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Investigation of gap filling ability of Ag–Cu–In brazing filler metals

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ABSTRACT

In an attempt to develop cadmium-free silver brazing filler metals, the ternary Ag–Cu–In alloys were investigated. The effect of varying indium content on melting temperatures and brazeability of Ag–Cu–In alloys on copper was ascertained in this article. Additionally, microstructures, hardness, and shear strength of the brazed joints were investigated. Investigation of brazeability was carried out using a varying gap test piece method adapted from ISO 5179-1983. With this method, the capillary rise height at different joint gaps was used as a quantitative measure for brazeability. The results from differential thermal analysis showed that with the increase of indium content in Ag–Cu–In, the solidus and liquidus temperatures of the filler metals decreased. However, the increase of indium contents showed no significant improvement to the capillary rise height. The limits of capillary rise height of each filler metal corresponding to the joint gaps of 50 and 100 μm were approximately 45 and 28 mm, respectively. Increasing of indium content led to the increase of an intermetallic phase in the brazed layer which subsequently increased the joint hardness. However, this slightly reduced joint shear strength. The average shear strength of the joint brazed with 60Ag–15Cu–25In filler metal was about 11% lower than that brazed with 60Ag–35Cu–5In filler metal.

1. Introduction

Silver brazing alloys of the American Welding Society's specification are well known as best suited filler materials for joining ferrous and non-ferrous metals, and alloys, except aluminum and magnesium [1,2]. In this alloy family, the alloys based on Ag–Cu–Zn–Cd system are brazing filler metals widely used for general purposes [1]. The addition of cadmium to silver–copper–zinc system reduces the solidus temperature and the melting range; reduces silver content; and improves the fluidity of the alloys [2,3]. However, the problem associated with cadmium-containing filler metals is the toxic fume generated during the brazing operation [3–5]. Cadmium in silver brazing filler metals also has high vapor pressure which is unsuitable for vacuum brazing [6]. Therefore, many attempts have been made to solve the problem of cadmium fume and to produce cadmium-free alloys that have similar characteristics of high fluidity and low melting point as those of cadmium-bearing alloys [7–16]. However, most of alloys that have been developed contain zinc which is also a volatile material. Therefore it is of interest to develop cadmium-free and zinc-free silver brazing filler metals as the alternatives. The ternary Ag–Cu–In alloys are attractive because indium has low melting temperature and low vapor pressure. However, investigation into this brazing filler alloys remains open.

When designing brazed joint, the knowledge of capillary gap filling of the brazing filling metal under well defined conditions is a valuable help [17,18]. It is also very important to know not only how the liquid filler metal wets the base metal surface but also how the same liquid behaves in different gaps between the joint components. To investigate these behaviors, a standard method for investigation of brazeability using a varying test piece (ISO 5179-1983) was established. However, the literature survey showed that this method has not been adopted.

In this study, silver brazing filler metals based on Ag–Cu–In system were studied. The effect of varying indium content on melting temperatures of Ag–Cu–In brazing filler metals was examined. Since copper is one of the base metals that is commonly brazed with cadmium-bearing silver brazing filler metals, it was chosen as a base metal in this study. The investigation of brazeability of Ag–Cu–In filler metals on copper was performed using a varying gap test piece method. Additionally, the microstructures, hardness, and shear strength of the brazed joints were investigated.

2. Experimental procedure

The nominal chemical compositions of Ag–Cu–In brazing filler metals investigated are presented in Table 1. Silver content was fixed at 60 wt.%. On the other hand, indium content was varied from 5 to 25 wt.%.

