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Review

Influences of Sn on Properties of Ag-Based and Cu-Based Brazing Filler Metals

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Abstract: Ag-based and Cu-based brazing filler metals, which are the most widely used brazing materials in industrial manufacturing, have excellent gap-filling properties and can braze almost all the metallic materials and their alloys, except for the low-melting-point metals such as Al and Mg. Therefore, Ag-based and Cu-based brazing filler metals have attracted great attention. In this review, three series of typical Ag-based filler metals: the Ag-Cu, Ag-Cu-Zn, and Ag-Cu-Zn-Sn alloys; and three series of Cu-based filler metals: the crystalline and amorphous Cu-P filler metals, as well as the Cu-Zn filler metals, were chosen as the representatives. The latest research progress on Sn-containing Ag-based and Cu-based brazing filler metals is summarized, and the influences of Sn on the melting characteristics, wettability, microstructure, and mechanical properties of the selected filler metals are analyzed. Based on these, the problems and corresponding solutions in the investigation and application of the Sn-containing Ag-based and Cu-based filler metals are put forward, and the research and development trends of these filler metals are proposed.

Keywords: Sn element; Ag-based filler metals; Cu-based filler metals; melting characteristics; wettability; microstructure; mechanical properties

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1. Introduction

The brazing filler metals can be divided into more than 10 series, such as those based on Ag, Cu, Al, Au, Ni, an Mn filler metals. Among these alloys, the Ag-based and Cu-based brazing filler metals are the most important filler materials, as they comprise a large proportion of fillers used and are widely used in joining of homogeneous or heterogeneous metals in the domestic appliance, electronic information, automobile, and other industries [1]. In the past decade, with the rapid development of household appliance refrigeration technology, the production and sales of the household appliance refrigeration industry keeps growing, and the demand for Ag-based and Cu-based filler metals increases continuously [2]. The traditional Cd-containing Ag filler metals were widely used due to their good comprehensive performance and high performance/cost ratio. However, with the strengthening of environmental protections, the toxicity of Cd has attracted increasing attention, and the application of Cd-containing materials has been prohibited in many fields in the USA, Japan, the European Union, and China [3]. In addition, the high price of Ag also restricts the application of Ag-based filler metals, and the applications of low-Ag filler metals and Ag-free, Cu-based filler metals are limited due to their high melting temperature and poor precision forming properties [4]. Therefore, the investigation and manufacture of the new green low-Ag or Ag-free filler metals have become hot topics in the brazing field.

Recently, most of the research has focused on the influences of the alloy elements on the variation rule of the microstructure and properties of the filler metals, as well as the action mechanisms of these elements, in order to make the brazing filler metals fulfill the required properties through modification of the alloy elements [5]. It was found that appropriate addition of Sn, In [6], Ga [7], Mn [8], Ni [9], or rare earth elements [10,11] could significantly optimize the microstructure and properties of the filler metals. Among these elements, Sn is a low-priced metal that can greatly decrease the solidus and liquidus temperatures and improve the flowability of the filler metals, giving it great application and research importance. In this review, we summarize the research advances regarding some Sn-containing Ag-based and Cu-based brazing filler metals, and analyze the influences of Sn on the melting characteristics, wettability, microstructure, and mechanical properties of the selected filler metals. Based on these, we present problems and corresponding solutions in the research and application of Sn-containing Ag and Cu filler metals, and propose the research and development trends of these filler metals. It is expected that this review can provide valuable theoretical support and reference for the development and application of new Ag-based and Cu-based filler metals.

2. Influences of Sn on Ag-Based Brazing Filler Metals

2.1. Influences of Sn on the Melting Characteristics of Ag-Based Brazing Filler Metals

The melting characteristics of the brazing filler metal are the important performance index, and affect not only the brazing temperature, but also the wettability, as well as the properties of the brazed joint [12,13]. The melting temperature of the Ag filler metals decreases with the increasing Ag content, and the filler metals with high Ag show excellent flow and spreading properties, but the material cost is very high. Through decreasing the content of Ag, the price of the Ag filler metal can be reduced, but the decrease in Ag will increase the melting point and raise the melting temperature range, which has a negative effect on the brazing properties of the filler metal [14].

The influences of the Sn content on melting characteristics of Ag60Cu brazing filler metals are presented in Table 1 [15,16]. It was seen that the addition of Sn could decrease both the liquidus temperature and the solidus temperature of the Ag60Cu filler metals. When the content of Sn was lower than 8%, the melting temperature range of the filler metals enlarged with the increasing Sn content. When the Sn content was higher than 8%, the melting temperature range tended to be stable, but still was much greater than the filler metals without Sn. In some other studies [17,18], similar conclusions were also reached; i.e., the addition of Sn could continuously decrease the melting point of the Ag-Cu filler metals. The obvious decrease in both the solidus temperature and the liquidus temperature of the filler metals was mainly attributed to the fact that the melting point of Sn is only 232 °C, as shown in Figure 1 [19], and Sn could partly dissolve into the phases of the filler metals [20].

Table 1. Melting characteristics of Ag60Cu filler metals with different contents of Sn [15,16].

