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Effect of B on microstructure and properties of joints brazed by In-situ Ag-Cu-Zn-Sn filler metal with high Sn content

Sujuan Zhong, Yunpeng Li, Yinkai Shi, Jian Qin, Hua Yu, Datian Cui and Weimin Long

1 School of Material Science & Engineering, Henan University of Science and Technology, Luoyang, 471003, People’s Republic of China
2 Zhengzhou Research Institute of Mechanical Engineering Co. Ltd., Zhengzhou, 450000, People’s Republic of China
3 National Joint Engineering Research Center for Abrasion Control and Molding of Metal Materials, Luoyang, 471003, People’s Republic of China
4 School of Material Science and Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450045, People’s Republic of China

E-mail: brazelong@163.com

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Abstract

The copper brazed joints were obtained by induction brazing using in situ synthetic high Sn content filler metals with different B contents and the effect of element B on the wettability of filler metals and microstructure and mechanical properties of the joints were studied. With the addition of element B, the spreading area of the filler metals on the copper increases. The microstructure of the joints mainly consists of silver-based solid solution and copper-based solid solution, and the distribution of silver-based solid solution in the brazing seam becomes dispersed with the addition of B. The width of the brazing seam increases significantly with the increase in B content. Meanwhile, the B element was mainly distributed in the Ag-based solid solution. The tensile strength firstly increased and then sharply decreased with B added. The maximum average tensile strength of 206.83 MPa was obtained with a 2% addition of B and the joint fracture pattern is a brittle fracture.

1. Introduction

The silver-based filler metals can be used to join a wide variety of ferrous and non-ferrous metals such as low-carbon steels, high-temperature nickel-based alloys and copper-based alloys, etc., with the exception of aluminum and magnesium [1-3]. Additionally, silver-based filler metals also play an increasing role in the joining of metal/ceramic [4, 5] and ceramic/ceramic [6, 7]. Although the earlier Cd-containing silver-based filler metals have excellent properties, the use of Cd-containing silver-based filler metals was prevented because Cd is a heavy metal with a toxic effect [8].

A number of studies have been carried out to find substitutes for silver filler metals containing cadmium. Li et al [9] developed a series of Ag–22Cu–xZn–ySn filler metals, the results showed that the increase of zinc and tin contents drastically decreases the solidus and liquidus temperatures, and the increase of zinc and tin in the filler metals helps the formation of eutectic structure. Ma et al [10] investigated the effect of In on low silver Ag-Cu-Zn filler metal and found that the addition of In lowered the solid and liquid phase temperatures of Ag-Cu-Zn filler metal, improved the wetting properties of the filler metal, and played a solid solution strengthening role in the joints formation process, enhancing the mechanical properties of the joints. However, it can only be used as a minor additive element because In is a precious metal.

According to the available research results, Ag-Cu-Zn-Sn filler metals are considered as a good substitute for cadmium-containing silver filler metals. However, with the continuous increase of the Sn element content, the Ag3Sn and CuSn brittle compounds in the filler metal structure increase significantly, resulting in a significant increase in the brittleness of the filler metal, and it is difficult to carry out conventional plastic deformation, so the high tin content of silver-based filler metals can only be used in the as-cast state, which seriously limits the promotion and application of filler metals [11]. A solution for in situ synthesis of high-strength silver filler metals...
during the brazing process was originally proposed by Long et al.\cite{12} and a study\cite{13} has shown that the in situ synthesis of high Sn silver filler metals by adding CuSn powders to the flux core can significantly improve the wettability of the filler metals and improve the mechanical properties of the brazed joint. Moreover, the effects of alloying elements on Ag-Cu-Zn-Sn filler metals have also attracted the interest of many researchers. For example, Khorunov et al.\cite{14} found that the addition of Ni and Mn improved the wettability of the Ag-Cu-Zn-Sn filler metal on cemented carbide and stainless steel, and the strength of the brazed stainless steel joints could reach 450 MPa. Yang et al.\cite{15} discovered that with the addition of rare-Earth Ce to silver-based filler metals, the microstructure of filler metals was more homogeneous, the solid-liquid phase temperature interval became narrower and the wettability improved. Xue et al.\cite{16} found that the added Ce easily formed high melting point Ce-Bi and Ce-Pb compounds with Bi and Pb in the silver filler metals, which inhibited the formation of harmful Bi and Pb singlet phases, thus improving the properties of the filler metals. Wang et al.\cite{17} developed a new low-silver lead-free solder, Sn-1.0Ag-0.5Cu-xB, the research results show that B plays a role in grain refinement and significantly improves the properties of solder joints.

