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A copper-base brazing alloy for electronics industries

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A copper-based alloy with suitable additives has been developed. Major applications are envisioned in the electronics and vacuum-tube industries. The developed alloy with only half the quantity of silver is less expensive than the standard Ag–Cu eutectic alloy and possesses comparable brazing characteristics.

1. Introduction

Brazing is a process for joining materials through the use of heat and filler metal. It involves the use of a non-ferrous filler alloy with liquidus temperature exceeding 450 °C but lower than that of the metal components to be joined [1].

The bulk of the brazing alloys which are widely used in electronics industries are based on nickel-, copper- and silver-based alloys.

Silver brazing alloys of the AWS BAg classification are best suited as filler metals for joining iron-, copper-, nickel- and silver-based alloys [2]. Powder metallurgical parts, metal–graphite composite and cemented carbide tool tips are also known to be readily brazed with BAg filler metals.

Most of the industrial silver brazing alloys are derived from the Ag–Cu system, either as Ag–Cu eutectic alloy or in combination with other elements as in the case of Ag–Cu–Zn and Ag–Cu–Zn–Cd alloys [3].

In view of high price of silver and toxicity of cadmium [4, 5], attempts have been made to develop cadmium-free brazing alloys with reduced silver. In an effort in this direction, Cu–P and Cu–Ag–P alloys have substituted BAg alloys in a number of applications joining copper alloys. Some of the silver-based alloys are further modified by replacing zinc and cadmium with tin or indium for vacuum-tube application where the high vapour pressure of zinc and cadmium cannot be tolerated [6].

Silver–copper eutectic alloy (72% Ag, 28% Cu) is widely used in electronics industries [7, 8]. As this alloy is expensive, alternative brazing alloys containing less silver, but with properties comparable to the standard eutectic alloy, are of interest.

The present work was directed towards substituting the standard 72% Ag–28% Cu eutectic alloy with a Cu–Ag base alloy with reduced silver content and other alloy additions such as silicon, tin, etc. Investigations were undertaken to induce desirable properties such as low melting point, high fluidity and wettability and low vapour pressure.

2. Experimental procedure

2.1. Materials

Silver, copper and tin were introduced as 99.99% purity, silicon metal was introduced into the system via a Cu–Si master alloy. The compositions of the developed alloy and the standard eutectic alloy are given in Table I.

2.2. Melting and casting

The melting of the alloy was done in an electric pot-type furnace using a graphite crucible, and was poured into a preheated graphite mould at about 900–950 °C. Experimental heats each weighing 0.5 kg were made.

2.3. Processing

The cast slabs were homogenized at 450–600 °C for 32 h. In some cases, homogenization was undertaken following cold working, reducing the time period. The homogenized slabs were processed into thin sheets by rolling.

2.4. Evaluation of physical properties

2.4.1. Melting point and electrical conductivity

The solidus and liquidus temperatures of the alloy were determined by differential thermal analysis (DTA) using a heating rate of 10 °C min^{-1}. Electrical conductivity was measured by a Foster Sigma Test instrument using a probe of 10 mm diameter.

TABLE I Chemical composition of the alloys (wt %)

Alloy designation	Alloy description	Ag	Si	Sn	Cu
A	Developed copper-based alloy	36.20	3.10	0.15	Bal.
B	Standard eutectic alloy	72.00	–	–	28

2.4.2. 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) [9] was taken and subjected to measurement.

2.5. Evaluation of mechanical properties

The mechanical properties, such as hardness, tensile strength and elongation, for Alloys A and B were determined. Additionally, microhardness, tensile, impact and shear strength for the brazed joints (copper to copper and nickel to nickel) were also determined.

For the tensile strength, an Instron tensile testing machine was employed making use of butt joint specimens (Fig. 2a). The impact and shear strength 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.