Sn/wt %	Solidus/°C	Liquidus/°C	ΔT/°C
0	778.7	814.1	35.4
2	756.3	809.9	53.6
4	694.4	797.6	103.2
5	680	767	87
8	604.9	776.7	171.8
10	602	718	116
15	580	680	100
20	521	640	119
25	514	609	95

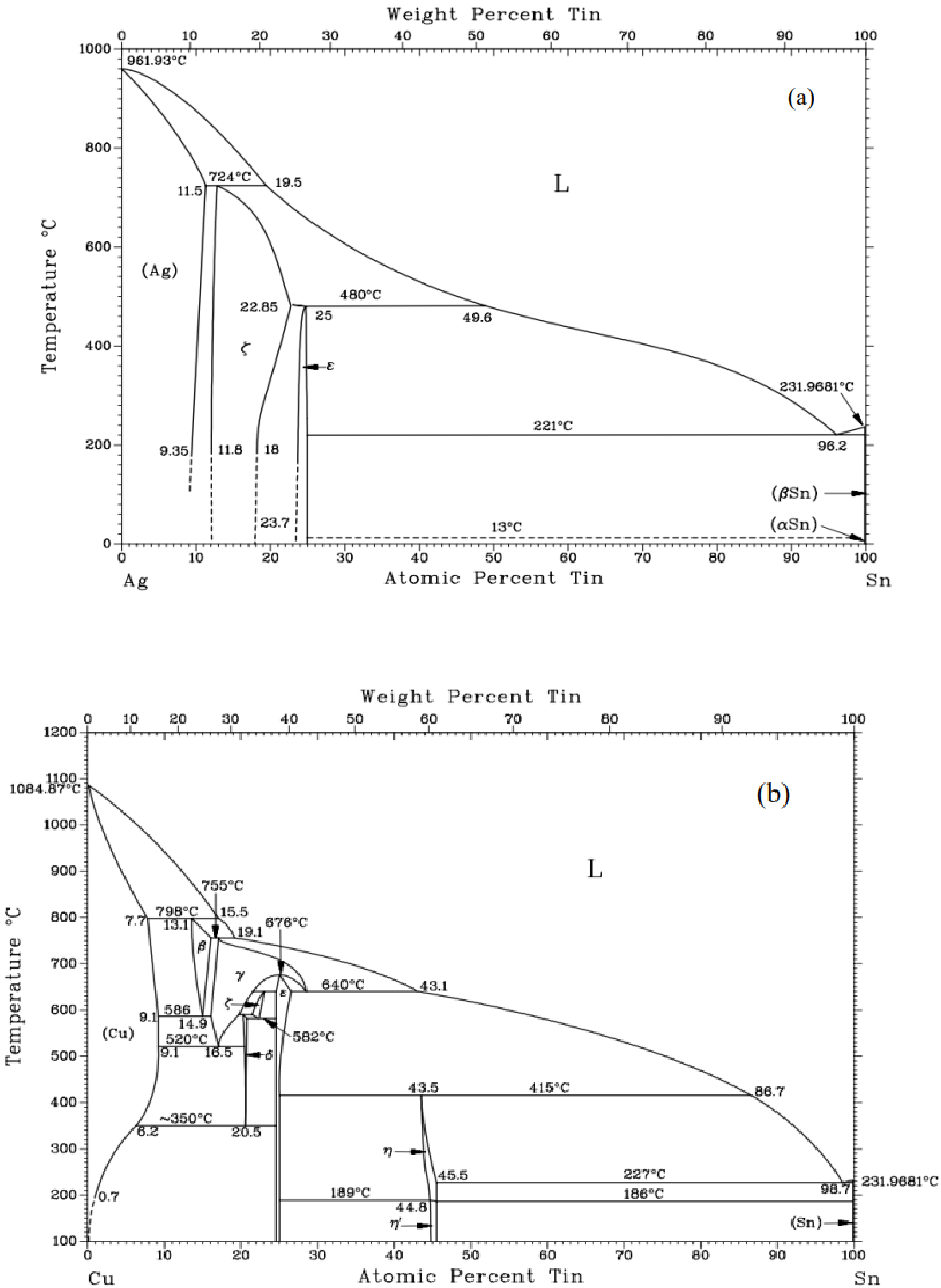

Figure 1. (**a**) Ag-Sn phase diagram; (**b**) Cu-Sn phase diagram [19].

Generally, Ag-based brazing filler metals with lower than 30% Ag content are considered to be low-Ag filler metals, and those with over 30% Ag content are classified as high-Ag filler metals. Through addition of Zn into the Ag-Cu alloys, the Ag-Cu-Zn series brazing filler metals with a lower melting temperature can be obtained, but the saturated vapor pressure of Zn is high, and the addition of Zn should not be excessive. Therefore, the addition of Sn is important for further reducing the Ag content without affecting the temperature of the brazing filler metals. Some research results on the influences of Sn content on melting characteristics of the Ag-Cu-Zn series brazing filler metals are listed in Table 2 [21–23]. It was found that the solidus temperatures and liquidus temperatures of both the high-Ag and the low-Ag Ag-Cu-Zn brazing filler metals decreased with the increasing content of Sn. The melting temperature range of the low-Ag filler metals increased gradually with the increasing Sn content, while that of the high-Ag filler metals showed an opposite trend.

Table 2. Melting characteristics of some Ag-Cu-Zn series brazing filler metals with different contents of Sn [21–23].