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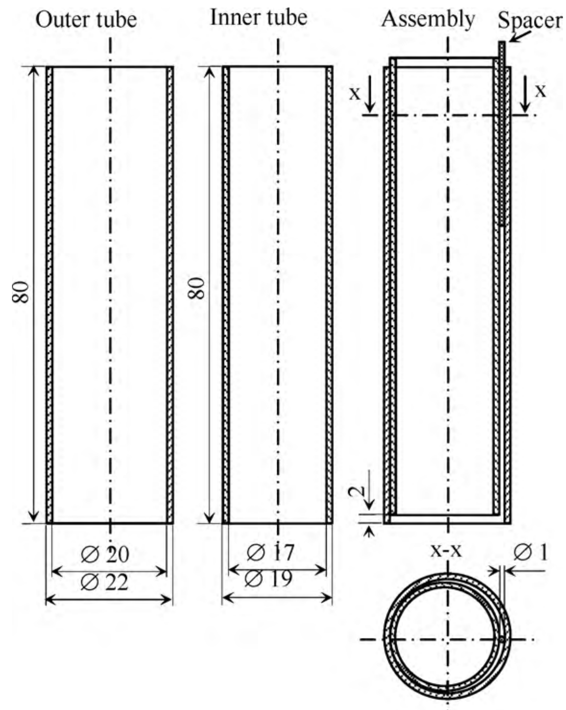


Fig. 1. A varying gap test specimen (in mm).

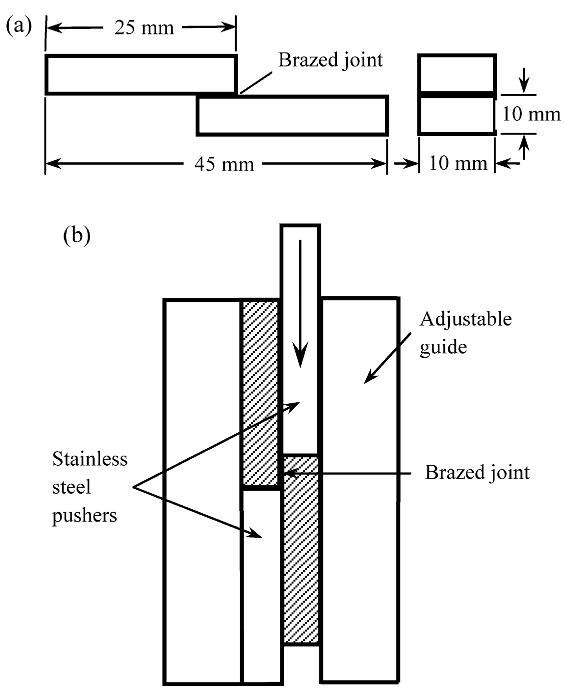


Fig. 2. (a) Shear test specimen, (b) schematic arrangement of shear test.

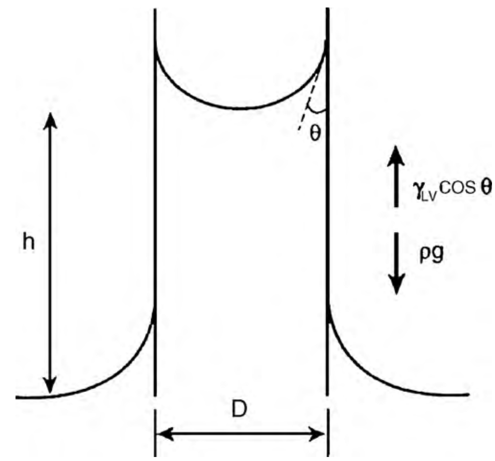


Fig. 3. Rise of a liquid between two parallel plates by capillary force.

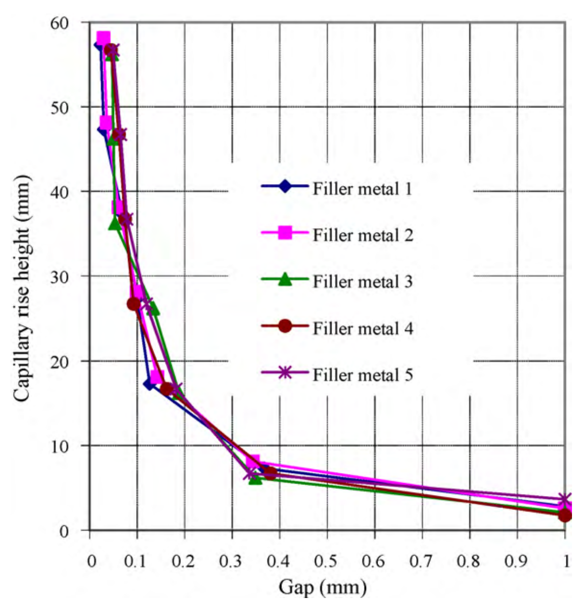


Fig. 4. Capillary rise height at different gaps.

