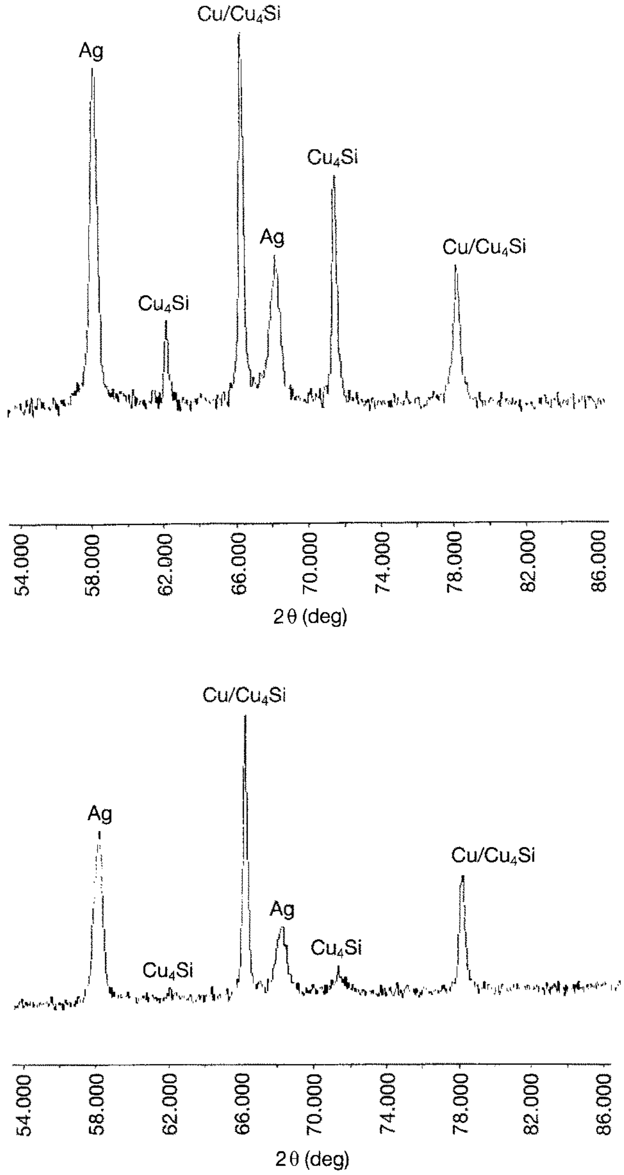


Figure 5 X-ray data of (a) alloy AC, and (b) alloy AR.

indicates that the amount of complex phases in the rapidly solidified material has definitely been reduced. This is indeed expected, because the extent of solid solubility in the rapidly solidified material has been increased. Another point may be noted regarding the nature of the intermetallics. While Yoshida and Morikawa [15] have identified these phases as Cu_7Si, in the present case the presence of Cu_4Si (in the air-cooled condition) in AC is strongly established.

Figs 6 and 7 represent the SEM characteristics of the alloy in AC and AR conditions. A point to be noted is the absence of the eutectic-like features entirely in the AR condition. This has been confirmed in many other samples, although only a few are reported here. The X-ray profile for copper (collected through energy dispersive analysis of X-rays) is also superimposed on the microstructure in each case. Broadly, the white areas and dark areas correspond to silver- and copper-rich regions, respectively.

The microstructures of nickel-to-nickel brazed joints with alloy AR and AC are shown in Fig. 8a and b. The micrographs show two distinct diffusion layers. A silver- and copper-rich layer is noticed close to the nickel base metal and adjacent to this layer, another layer, rich in nickel and silicon, exists. The nickel- and silicon-rich layer is also known to contain some copper. The formation of two diffusion layers is also reported by other investigators [15]. This is possibly due to the dissolution of nickel base metal first in the brazing alloy and, as the silicon in the filler alloy has greater affinity for nickel (than copper), the dissolved nickel forms a nickel–silicon compound. Because the resultant nickel–silicon compound has a higher melting point than the brazing temperature (830 °C), it resolidifies and is isolated from the base metal. Consequently, a copper- and silver-rich layer exists adjacent to nickel base metal, and a nickel- and silicon-rich layer is located close to this layer. Apart from this, the micrographs also reveal that the distribution of the dark phase (Cu_4Si/Cu_5Si) is more uniform in the brazed joint with alloy AR than in the alloy AC. This is again a result anticipated in the RSP alloy, because the rapid solidification induces higher chemical homogeneity and also induces greater diffusion due to a higher concentration of vacancies and very fine grain size.