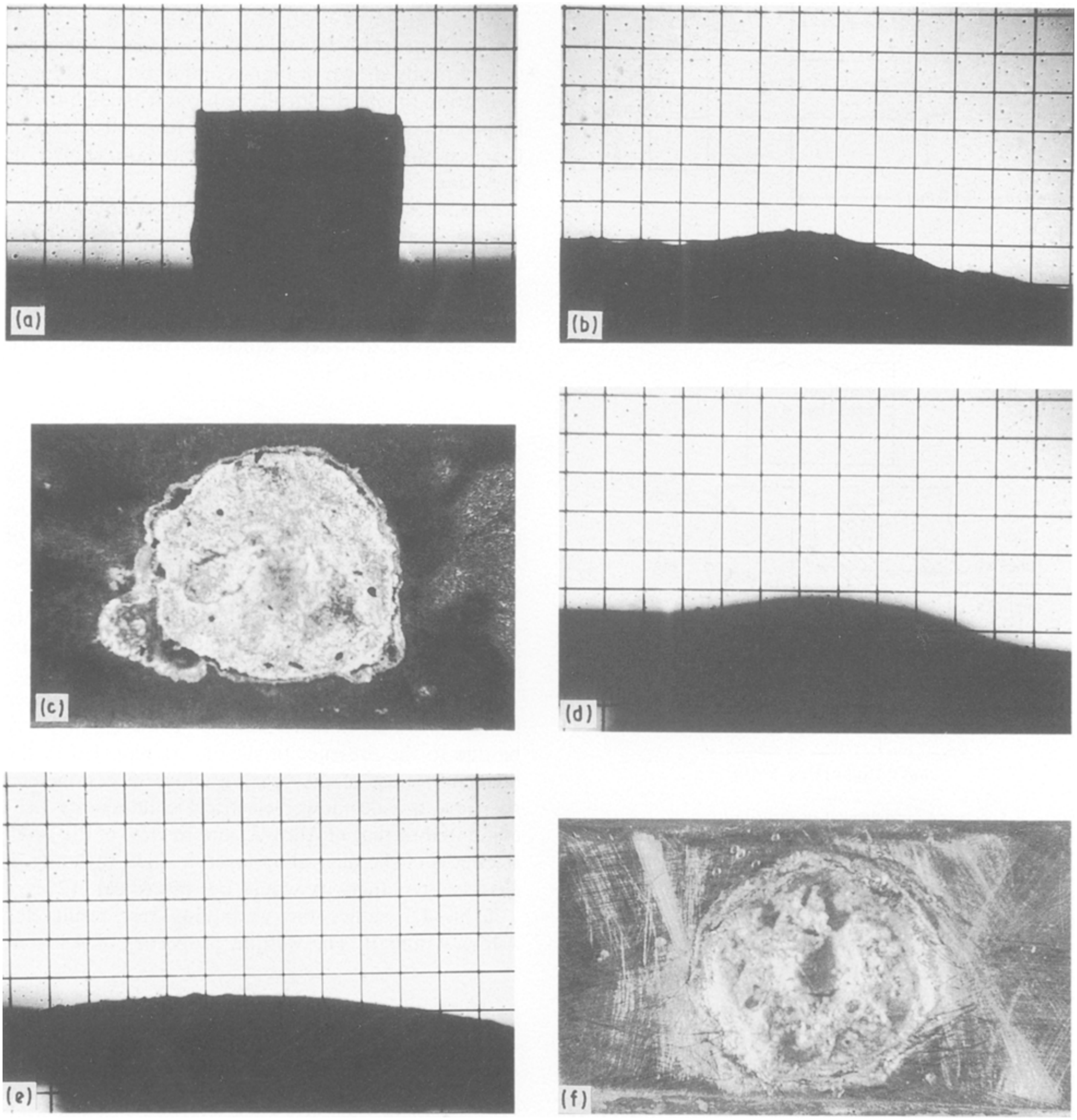

Figure 1 Solidified contact angle and wetted area. (a) Wettability test sample on base metal platelet. (b) Contact angle ($\theta = 10°$), Alloy A on nickel base plate. (c) Wetted area, Alloy A on copper base plate. (d) Contact angle ($\theta = 12°$), Alloy A on copper base plate. (e) Contact angle ($\theta = 10°$), Alloy B on copper base plate. (f) Wetted area, Alloy B on copper base plate.