No.	Ag%	Cu%	Zn%	Sn%	Ni%	Temperature/°C	Melting Temperature Range/°C
1	20	Bal	38	1.5	1.3	763.9–803.7	39.8
	20	Bal	32	2.5	-	735–782	47
	20	Bal	36.5	4	1.2	696.9–787.5	70.6
	20	Bal	32	4.5	-	737–771	34
	20	Bal	32	6.5	-	670–750	80
	20	Bal	32	7.5	-	656–738	82
2	Bal	20	12	-	-	665–760	95
	Bal	20	16	5	-	612–678	66
	Bal	22	18	8	-	590–635	45

The traditional Ag-Cu-Zn-Cd brazing filler metals have superior comprehensive properties among all the Ag filler metals, and were widely used. However, the addition of the toxic Cd into the brazing filler metals has been prohibited, since the concept of green environmental protection strikes a deep chord in the hearts of the people. Through a large quantity of investigations, it was found that only the In and Sn elements can replace Cd in Ag-based filler metals, and the price of In is high. Therefore, the Ag-Cu-Zn-Sn filler metals are recognized as a substitute for the Ag-Cu-Zn-Cd filler metals [24].

To reveal the effects of Sn on the melting characteristics of Ag-Cu-Zn-Sn filler metal, Wang et al. prepared a thin Sn layer on the BAg34CuZnSn (Ag34-Cu36-Zn27.5-Sn2.5) filler metals following a process of electric cleaning, water washing, activation, water washing, brush plating, and water washing. Table 3 presents the melting characteristics of the BAg34CuZnSn filler metals with different weight ratios of the brush-plated Sn layer to the BAg34CuZnSn alloy [25]. It is obvious that with the increasing Sn content, the solidus temperature and the liquidus temperature of the filler metals showed a linear decreasing trend, and the melting temperature range decreased gradually; whereas, compared with the method of adding the Sn element into the filler metals through smelting, the brush-plated Sn has less of an effect on the melting characteristics.

Table 3. Melting characteristics of BAg34CuZnSn brazing filler metals with different contents of the brush-plated Sn layer [25].

Weight Ratio of the Sn Layer to the BAg34CuZnSn	Solidus/°C	Liquidus/°C	Melting Temperature Range/°C
0	700.0	731.0	31.0
0.5	697.5	724.0	26.5
1.0	693.0	717.0	24.0
1.5	690.0	712.0	22.0
2.0	686.0	705.5	19.5

2.2. Influences of Sn on the Wettability of Ag-Based Brazing Filler Metals

The wettability of the brazing filler metals is crucial to the gap-filling ability and quality of the brazed joints, and is usually measured through the gap-filling test and the spreading test [20]. It has been revealed that the wettability of the Ag60Cu brazing filler metal with 4 wt % of Sn was close to that of the Ag72Cu filler metal [16], and both the two filler metals showed a superior spreading property on the Cu substrate. Figure 2 shows the capillary rise heights of the Ag60Cu-xSn filler metals in gaps with different widths [15]. In the figure, it can be seen that when the gap width was lower than 0.1 mm, the capillary rise heights of the filler metals with the increasing contents of Sn were almost the same, demonstrating that the content of Sn had little influence on the capillary rise height.

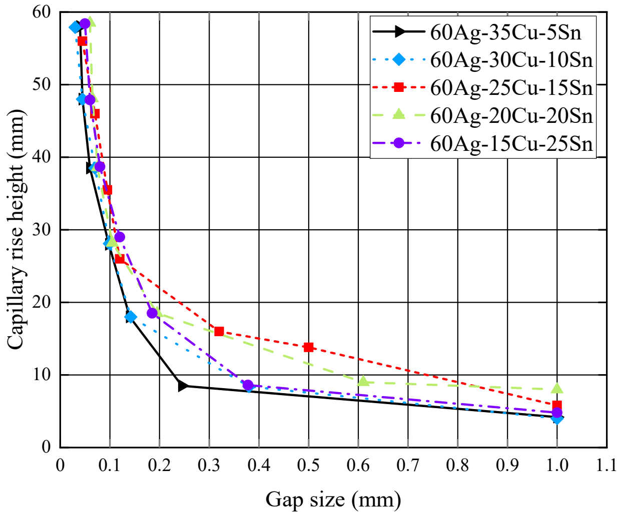

Figure 2. Capillary rise heights of Ag60Cu-xSn brazing filler metals in gaps with different widths [15].

Figure 3 shows the influence of Sn on the spreading performance of the BAg20CuZn (Ag20-Cu44-Zn36) filler metals bearing 1.5% In. As in the figure, with increasing Sn content, the spreading area of the filler metal showed an an increasing trend [26]. When the content of Sn increaseds from 1.5 wt % to 3.0 wt %, the spreading area increased from 207.7 mm^2 to 320.6 mm^2, indicating that the wetting property of the filler metal had been greatly improved. The reason was that the flowability of the liquid metal could be measured by its viscosity, and higher viscosity corresponded to worse flowability, while the viscosity was inversely proportional to the superheated degree of the liquid metal [27]. Therefore, at the same brazing temperature, the brazing filler metal, with a lower melting temperature, had a higher superheating degree, resulting in lower viscosity and higher flowability. On the contrary, when the melting temperature of the filler metal increased, the flowability decreased [28,29].