Measurement of the solidus and liquidus temperatures of filler alloys was performed using differential thermal analysis (DTA). Assessment of brazeability of Ag–Cu–In brazing filler metals on copper was carried out using a method adapted from ISO 5179-1983 [19], investigation of brazeability using a varying gap test piece. The specimen configuration is schematically shown in Fig. 1. A small copper tube was fixed to the inside of a larger copper tube by inserting a spacer between the outer portion of the small tube and the inner portion of the big tube. The joint width then varies gradually from 0 to 1 mm. The two tubes were also assembled in such a way that there was clearance (2 mm) between the bases of two tubes to allow the molten filler metal to flow from the bore of the inner tube into the capillary gaps. The bottom portion of the tubes assembly was then fitted into a hollow (12 mm deep) of a non-wettable graphite block and 35 g of filler metal was introduced into the bore of the small tube. Brazing was carried out in a Nitrogen atmosphere in an OXYNON conveyer-type furnace [20] at 50 °C above the liquidus temperature of each filler metal. The brazing time at brazing temperature was 10 min. Since the heating chamber of the furnace was protected with carbon walls and brazing atmosphere was nitrogen, the oxygen level during brazing was very low.

Table 1
Nominal composition (wt.%) and property of Ag–Cu–In alloys.

Filler metal	Ag	Cu	In	Solidus (°C)	Liquidus (°C)	Melting range (°C)
1	60	35	5	728	770	42
2	60	30	10	673	748	75
3	60	25	15	610	704	94
4	60	20	20	612	685	73
5	60	15	25	605	677	72

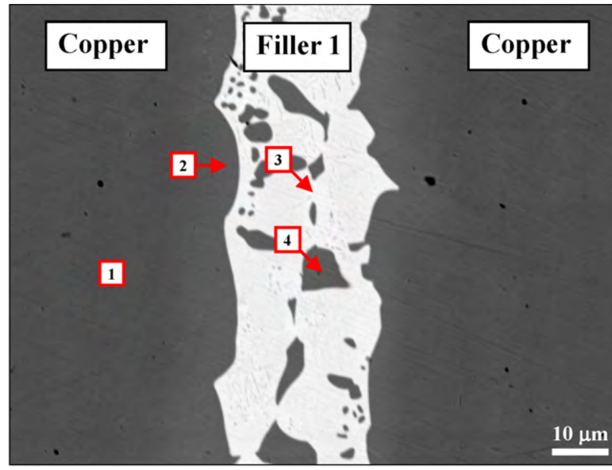
In order to determine the gap width for a given capillary rise height, the varying gap test pieces were cut at every 10 mm along their height. At the polished cross-section, the measurement was then made at mouth of gap which was filled with the filler metal using a profile projector. Note that the capillary rise height was measured from the bottom of the meniscus of the molten metal located at the bottom of the test piece. Microstructure inspection of the cross-section of the brazed joint was performed using an optical microscope and a SHIMADZU electron probe micro-analyzer (EPMA).

At different vertical sections of the varying gap test piece, hardness measurement was performed at the center of 50 μm brazed seams using a Vicker hardness tester. The number of indents taken per hardness data was 3. Assessment of brazed joint shear strength was also conducted using a simple lap-joint specimen and a pushing method as shown in Fig. 2. Initial joint gap of 50 μm was obtained using a special jigging system and brazing filler metals were preplaced at the mouth of the joints. The shear strength value was an average of 3 specimens.

3. Results and discussion

3.1. Thermal analysis

Solidus and liquidus temperatures of Ag–Cu–In brazing filler metals obtained from DTA are tabulated in Table 1. The solidus and liquidus temperatures of the alloys were suppressed by increasing indium content. With the increase of indium content from 5 to 25 wt.%, the solidus and liquidus temperatures of the filler metals decreased from 728 to 605 °C and from 770 to 677 °C, respectively. However, with the increment of indium from 5 to 15 wt.%, the melting range increased from 42 to 94 °C. Further increase of indium content (20–25 wt.%), causes the melting range to become slightly narrower. The decrease of both solidus and liquidus temperatures is believed to be attributed to the low melting temperature of indium.