In this work, to further improve the overall performance of the filler metals, certain content of B element was added to the silver-based filler metals with high Sn content, and the effect of B element on the wettability of silver-based filler metals with high Sn content was investigated. The copper joints were brazed by the induction brazing method, the microstructure changes of the joints were analyzed, their mechanical properties were measured and their fracture morphology was studied.

### 2. Experimental materials and methods

The outer skin of the flux-cored silver filler metal is BAg30CuZnSn, its chemical composition is shown in table 1. And the flux-core component is a mixture of flux, Cu60Sn40 alloy powder with a particle size of 48 μm (purity of 99.9%) and B powder with a particle size of 45 μm (purity of 99.95%), figure 1 shows the microstructure of the Cu60Sn40 powder and B powder. Different masses of flux, Cu60Sn40 powder and B powder were weighed, mixed thoroughly using a planetary stirrer and then filled into the BAg30CuZnSn to prepare flux-core silver filler metals with the composition shown in table 2. And the schematic diagram of filler metals cross section is shown in figure 2.

![Figure 1. The microstructure of (a) Cu60Sn40 powder and (b) B powder.](image)

**Table 1.** Chemical composition of BAg30CuZnSn silver filler metal (wt%).

| Composition   | Ag  | Cu  | Zn  | Sn  |
|---------------|-----|-----|-----|-----|
| BAg30CuZnSn   | 29.0| 35.0| 30.0| 0.5 |
| ~ 31.0        | ~ 37.0| ~ 34.0| ~ 1.5 |

The melting characteristic of the filler metals was determined using differential thermal analysis (DTA) under an argon atmosphere with heating at a rate of 10 °C min⁻¹. The spreading test was performed according to China’s National Standard GB/T 11364-2008. Cuttings of about 0.2 g of filler metals were placed on T2 copper (40 mm × 40 mm × 2 mm) for spreading experiments, and the specimens were heated at 810 °C for 5 min in a
Each filler metal is experimented with three times under the same conditions and the results are obtained as an average. The spreading area was calculated using the software Image-J. And then the copper joints were brazed by induction brazing with a lap length of 2 mm. The detailed process is as follows: The filler metal is first heated at a current of about 28 A until the powder core melts, then the current is adjusted to about 42 A for 30 s and then cooled in the air to obtain the brazed joints. The schematic and macroscopic morphology of the brazed joint is presented in figure 3. The obtained copper brazed joints were cut, inlaid, ground and polished, and their microstructure was observed by the JSM-IT800 SHL Field emission Scanning Electron Microscope (SEM) and the elemental distribution was analyzed Energy Dispersive Spectrometer (EDS). Since general detection methods cannot accurately detect the distribution of B elements, Electron probe microanalysis (EPMA) is used to detect the distribution of B elements.

For the mechanical characterization, SHIMADZU AG-I250KN precision universal electronic tensile testing machine was used to test the tensile strength of the joints under room temperature with the stretching rate of 1.0 mm min$^{-1}$, multiple tests are carried out and the average is taken as the final result. And SEM was used to analyze the fracture microstructure obtained by the tensile test, and the fracture pattern were studied.