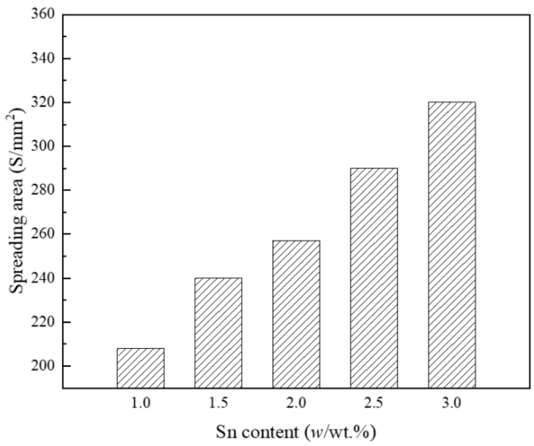

Figure 3. Variations in the wetting area of BAg20CuZnIn filler metals with increasing Sn content [26].

In another study, the Sn layers were plated on BAg34CuZnSn filler metals by the combination of electroplating and thermal diffusion; the variation of the wetting area with the change in the Sn content is shown in Figure 4 [30], in which it can be seen that the wettability of the filler metals increased with the increasing content of the surface-plated Sn. Some other reports investigated the wettability of BAg35CuZnSn filler metals with electroless-plated Sn [31] and BAg34CuZnSn filler metals with brush-plated Sn [25], and the same conclusion was reached, demonstrating that the Sn element is effective in optimizing the wettability of Ag-Cu-Zn-Sn brazing filler metals.

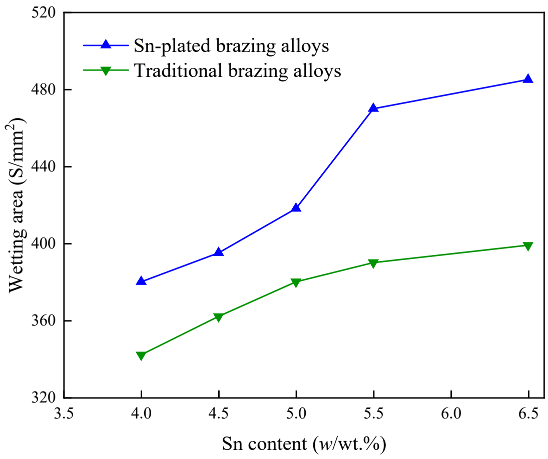

Figure 4. Variations in the wetting area of BAg34CuZnSn brazing filler metal with the increasing content of plated Sn [30].

2.3. *Influences of Sn on the Microstructure of Ag-Based Brazing Filler Metals*

The properties and processing technologies of brazing filler metals are determined by their microstructure [32]. Therefore, it is particularly important to reveal the effect of Sn addition on the microstructure of Ag-based filler metals. Figure 5 shows scanning electron microscope (SEM) images of Ag60Cu filler metals with different contents of Sn that reveal that the microstructure of the filler metals changed obviously with the increasing Sn content [16]. The energy-dispersive X-ray spectrometry (EDS) analysis of the phases of the filler metals showed that the Ag60Cu filler metals were composed mainly of the Cu-rich phase with a Ag solute element (α-Cu) and a Ag-Cu eutectic. With the addition of 2% or 4% of Sn, the filler metals were composed of the α-Cu, the Ag-rich phase with a Cu solute element (α-Ag), and some Ag-Cu-Sn ternary eutectic. With the addition of 8% Sn, a Cu-rich phase with a Sn solute element (β-Cu) appeared. As the α-Cu and α-Ag were ductile phases but the β-Cu was a brittle phase, and a large amount of Cu_6Sn_5 intermetallic compound (IMC) was produced, the forming properties of the Ag60Cu filler metal with 8% of Sn deteriorated sharply. Liu et al. attempted to add Sn and In with a total content of 20% to Ag58Cu22 filler metals, and found that the filler metals had good forming properties only when the content of Sn was lower than 12%, while the filler metals became too brittle to be formed when the content of Sn was higher than 15% [33].

The major phases in Ag-Cu-Zn filler metals include the Ag-based solid solution, the Cu-based solid solution, the Cu-Zn IMC, etc. When the content of Sn in Ag-Cu-Zn filler metals is lower than 4%, the alloys are composed mainly of the Cu-based solid solution, the Cu-Zn IMC, and the needlelike or bulk Ag-based solid solution. With increasing Sn content, the large blocky structure consisted mainly of the Ag-based solid solution, a small portion of Cu-Zn IMC increased obviously (see Figure 6), and the forming properties of the filler metals were optimized accordingly [22]. When the content of Sn in the Ag-Cu-Zn filler metal exceeded 4.5%, the filler metals were composed mainly of the Cu-rich phase, the Ag-rich phase, the Cu-Zn IMC, the $Cu_{5.6}Sn$ IMC, the $Cu_{40.5}Sn_{11}$ IMC, and Cu_3P compounds. Meanwhile, coarse dendrites with a certain directionality appeared in the filler metal, resulting in an obvious decrease in the performance of the filler metals [28].

Figure 7 shows the microstructure of the Cu-20Ag-Zn-xSn alloys with 6.5% and 7.5% Sn, in which more Sn bronze phases appeared, and the segregation was more serious with increasing Sn content, which led to a gradual increase in the brittleness of the filler metals, as the Sn bronze was a brittle phase [21].