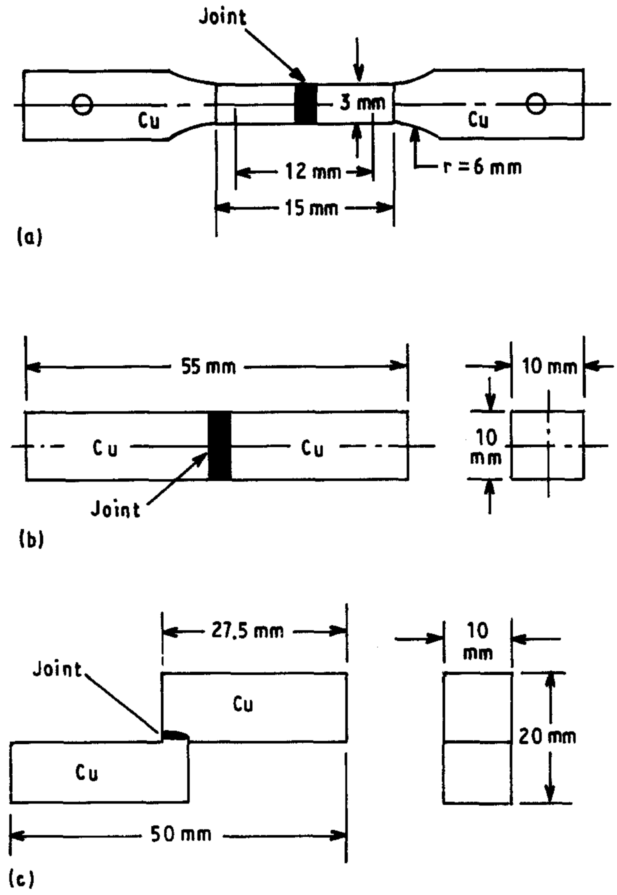

Figure 2 Test pieces for brazed joint mechanical properties. (a) Tensile test piece, (b) impact test piece, (c) shear test piece.

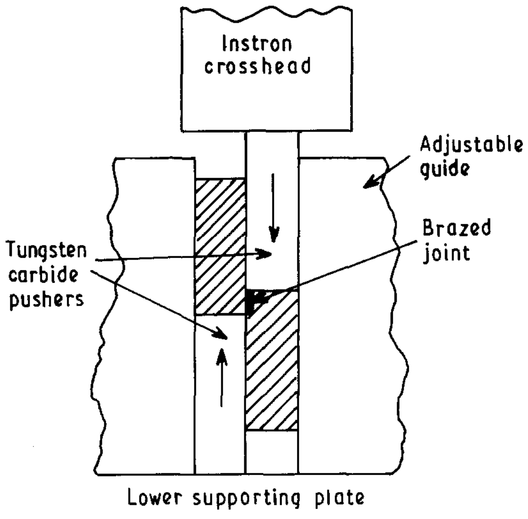

Figure 3 Schematic arrangement of shear test.

2.6. Corrosion studies

Corrosion studies, such as impressed current, anodic and cathodic polarization and H_2S exposure, were carried out on copper to copper brazed joint samples made with Alloys A and B.

In the impressed current studies, 5 mA current was passed for 52 h. A 1 cm^2 area covering parts of both brazed portion and copper base was taken and exposed separately to 3.5% NaCl and 1% Na_2S solutions at room temperature. The remaining areas of the brazed joint samples were covered with microcrystalline wax.

Anodic and cathodic polarization were carried out on a 1 cm^2 area exposed to 3.5% NaCl and 1% Na_2S solutions. Open circuit potential (OCP) and corrosion current were calculated from the polarization curves using a computerized potentiostat (Parc, Model-320).

In H_2S exposure studies, the brazed joint samples were exposed in 100 p.p.m. H_2S for 30 days. The effect of H_2S at the brazed joint line and adjoining areas was noted.

2.7. Structural characterization

Optical microscopic studies were carried out on the cast, homogenized and brazed joint samples. Additionally, some observations with XRD and SEM were also done.