![Figure 2. Schematic diagram of filler metals cross section.](image-url)

![Figure 3. The schematic (a) and macroscopic morphology (b) of the brazed joint.](image-url)

| Filler metals | Composition of flux-core, wt% |
|---------------|-----------------------------|
|               | Flux | CuSn | B  |
| 1             | 40   | 60   | 0  |
| 2             | 38   | 60   | 2  |
| 3             | 37   | 60   | 3  |

Table 2. Chemical composition of flux-cores in the filler metals.
3. Results and discussion

3.1. Melting temperature and wettability of the flux-cored silver filler metals

The melting characteristic curves for BAg30CuZnSn and Cu60Sn40 are displayed in figure 4. It can be seen that the melting characteristic curve of the filler metal crust BAg30CuZnSn only has one heat absorption peak, which suggests that a heat absorption reaction takes place during the melting process, and the initial melting temperature of BAg30CuZnSn was 666.79 °C and the end melting temperature was 776.49 °C, corresponding to a melting point of 776.49 °C and a melting temperature interval of 109.7 °C [18]. Likewise, the Cu60Sn40 alloy has an initial melting temperature of 721.77 °C and an end melting temperature of 759.27 °C. The melting point of B is known to be 2076 °C based on the related literature [19].

The spreading area of various flux-cored silver filler metals on T2 copper is shown in figure 5. It is clear that the average spreading area of the filler metals on copper was only 158.86 mm² without the addition of B, and the spread area rose by 32% to 210.39 mm² with the addition of 3% B, indicating that the filler metal wettability on
Cu was greatly enhanced by the addition of element B. This is most likely because element B is a surface active element and makes the liquid filler metal appear positively adsorbed when it is added in tiny amounts. The emergence of the positive adsorption phenomena decreases the liquid filler metal surface tension, facilitating the filler metal to spread out on the base materials and enhancing its spreading ability [20].

Combining the melting point of the alloy powder and the melting characteristics curve of BAg30CuZnSn, the spreading process of the filler metal is analyzed. First, the flux is liquefied and spread to remove impurities such as oxide film on the copper surface. Then, the CuSn alloy melts and spreads on the copper (carrying B powder out) to form a thin layer of molten CuSn liquid alloy, reducing the solid-liquid surface tension on the base material. Subsequently, BAg30CuZnSn melts and spreads on the molten CuSn liquid thin layer, while interacting and fusing with each other to form a high Sn content liquid filler metal [13].

3.2. Microstructure of the brazing joints
The microstructure of the brazed joints brazed by in situ synthesis of high Sn content silver filler metals with different B contents and the elemental distribution of the corresponding area is shown in figure 6. It can be seen that the width of the brazing seam is about 38 μm without the addition of B. The brazed joint is mainly composed of two parts, a coarse copper-based solid solution directly connected to the base material with a large amount of solid solution of Zn elements, and a silver-based solid solution distributed in the middle of the brazing seam with a large amount of solid solution of Sn elements, and the formation of Ag-Cu eutectic in this region. Moreover, no defects such as voids and micro-cracks were found at the interface, indicating that the filler metal and the base material have good metallurgical bonding.

When 2% B is added, the width of the brazing seam increases to 86 μm. This is due to the fact that the CuSn alloy powder in the filler metal first melts and carries the B element into the brazing seam through capillary action during the brazing process. While the B atoms have a small radius and diffuse rapidly, making it easy to diffuse into the base material during the brazing process. Furthermore, B acts as a element that lower the melting point, lowering the melting point of the substrate in the interface area and making the width of the brazing seam increase [21, 22]. In addition, the microstructure of joints has changed significantly. The grey-black copper-based solid solution becomes finer than that without the addition of B, and grows in a columnar pattern towards the inside of the brazing seam. The grey-white silver-rich phase grows towards the sides of the base material and is more evenly distributed in the brazing seam, and a bright white needle-like phase is formed in the area where the silver-rich and copper-rich phases meet, which is presumed to be the Ag5Sn phase. Additionally, Ag-Cu eutectic phase is also present within the silver-rich phase.