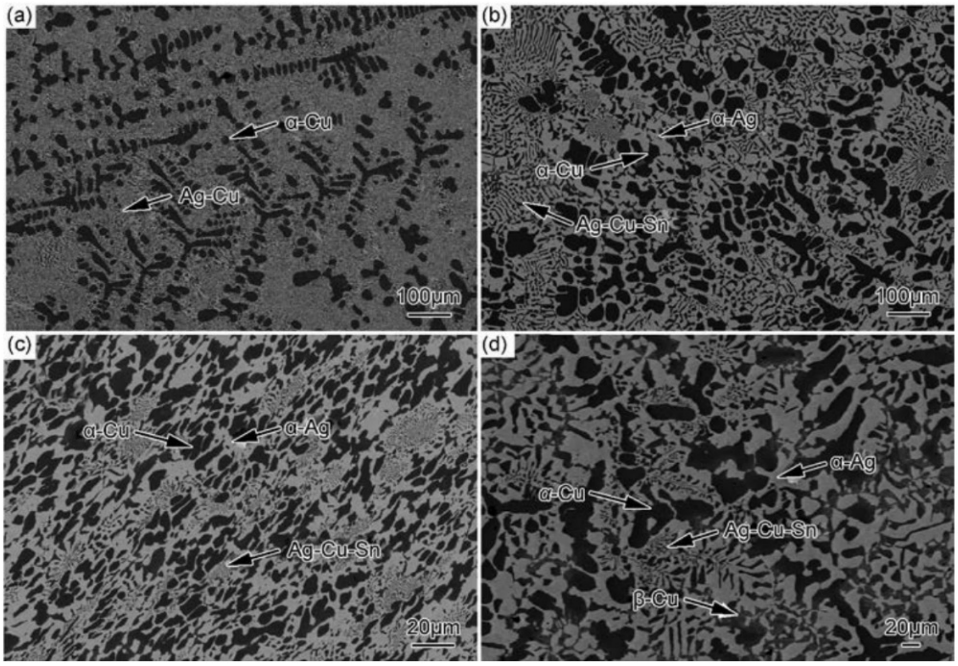

Figure 5. Microstructures of Ag60Cu-xSn filler metals containing (**a**) 0%, (**b**) 2%, (**c**) 4%, and (**d**) 8% Sn [16].

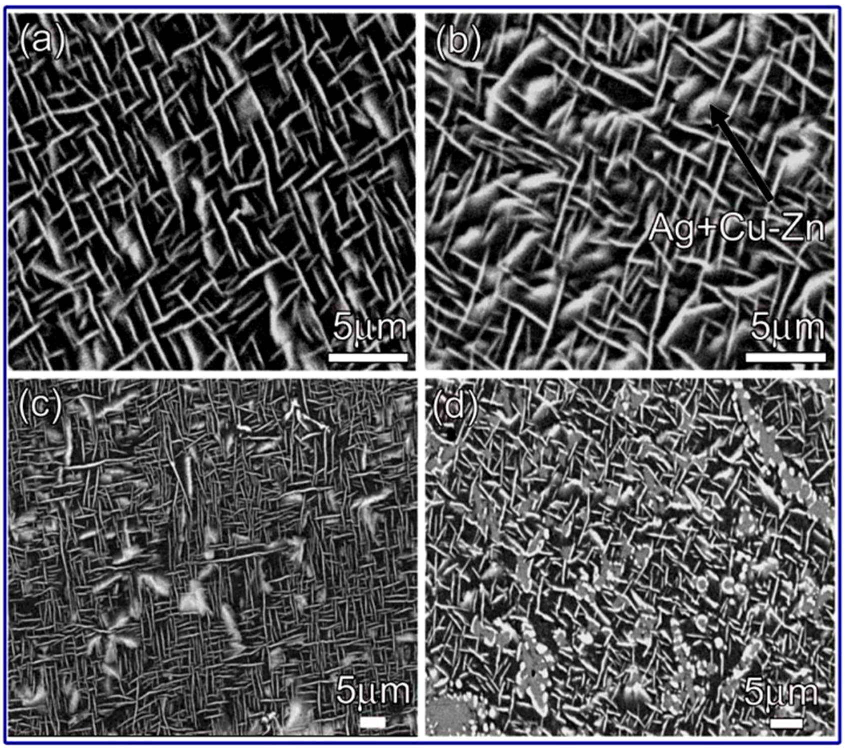

Figure 6. BSE images of Ag-Cu-Sn filler metals with (**a**) 1.5%, (**b**) 2.2%, (**c**) 3%, and (**d**) 4% Sn [22].

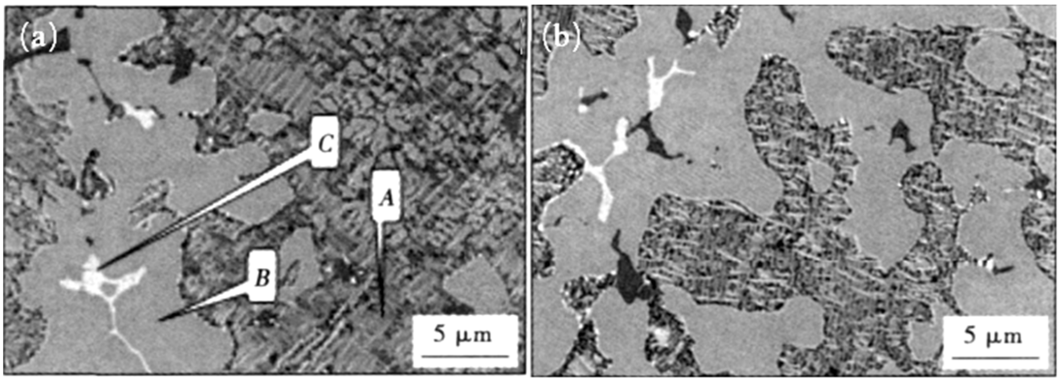

Figure 7. Microstructures of Cu-20Ag-Zn-xSn with (**a**) 6.5% and (**b**) 7.5% Sn [21].