Zone	Ag		Cu		In	
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
1	0	0	100	100	0	0
2	4.43	2.66	95.56	97.33	0	0
3	78.77	73.57	11.02	17.47	10.20	8.95
4	3.62	2.18	94.98	97.03	1.38	0.78

Fig. 5. BSE image and chemical analysis of Cu/filler metal 1/Cu joint.

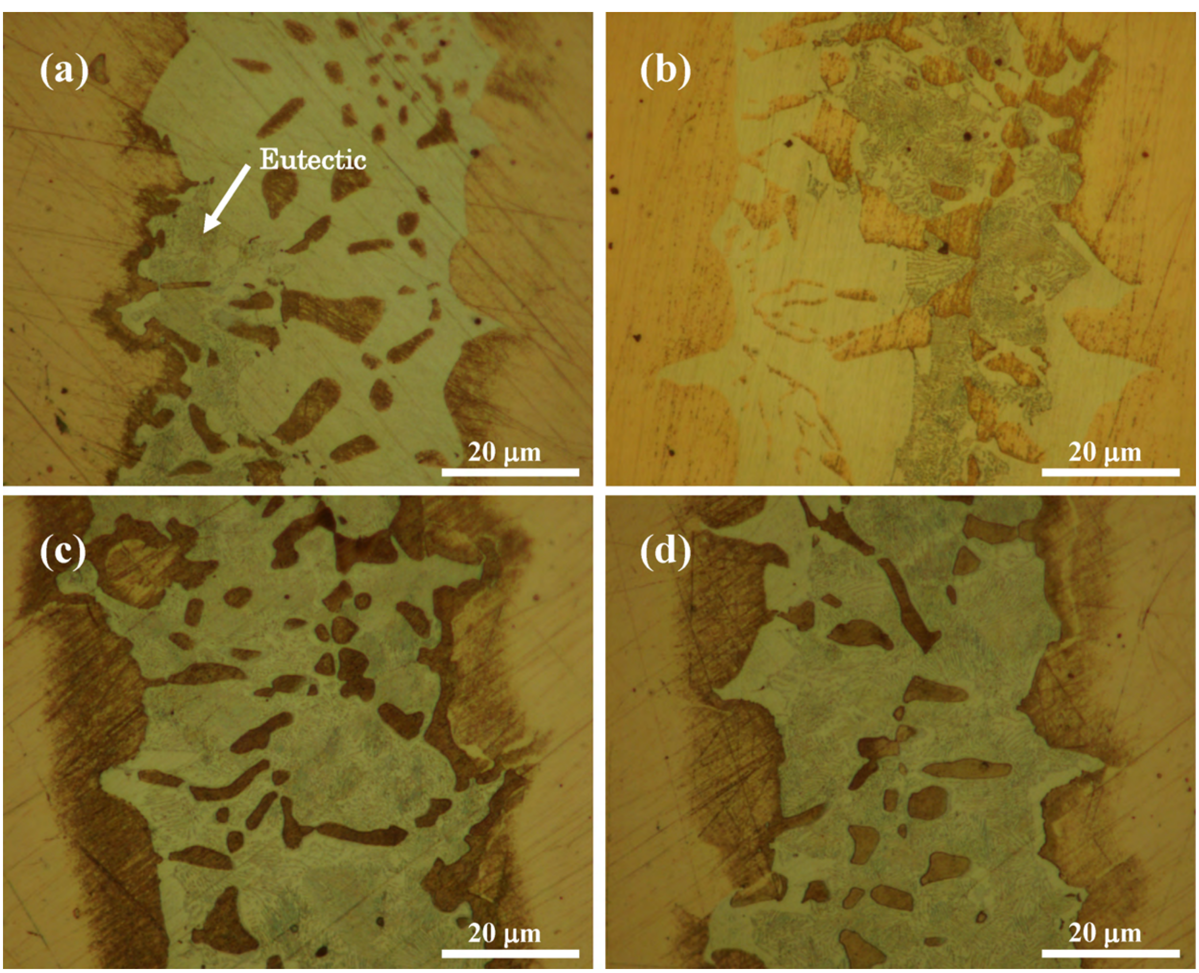


Fig. 6. Microstructure of copper joints brazed with: (a) filler metal 2, (b) filler metal 3, (c) filler metal 4, and (d) filler metal 5.