The microstructure of the brazed joint became more homogeneous as the B content was raised to 3%, and the width of the brazing seam has been increased to 182 μm, indicating that a stronger interaction occurred between the base material and the liquid molten filler metal during the joint formation process.

The copper-based solid solution joined to the base material grows in columns towards the inside of the brazing seam, as shown in figure 6(k), but the length of columnar copper-based solid solution at the interface becomes shorter compared to the addition of 2% B. At the same time, a large amount of grey-black massive Cu-rich phase exists inside the brazing seam, presumably separated by other phases when the Cu-rich phase extends and grows, resulting in a discontinuous distribution in the brazing seam. According to the elemental...
distribution diagram (Figure 6(f)–(o)), it can be seen that the grey-white silver-rich phase is mainly distributed around the Cu-based solid solution and the region that discontinuously distributed the Cu-based solid solution in the center of the brazing seam.

The elemental distribution of the brazing seam of the brazed joints with 3% B was examined and analyzed using EPMA, as shown in Figure 7. It can be observed that the distribution areas of Cu and Zn are highly overlapping, indicating that Zn is mainly solid-soluble in Cu to form a Cu-based solid solution, Ag is mainly distributed in the Cu-poor zone, Sn is distributed in both the Ag-rich and Cu-rich zones, and the concentration of B is higher in the silver-rich phase than in the Cu-rich phase.

Chemical affinity can be used to characterize the strength of the interaction between elements, the larger the chemical affinity parameter between elements, the stronger the tendency to interact. The value of the chemical affinity parameter between any two elements in the Ag-Cu-Zn-Sn-B filler metal can be calculated as follows [23].

\[ \eta = \frac{(z/\gamma_k)_A}{(z/\gamma_k)_B} + \Delta X \]  

Where \( \eta \) is the chemical affinity parameter, \( (z/\gamma_k)_A \) is the ratio of the charge to the atomic radius of the element, and \( \Delta X \) is the difference in electronegativity between elements A and B. The value of \( (z/\gamma_k)_A/(z/\gamma_k)_B \) is always the smaller value of \( (z/\gamma_k)_A \) as the denominator, so \( (z/\gamma_k)_A/(z/\gamma_k)_B \) is always greater than 1. The data required for the calculations were taken from the literature [24] and the results are presented in Table 3. It can be observed that the value of the chemical affinity parameter of element B and element Ag is larger than that of Cu and Zn, which means that element B is more likely to interact with Ag and there is a ‘pro-Ag’ effect exists. This is consistent with the previous EPMA findings. Similarly, both Cu and Ag elements are more likely to combine with Sn elements, forming the Cu₆Sn₅ phase and Ag₃Sn phase respectively.

| Binary System (A-B) | Charge-radius ratio | Element electronegativity | Chemical Affinity Parameters \( \eta \) |
|---------------------|---------------------|---------------------------|------------------------------------------|
|                     | \( (z/\gamma_k)_A \) | \( (z/\gamma_k)_B \) | \( \frac{(z/\gamma_k)_A}{(z/\gamma_k)_B} \) | \( X_A \) | \( X_B \) | \( \Delta X \) | |
| B-Ag                | 15.00               | 0.79                      | 18.99                                    | 2.04  | 1.93  | 0.11   | 19.10        |
| B-Cu                | 15.00               | 1.04                      | 14.42                                    | 2.04  | 1.90  | 0.14   | 14.56        |
| B-Zn                | 15.00               | 2.70                      | 5.56                                     | 2.04  | 1.65  | 0.39   | 5.95         |
| B-Sn                | 15.00               | 5.64                      | 2.66                                     | 2.04  | 1.96  | 0.08   | 2.74         |
| Sn-Ag               | 5.64                | 0.79                      | 7.14                                     | 1.96  | 1.93  | 0.03   | 7.17         |
| Zn-Cu               | 2.70                | 1.04                      | 2.60                                     | 1.65  | 1.90  | −0.25  | 2.35         |
| Sn-Cu               | 5.64                | 1.04                      | 5.42                                     | 1.96  | 1.90  | 0.06   | 5.48         |