The XRD spectrum and interfacial morphology of the BAg34CuZnSn filler metal with a brush-coated Sn layer are shown in Figure 8 [34]. As exhibited in Figure 8a, the crystalline grains of the brush coated Sn showed an obvious preferred orientation of (200) and (112). In Figure 8b, it can be seen that the bonding interface between the filler metal and the Sn coating was flat and compact, and the Sn coating was uniform in microstructure, with no defects such as pores and inclusions. The results demonstrated that the plating method could decrease the internal stress between the Sn coating and the filler metal substrate, and improveds the bonding between the coating and the filler metal, making the bonding between the filler metal and the Sn coating dense, and without defects. In this way, forming of the AgCuZnSn filler metal with high Sn content could be realized.

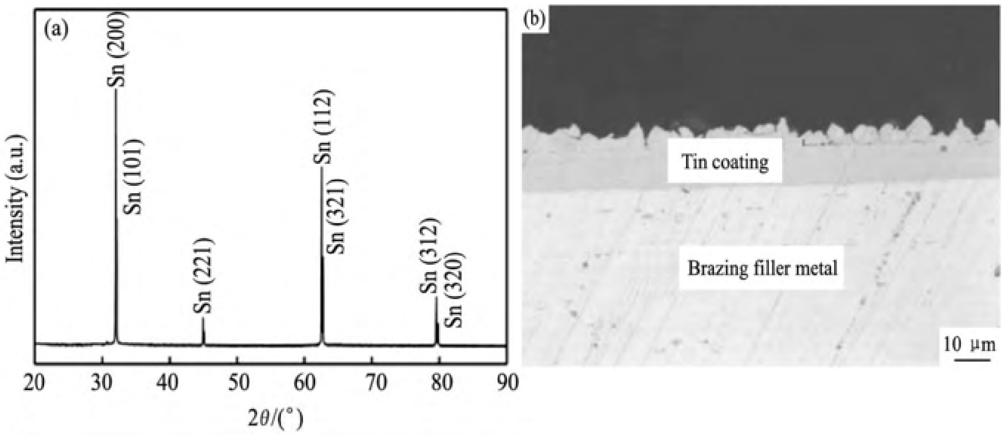

Figure 8. Analysis results of BAg34CuZnSn filler metals with a plated Sn coating: (**a**) XRD spectrum of the Sn coating; (**b**) interface morphology [34].

2.4. Influences of Sn on the Mechanical Properties of Joints Brazed by Ag Filler Metals

During the service process of brazed devices, the mechanical properties of the brazed joints are the key factors that affect the reliability of the joints [35]. At present, investigations of mechanical properties of brazed joints focus mainly on the shear strength and the tensile strength. The shear strength of Cu/Cu joints brazed by using Ag60Cu filler metals with different contents of Sn is shown in Figure 9. As shown in the figure, when the content of Sn was 5%, the average shear strength of the brazed joints was 210 MPa. When the content of Sn increased to 10%, the shear strength increased by 9%. In contrast, when the Sn content was over 10%, the shear strength of the brazed joints decreased [15], because the volume ratio of the brittle Cu-Sn IMCs increased with the increasing Sn content [36].

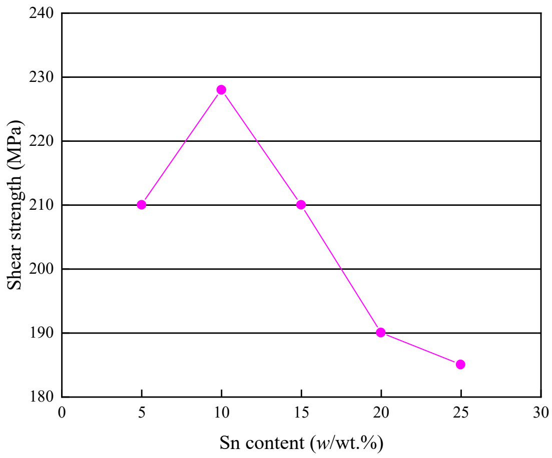

Figure 9. Shear strengths of Cu/Cu joints brazed by using Ag60Cu filler metals with different contents of Sn [15].

Figure 10 shows the shear strength of the stainless steel/stainless steel joints brazed by using Ag-Cu-Zn filler metals with different contents of Sn [22]. As shown in the figure, the shear strength increased firstly and then decreased with the increasing Sn content in the filler metals, because the alloying of Sn could decrease the brazing temperature of the filler metals, which made grain coarsening less likely to occur in the joining zone of the substrate material, and the lower temperature could decrease the residual stress. In addition, the addition of Sn improved the strength of the Ag-based filler metals through solid solution strengthening, and the introduction of Sn formed a Cottrell atmosphere that pinned the dislocation and hindered the dislocation slip [37], thus the joints' strength was improved. However, when the content of Sn was too high, a brittle structure appeared in the brazing filler metals and sharply decreased the joints strength. Similarly, some other reports also obtained the same test results [21]. Wang et al. plated the Sn coating on BAg45CuZn [38] and BAg50CuZn filler metals [39], and found that when the content of Sn was too high, the brittle phases that appeared in the filler metals were Cu_5Zn_8, $Cu_{41}Sn_{11}$, Cu_3Sn, and Ag_3Sn, and the brazed joints fractured mainly in a brittle mode, with a small ductile fracture.