3. Results and discussion

3.1. Homogenization and processing

It is evident from the steps of processing (which are schematically shown in Fig. 4a and b) that the homogenization time is drastically reduced from 32 h to 5 h by preceding it by cold rolling. The microstructures of the cast and homogenized samples are shown in Fig. 5a–c.

Dendrites disappear (Fig. 5a–c) following both conventional, as well as modified homogenization processes. The beneficial effect of initial cold reduction in improving the kinetics of homogenization may be understood on the basis of the reduction in the effective diffusion distances which, in turn, lowers the relaxation time [10].

3.2. Physical properties

The solidus and liquidus temperatures of Alloy A are 770 and 790 °C, respectively. These are very close to the eutectic solidification temperature (780 °C) of Alloy B. Further, the melting range for Alloy A is also very narrow (20 °C).

The density of Alloy A is 9 $g\,cm^{-3}$ which is only slightly lower than that of Alloy B, as would be expected from the composition (Table II).

The electrical conductivity value of Alloy A is lower than that of the standard Alloy B (Table II); this may be due to the presence of silicon. As reported in the literature, most of the brazing alloys in commercial use have a much lower electrical conductivity [11] compared to that of Alloy A, and in view of the small thickness of the filler alloy layer, a slight lowering in electrical conductivity would not be critical [12].

Table III shows the wettability test results for Alloys A and B. The wetting properties of Alloy A,

TABLE II Physical properties of the alloys

Alloy	Temperature (°C)		Density ($g\,cm^{-3}$)	Electrical conductivity (% IACS)
	Solidus	Liquidus		
A	770	790	9.0	20–22
B	780	780	9.9	65

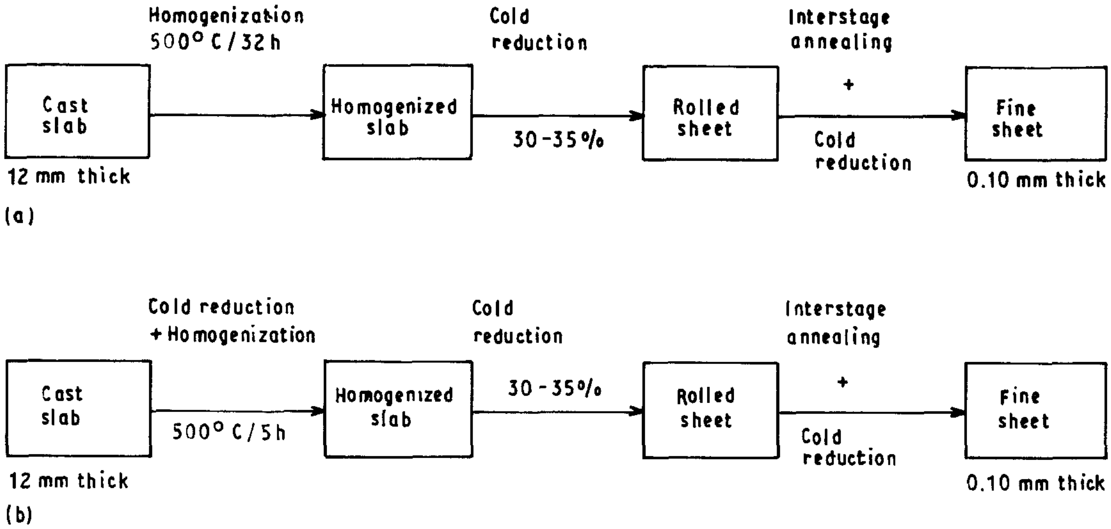

Figure 4 Processing schedule of the alloy: (a) conventional, (b) modified.