Figure 7. Elemental mapping results of the brazing seam of the joints with addition of 3%B by EPMA (a) Analytical area, (b) Ag, (c) Cu, (d) Zn, (e) Sn, (f) B.
3.3. Effect of B on the shear strength of brazing joints

The load-displacement curves and average tensile strength of the brazed joints are performed in figure 8, it can be seen that the load-displacement curves of brazed joints with different B additions have the same trend, whereas the brazed joints with 2% B additions are characterized by larger loads and longer displacements, which indicates that the joints have high strength and good ductility. The average tensile strength of the joint brazed with filler metal that 2% B was added achieved 206.83 MPa and about 34% more than the joint brazed without B addition. The average tensile strength of joints, however, dropped when B content was raised to 3%. The brazed joints without B addition had an average tensile strength of 157.5 MPa, which was lower than the tensile strength of joints brazed with 3% B addition.

The mechanical properties of brazed joints are usually highly relevant to their microstructure. As shown in figure 6, the braze joint is mainly composed of copper-based solid solution and silver-based solid solution, and the addition of B has a great influence on the microstructure morphology of the braze joint, mainly acting as a solid solution reinforcement and enhancing the strength of the brazed joint. A similar result was found by Ma et al [25] for the addition of Ga to the filler metals. Moreover, the length of columnar copper-based solid solution growing toward the center of the brazing seam increases, and when subjected to an applied load, the columnar Cu-based solid solution in the brazed joints can act as a nail, which has a positive effect on the brazing seam [18]. With the addition of B up to 3%, the length of the columnar Cu-based solid solution into the brazing seam decreases, making it difficult to perform the nailing effect. In addition, the Ag-Cu eutectic phase, which can improve the strength of the brazed joints, is reduced and becomes coarser within the brazing seam, leading to a reduction in the strength of the brazed joints.

Figure 9 depicts the fracture morphology of the brazed joints, and table 4 displays the results of the element composition at each site. The addition of B seems to have a significant impact on the morphology of fracture. A considerable number of dissociation surfaces and a limited number of tough nests were observed at the joint fracture without the addition of B. The fracture mode was thus judged to be a mixed tough-brittle fracture with a predominantly brittle fracture, which occurred in the silver-based solid solution. When 2% B is added, the fracture morphology has obvious tearing edges, indicating that the fracture pattern is a brittle fracture. As shown
in figure 9(c), the fracture morphology of the joint with the addition of 3%B exhibits typical quasi-cleavage fracture characteristics, and it can be seen from the energy spectrum results that the Sn content at the fracture is as high as 11.26%, so it is speculated that the excessive Sn is the main reason for the decrease in mechanical properties of joints.

4. Conclusions

The effect of B addition on the wettability of in situ synthetic high Sn content silver filler metals and microstructure and mechanical properties of the joints were investigated. The following conclusions can be obtained from the experimental results:

(1) The spreading area of the filler metals on the copper gradually increases with increasing B content. The average spreading area reaches 210.39 mm² when the B content is 3%.

(2) The microstructure of the brazed joint is mainly composed of silver-based solid solution and copper-based solid solution. With the increase of B element content, the width of the brazing seam becomes wider, the silver-based solid solution in the brazing seam diffuses to the base metal on both sides, and the distribution of copper-based solid solution becomes more and more dispersed. And the B element is mainly distributed in the Ag-based solid solution.

(3) The addition of B can significantly improve the strength of copper brazed joints, and the tensile strength of the brazed joint is the highest when the addition of B is 2%. But as the B content continued to increase, the joint strength decreased.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

The authors declare no conflict of interest.

ORCID iDs

Yunpeng Li https://orcid.org/0000-0002-1734-6951
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