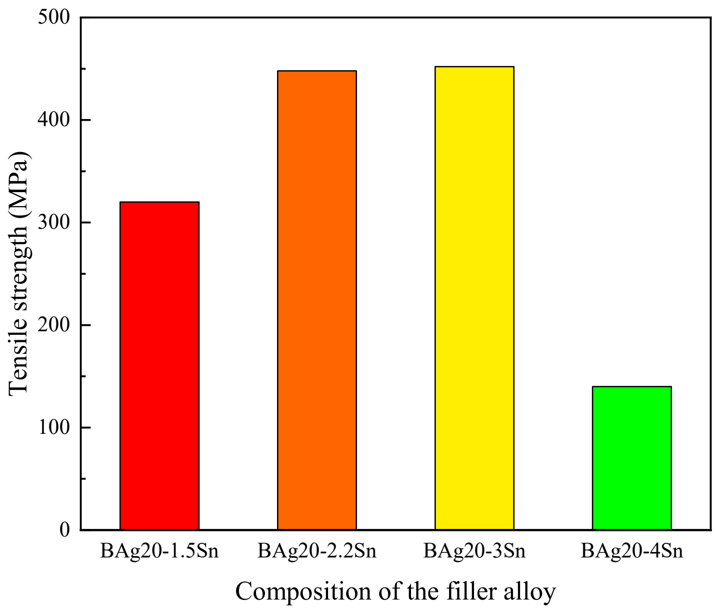

Figure 10. Tensile strengths of stainless steel/stainless steel joints brazed by using Ag-Cu-Zn filler metals with different contents of Sn [22].

The tensile strength of the stainless steel/stainless steel joints brazed by using Ag-Cu-Zn-Sn filler metals were higher than 300 MPa and could satisfy the application requirements in most cases [40]. Figure 11 shows the tensile strength of the 316LN stainless steel joints brazed using a BAg34CuZnSn filler metal with a plated Sn coating, and a filler metal of the same composition but manufactured through the traditional melting and drawing processes [41]. At the same Sn content, the joints brazed using the traditional filler metal were a little higher, because the Sn distribution in the traditional filler metal was more uniform, and the Sn mainly played the role of solid solution strengthening and precipitation strengthening, with Ag_3Sn and $Cu_{41}Sn_{11}$ as the main strengthening phases [23]. In contrast, the Sn coated on the Ag filler metal strengthened mainly through an aging strengthening mechanism. The Sn was relatively uniform in the filler metal, but there was local segregation, and the strengthening phases were mainly Ag_3Sn and Cu_3Sn [39]. When the content of Sn was 5.5%, the brazed joints showed the highest tensile strength.

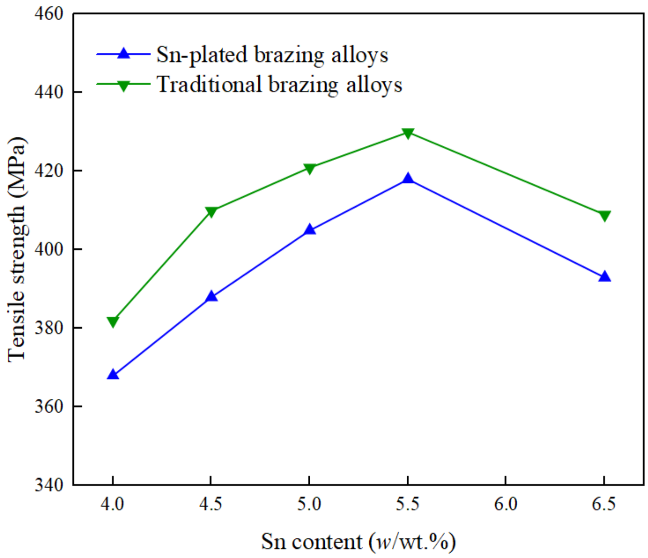

Figure 11. Tensile strengths of 316LN stainless steel joints brazed using BAg34CuZnSn filler metals with a plated Sn coating and a filler metal of the same composition but manufactured through the traditional melting and drawing processes [41].

3. Influences of Sn on Cu-Based Brazing Filler Metals

3.1. Influences of Sn on the Melting Characteristics of Cu-Based Brazing Filler Metals

Cu-based brazing filler metals have a great variety and are widely used. Among the Cu filler metals, the Cu-P series filler metals have a low melting point, good flowability, a low price, and a self-brazing property when brazing pure Cu, so they are widely used to braze pure Cu [42,43]. However, for brazing of low-melting-point Cu alloys such as brass, the melting temperature of Cu-P solder is too high. If using Cu-P filler metal containing Ag, the cost will be much higher, which limits its application [44]. Therefore, to decrease the melting point of Cu-P filler metals and reduce the use of Ag, Sn is usually added into Cu-P filler metals, and ternary or multicomponent Cu-P-Sn-based filler metals can be obtained.

It was found that the addition of 1% Sn into a Cu-6P alloy could obviously decrease the liquidus temperature, and the liquidus temperature decreased by about 100 °C when the content of Sn was increased to 6% [4]. Table 4 presents the melting temperature of Cu-5P filler metals with different contents of Sn, in which it can be seen that the melting point of the filler metals decreased with the increasing Sn content [45].