3.2. Capillary gap filling limit

When a pair of parallel plates partly immersed into a liquid (Fig. 3), provided that the wetting contact angle θ is less than 90°, the liquid will climb up by the capillary force to an equilibrium height h at which the capillary force is in balance with the hydrostatic force [3]. The theoretical capillary rise height is express by:

$$h = \frac{2\gamma_{LV} \cos\theta}{\rho g D} \quad (1)$$

where γ_{LV} is the surface tension between liquid and vapor (N/m), ρ is the density of the liquid (kg/m^3), g is the acceleration due to gravity (m/s^2), and D is the gap between two plates (m). It would be expected from this equation that the height capillary rise increases when the values of contact angle and the gap become small. In brazing, however, the real situation is rather complex as spreading nature is irreversible and the wetting contact angle is time independent. Besides, brazing process generally involves base metal dissolution by the molten filler alloy which leads to the change of filler metal composition [3].

In the present study, the capillary rise height was determined experimentally. The experimental results obtained from varying gap test pieces are shown in Fig. 4. It depicts capillary rise heights of different filler metals at various joint gaps. The data of the vertical joint filling limits of each filler metal at different joint gaps are very important in brazed joint design. As expected, the capillary rise height increased as the joint clearance gets narrower. The height of capillary rise gradually increased when the joint gap decreased from 1 to 0.2 mm, but sharply and almost linearly increased when the gaps are smaller than 0.2 mm. Since the values of capillary rise height at joint gaps greater than 0.2 mm were relatively low, these gaps are not suitable for brazing. In fact, the joint gaps of less than 0.15 mm were recommended when designing the brazed joint. It can also be noticed that each brazing filler metal investigated exhibited similar result, indicating that the variation of indium content in Ag–Cu–In filler metals showed no significant effects on capillary rise height. The limit of capillary rise height of each filler metal corresponding to the joint gaps of 50 and 100 μm are approximately 45 and 28 mm, respectively.

3.3. Microstructural observation

Back scattered electron image and chemical analysis results (Fig. 5) obtained from EPMA showed that copper joint brazed with filler metal 1 which contains 5% of indium consists of three phases: copper base metal (zone 1), copper solid solution at the joint interface and in the brazed layer (zones 2 and 4), silver solid solution (zone 3).

Fig. 6 showed copper joints at approximately 50 μm brazed seams made with filler metals containing different indium contents. It was found that copper joints made with brazing filler metals that contain indium from 10 to 25%, consist of additional very fine eutectic structures in the brazed layer. This fine eutectic structure comprised white silver solid solution and a gray phase. The amount of eutectic structure increased as indium content increased, whereas the amount of silver solid solution decreased. However, the amount of copper solid solution seemed to remain unchanged. Fig. 6 also showed that the microstructures of copper joint made with filler alloys 4 and 5 were very similar. Results from EPMA elemental mapping (Fig. 7) at copper joint brazed with brazing filler metal 3 indicated that copper and indium co-existed in the gray phase (at the center of the brazed layer). With reference to a Cu–In binary phase diagram [21], the solid solubility of indium in copper is very limited and vice versa. At room temperature they form an intermetallic phase, δ (Cu_7In_3). Therefore, the gray phase was probably the δ phase.