TABLE III Wettability test results

Alloy	Base metal used	Brazing temp. (°C)	Protective medium	Wetted area (in^2 (mm^2))	Contact angle (deg)	Wetting index
A	Copper	850	Argon	0.225 (145)	12	0.22
	Nickel	850	Argon	0.255 (164)	$\leqslant 10$	0.25
B	Copper	850	Argon	0.200 (130)	$\leqslant 10$	0.20
	Nickel	850	Argon	0.230 (148)	$\leqslant 10$	0.23

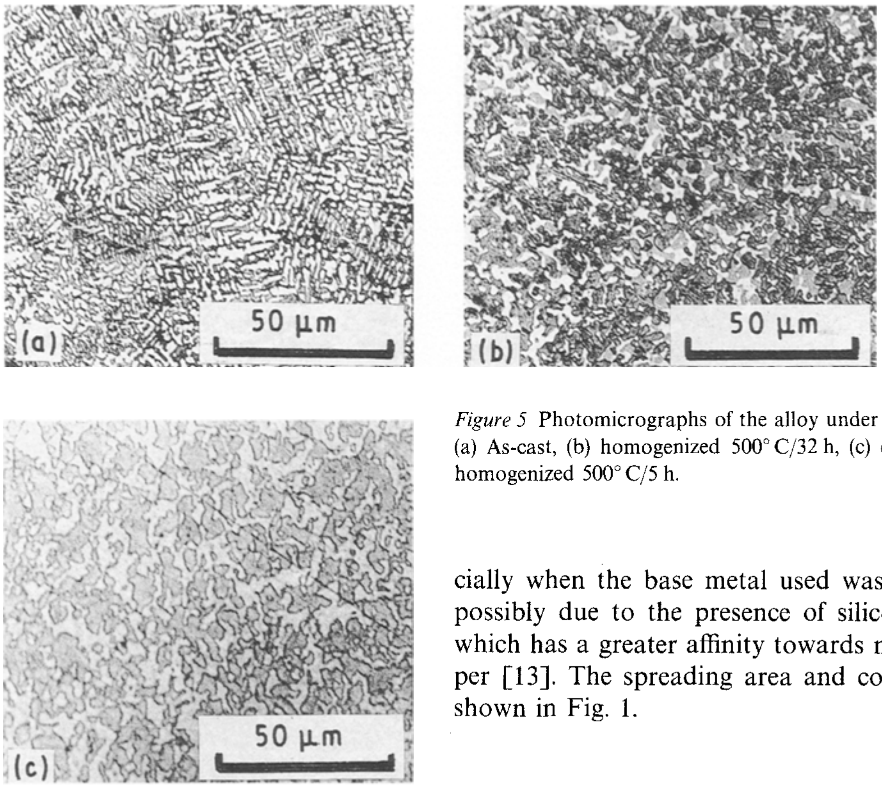

Figure 5 Photomicrographs of the alloy under various conditions. (a) As-cast, (b) homogenized 500° C/32 h, (c) cold reduction and homogenized 500° C/5 h.

such as contact angle, spreading area and wetting index of molten metal on different base metals (nickel or copper) under specified test conditions, are comparable to those obtained with Alloy B. In fact, Alloy A reveals better wetting properties than Alloy B, especially when the base metal used was nickel. This is possibly due to the presence of silicon in the alloy which has a greater affinity towards nickel than copper [13]. The spreading area and contact angle are shown in Fig. 1.

3.3. Mechanical properties

3.3.1. Properties of the brazing alloy

It is observed from Table IV that the ultimate tensile strength (UTS) and hardness values of Alloy A are higher, and the elongation percentage is lower, compared to those for Alloy B. However, an elongation of higher than 25% for Alloy A is expected to fulfil all the requirements in routine operations.

3.3.2. Properties of the brazed joints

The mechanical properties, such as tensile, impact and shear strength, of the brazed joints (copper to copper) are given in Table V. It is evident that these properties are either comparable or superior to those for the brazed joint made with Alloy B.

3.4. Corrosion properties

Micrographs of exposed samples are shown in Fig. 6. It is observed that grooving at the joint areas under the conditions of study has taken place in the case of joint samples made with Alloy B. No such grooving under similar conditions is observed in samples brazed with Alloy A. The superiority of Alloy A in NaCl and Na_2S solutions is noticeable from the electrochemical and exposure studies. The OCP of Alloy A is more positive than that of Alloy B (Table VI). The I_{corr} in both 3.5% NaCl and 1% Na_2S solutions is lower compared to those of Alloy B. The corrosion rate (1.24) of Alloy A is much lower than that of Alloy B (18.00).