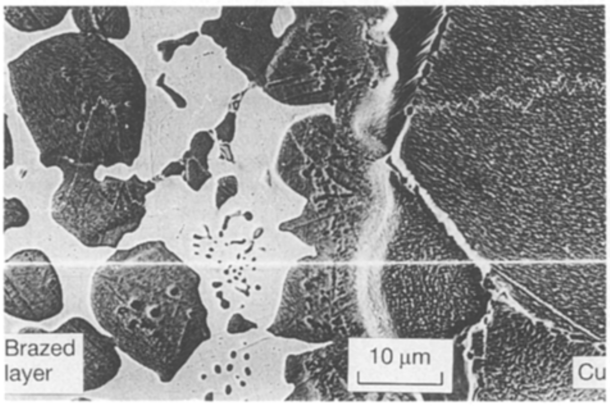


Figure 6 Scanning electron micrograph of a brazed joint copper-to-copper with alloy AC showing silver-rich and copper-rich areas. Superimposed is the X-ray profile (EDAX) for copper.

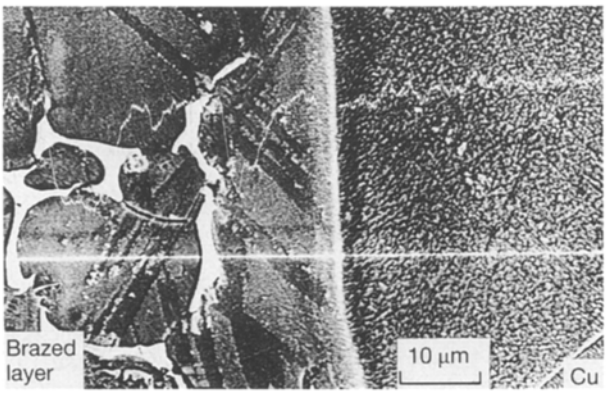


Figure 7 Scanning electron micrograph of a brazed joint copper-to-copper with alloy AR revealing silver and copper regions. Superimposed is the X-ray profile (EDAX) for copper.

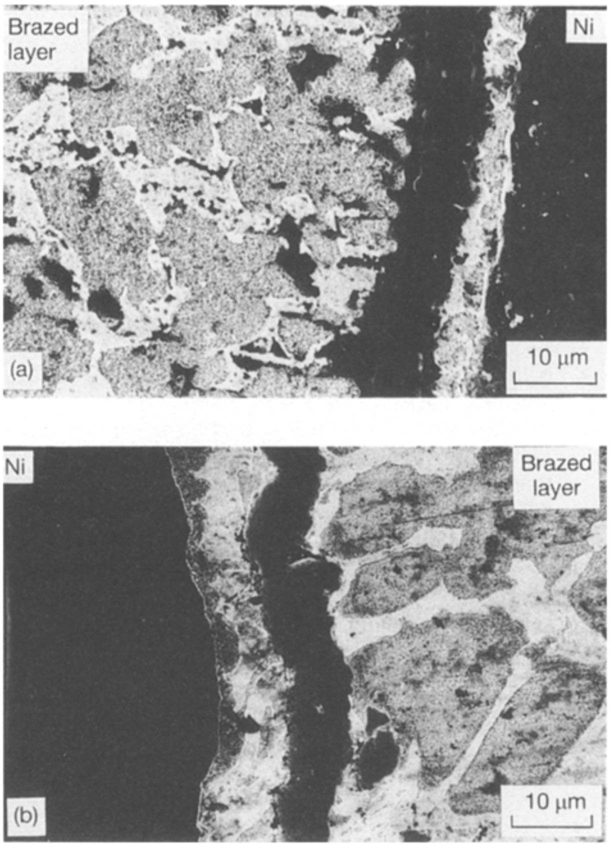


Figure 8 Scanning electron micrographs of brazed joints nickel-to-nickel with (a) alloy AR, (b) alloy AC, showing two distinct diffusion layers (a silver- and copper-rich layer close to the nickel base metal and, adjacent to this, a nickel- and silicon-rich layer).

4. Conclusion
Rapidly solidified low-silver brazing alloy shows superior wettability on copper and nickel. Mechanical properties of the brazed copper-to-copper and nickel-to-nickel joints also reveal superiority for the RSP brazing alloy than when conventionally processed at the same composition.

The alloy following RSP shows much better microstructural homogeneity in comparison to its conventionally cast counterpart. This results in uniform melting and flow in the joint areas during brazing. The brazed joints are free from voids and segregation.

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