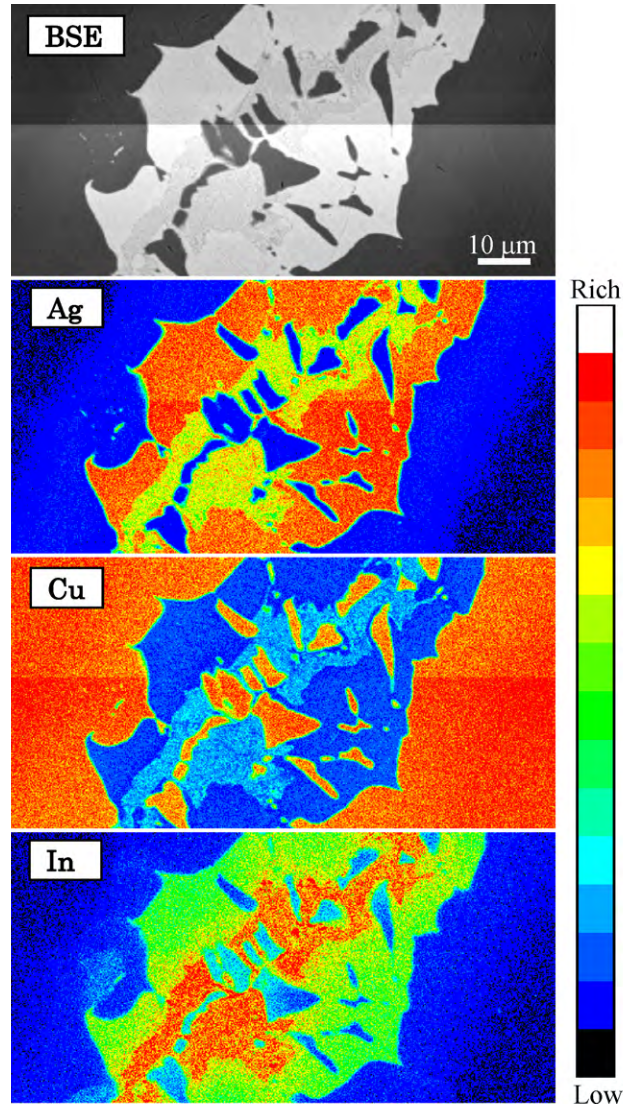


Fig. 7. EPMA elemental mapping of Cu/filler metal 3/Cu joint.

The brazed joint microstructures at 50 and 100 μm brazed seams showed similar appearance. A typical microstructure at approximately 100 μm brazed seam of copper brazed with filler metal 5 is shown in Fig. 8. The microstructures at wider brazed seams (greater than 0.2 mm) were not discussed here because the values of capillary rise height corresponding to these gaps were small. In other words, these gaps are not suitable for brazing as mentioned previously.

Microstructure observation at about 50 μm brazed seams along different vertical sections of the specimens revealed that the microstructures were similar. This implies that although the brazing filler metals possess wide melting range, their effect on liquation was negligible. It could be due to rapid heating during brazing in the OXYNON conveyer-type furnace because, during brazing, the specimen moved into the heating zone where brazing temperature was already preset.

3.4. Brazed joint mechanical properties

Fig. 9 illustrates average hardness at the center of 50 μm brazed seam made with different brazing filler metals. The hardness value strongly increased with the increment of indium content in the brazing filler metals. The average hardness value of the

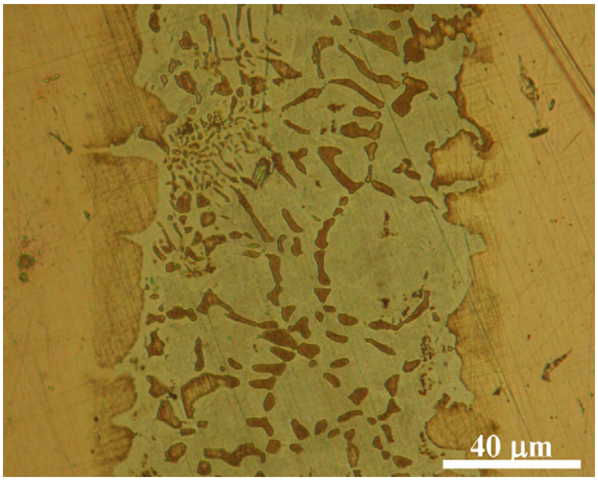


Fig. 8. Cu/filler metal 5/Cu microstructure at about 100 µm brazed seam.