In the H_2S exposure test too, the attack at the brazed joint line is less in the case of the joint sample made with Alloy A than with Alloy B.

TABLE IV Mechanical properties of the alloys

Alloy	Hardness (VPN)	Tensile strength ($kg\,mm^{-2}$)	Elongation (%)
A	130–135	41.5	25.5
B	110–115	28.4	35.0

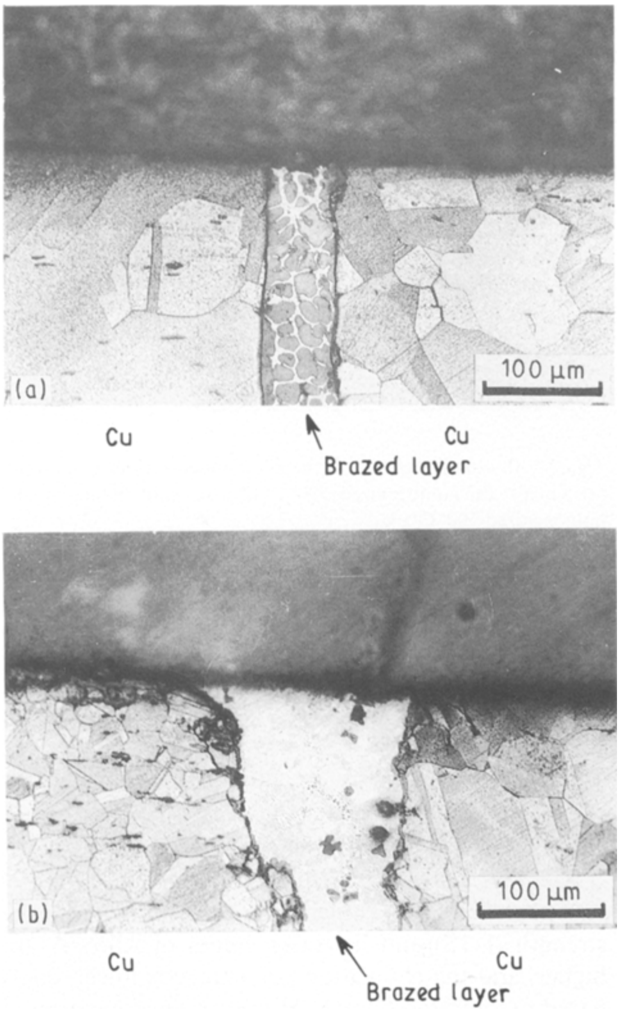

Figure 6 Micrographs of exposed samples (in Na_2S). Copper to copper brazed joint with (a) Alloy A, (b) Alloy B.

3.5. Microstructural features in brazed joints

Fig. 7 represents the optical microfeatures of the brazed joints. On comparing the microstructural features in the brazed alloy (in the joint) with that of the as-cast material (Fig. 5) one notices some differences. In the brazed joint, one finds primary copper-rich dendrites together with the Cu–Ag eutectic, and also some silver-rich globular areas. The as-cast microstructure, on the other hand, shows fine copper-rich dendrites with extremely fine eutectic in the interdendritic region, hardly resolvable at the same magnification. Comparing these two microstructures, one may conclude that the brazing alloy, cast in a graphite mould (as-cast material) displays a faster cooling rate bringing about a refinement. The corresponding scanning electron micrographs of the brazed joint are given in Fig. 8a and b. These photographs also carry the X-ray mapping using the EDAX. The microstructural features in the joint are similar to those seen by optical microscopy, namely distinct copper- and silver-rich primary regions and typical eutectic areas. The X-ray data (Fig. 9) also support the occurrence of near-pure copper and silver regions, in addition to some Cu–Si intermetallics. Microhardness data for joints with Alloys A and B are shown in Table VII. It is revealed from the table that the dark areas (Fig. 7) are essentially Cu_nSi (either Cu_4Si or Cu_5Si), where the hardness is higher than that in the pure copper areas.

TABLE V Mechanical properties of brazed joints (copper to copper) (mean of three tested samples)

Alloy	Tensile strength ($kg\,mm^{-2}$)	Impact strength		Shear strength ($kg\,mm^{-2}$)
		(kg m)	(ft lb)	
A	17.00	1.40	(10)	12.00
B	15.76	1.30	(9.3)	10.25

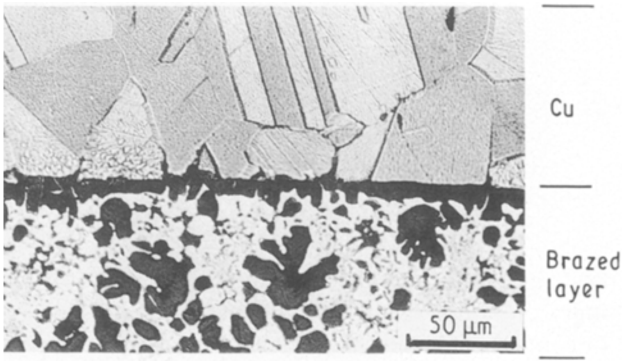

Figure 7 Micrograph of brazed joint copper to copper with Alloy A.

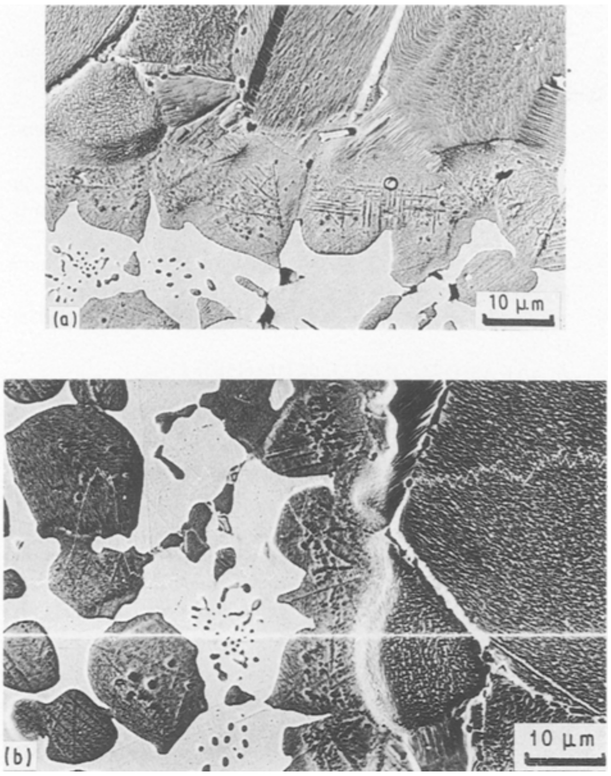

Figure 8 (a) Scanning electron micrograph of brazed joint copper to copper with Alloy A. (b) EDAX line scanning of brazed joint (copper to copper) with Alloy A (Cu K_α).

TABLE VI Polarization data of brazed alloys in 3.5% NaCl and 1% Na_2S at room temperature

Sample	3.5% NaCl		1% Na_2S		Corr. rate
	Ocp (− mV)	I_{corr} (μA cm^{-2})	Ocp (− mV)	I_{corr} (μA cm^{-2})	(mpy^{-1})
A	375	4.55	1050	3.10	1.44
B	450	23.65	1050	38.30	18.00

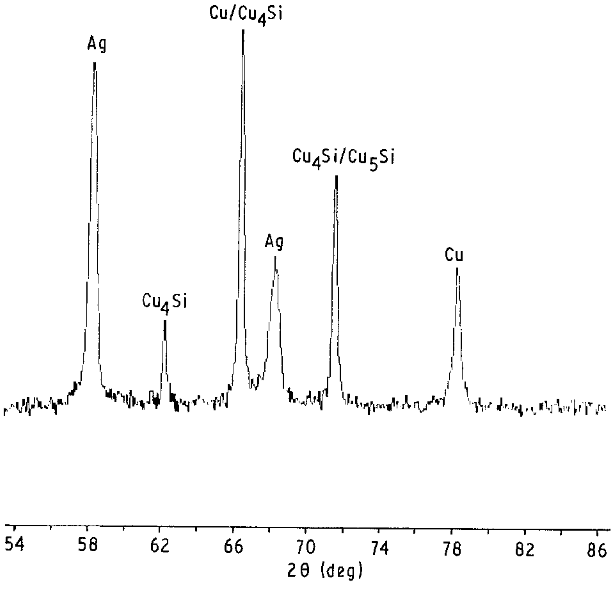

Figure 9 X-ray data for Alloy A.