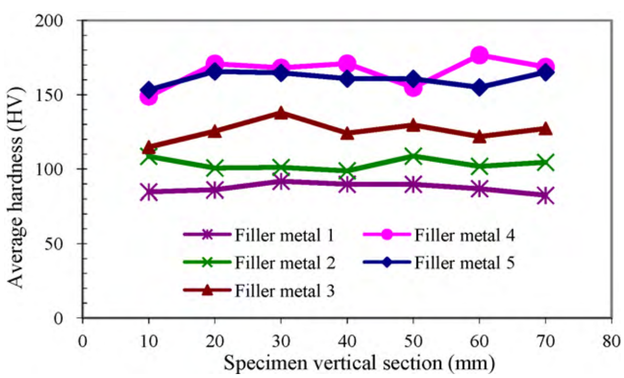


Fig. 9. Hardness at center of brazed seam at different vertical sections.

joint brazed with filler metal 5 was twice higher than that of the joint brazed with filler metal 1. This is clearly associated with the microstructures of the joints. That is, the amount of copper–indium intermetallic phase increased with increasing indium content, thus increasing the hardness. Copper joints made with brazing filler metals 4 and 5 have identical hardness value because of their similar microstructures. It is also noticeable that, for each filler metal, the values of hardness at different vertical sections of the specimen seemed to be similar. This is undoubtedly because of the similarity of the microstructures at different vertical sections.

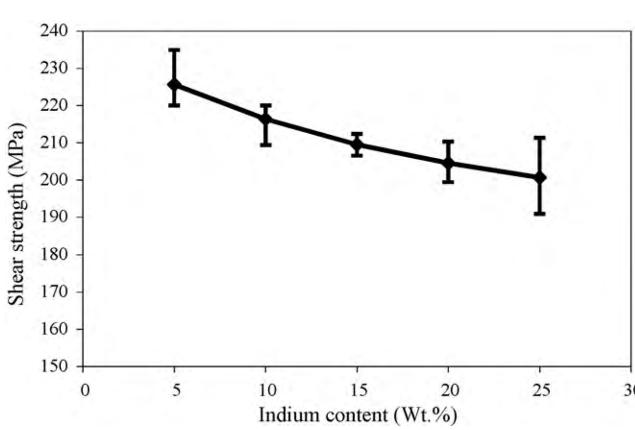


Fig. 10. Effect of indium content on brazed joint shear strength.

Fig. 10 showed the effect of varying indium content in Ag–Cu–In filler metals on brazed joint shear strength. The average shear strength only slightly declined when indium content was increased. The average shear strength of the joint brazed with filler metal 5 which contains 25 wt.% of indium was 200 MPa, which is about 11% lower than that brazed with filler metal 1 which contains 5 wt.% of indium. This indicated that although intermetallic compounds are usually hard and brittle [3], the copper–indium intermetallic phase (Fig. 6) did not severely affect the joint strength because it was finely distributed in silver solid solution in the brazed layer.

4. Conclusions

The effects of indium addition on melting temperatures and brazeability of Ag–Cu–In alloys on copper were investigated along with the brazed joint microstructures, hardness, and shear strength. The conclusions are summarized as follows:

1. With the increase of indium content, the solidus and liquidus temperatures of the filler metals decreased from 728 to 605 °C and from 770 to 677 °C, respectively. However, with the addition of indium (from 5 to 15 wt.%), the melting range increased from 42 to 94 °C. Further increase of indium content (from 20 to 25 wt.%) slightly narrows the melting range of the alloys.
2. The increase of indium content in Ag–Cu–In filler metals showed no significant effects on capillary rise height.
3. The joint gaps greater than 0.2 mm were not suitable for brazing with Ag–Cu–In fill metals since the values of capillary rise height were low. Indeed, the recommended joint gaps should be less than 0.15 mm.
4. With the increment of indium from 10 to 25 wt.%, the joint microstructures consist of additional very fine eutectic structure which increased as indium content increased. This subsequently increased the joint hardness, but slightly decreased the joint shear strength. The average shear strength of the joint brazed with 60Ag–15Cu–25In filler metal was about 11% lower than that brazed with 60Ag–35Cu–5In filler metal.

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