TABLE VII Microhardness data for brazed joints (copper to copper) with alloys A and B

Area (Fig. 10a, b)	Microhardness (VHN), load 25 g	
	Alloy A	Alloy B
I	95	90
II	115	120
III	102	108
IV	130	115
V	140	110
VI	135	–
VII	145	–
VIII	290	–

4. Conclusion

In the currently developed (reduced silver) alloy, the melting point, fluidity and wetting properties are as good as in the conventional Ag–Cu eutectic alloy.

The new alloy possesses higher strength and good workability; hence should be amenable to forming

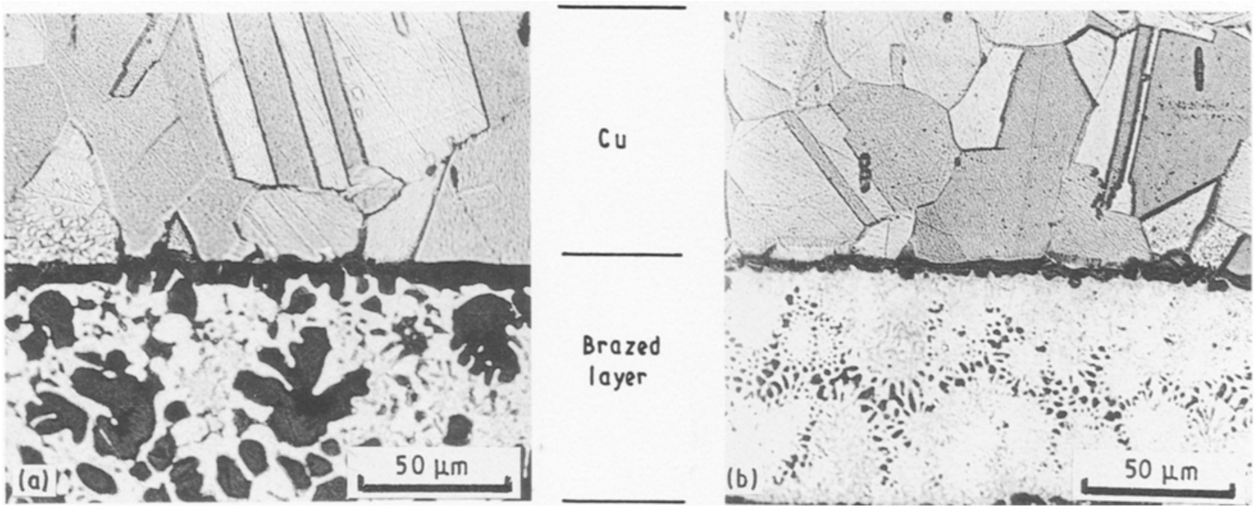

Figure 10 Brazed joints (copper to copper) with (a) Alloy A, (b) Alloy b. (a) I, twins in the copper side; II, eutectic in brazed layer; III, joining line towards the copper side; IV, joining line towards the brazed alloy layer; V, eutectic and small dark phases; VI, small dark phases; VII, small and medium dark phases; VIII, a big dark phase. (b) I, twins in the copper side; II, eutectic in brazed layer; III, joining line towards the copper side; IV, joining line towards the brazed layer; V, eutectic and white area.

foils or wires industrially. The mechanical properties of the brazed joints (copper to copper) using the new alloy are comparable to those of eutectic brazed joints.

The corrosion properties of the brazed joints (copper to copper) using the new alloy are much better than the eutectic brazed joint. Thus the new alloy with 50% saving in silver, should be a potential substitute for the conventional 72% Ag and 28% Cu eutectic alloy.

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