Table 4. Melting temperatures of Cu-5P filler metals with different contents of Sn [45].

Cu-5P Filler Metals with Different Contents of Sn	Liquidus Temperature Measured by DSC/°C
Cu-5P	923
Cu-5P-1Sn	729
Cu-5P-4Sn	676
Cu-5P-10Sn	659

Amorphous Cu-P filler metal is a new brazing material with an atomic arrangement that basically retains the structure of the liquid metal; that is, the long-range disorder and short-range order. This structure feature gives it many excellent properties [46]. In the mid-1970s, the "amorphous" technology moved from laboratory to industrial application in industrially developed countries. The "Allied" company of the United States systematically investigated the amorphous Cu-P filler metal and named it as the MBF2000 series, but this filler metal was brittle and had a low strength [47]. At present, Cu-Ni-P amorphous filler metals have acquired a relative wide application. For example, the Cu-Ni-Sn-P amorphous filler metal named STQ501 has excellent properties, and the addition of Sn decreases its melting temperature. In the past 20 years, in order to further explore the influence of Sn on properties of amorphous Cu-Ni-P filler metals, many experts and scholars have been committed to this field. Zhang et al. prepared amorphous Cu68.5Ni15.7Sn9.3P6.5 alloys by rapid solidification technology, and the differential thermal analysis (DTA) measurement results revealed that the addition of Sn made the solidus temperature and the liquidus temperature of the amorphous alloys much lower than that of Cu-6.5P alloys [48]. Figure 12 shows the liquidus temperature of amorphous Cu-5P-2Ni filler metals with different contents of Sn [49], and demonstrates that the Sn addition greatly decreased the melting temperature of the Cu-5P-2Ni filler metals. With further addition of Sn, the rate of decrease in the melting temperature slowed, which was similar to the variation law in melting temperature of Cu-P-Sn ternary filler metals with an increasing Sn content [4].

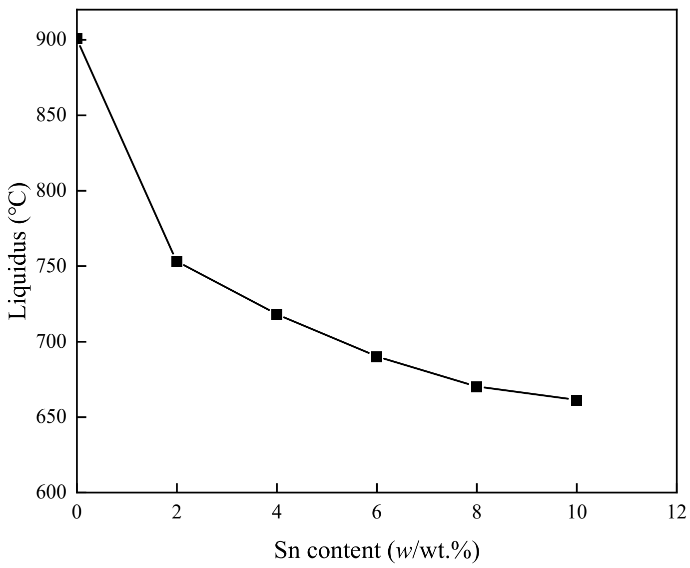

Figure 12. Liquidus temperatures of amorphous Cu-5P-2Ni filler metals with different contents of Sn [49].

The Sn element added into Cu-Zn filler metal through smelting can decrease the melting temperature, but the Sn contents in the Cu-Zn-Sn filler metals manufactured in this way are very low; for example, they are only 1% in HS221. If the Sn content is too high, the plasticity of the filler metal will deteriorate, and it will be difficult to be formed [50]. As a result, application of Cu-Zn filler metals with high Sn content is greatly limited.

Dong et al. prepared a Sn layer on BCu68Zn filler metal through hot dipping, which significantly increased the Sn content in the filler metal, and a metastable Ag-saving, Cu-based filler metal was obtained. The melting characteristics of the BCu68Zn filler metals with different contents of Sn (wt %) are presented in Table 5 [51].

Table 5. Melting characteristics of BCu68Zn filler metals with different contents of Sn [51].

Content of Hot-Dip-Coated Sn/wt %	Solidus/°C	Liquidus/°C	ΔT/°C
0	919.0	949.0	30.0
1.6	911.8	940.5	28.7
3.2	896.2	920.3	24.1
4.8	872.5	894.5	22.0
6.4	856.0	875.0	19.0

3.2. Influences of Sn on the Wettability of Cu-Based Brazing Filler Metals

An experiment carried out by Huang et al. revealed the optimization mechanisms of the Sn element on the wettability of Cu-6.5P filler metals [52]. The solubility of Sn in Cu was very low, and an appropriate amount of Sn could form a solid solution with Cu to improve the wettability of the filler metals, but an excess amount of Sn could not completely dissolve into the Cu. Meanwhile, the Sn oxide could hardly be reduced by P, resulting in poor wettability. This explanation fits with the wetting and spreading test results for Cu-5P filler metals obtained by Yang et al. [45].

The addition of Sn can also significantly improve the wettability of amorphous Cu-P filler metals, especially the wettability of ferrous metals such as Fe and Ni. Yang et al. [49] found that the melting range of Cu-5P-2Ni filler metal was quite wide. When the filler metals were heated to the two-phase zone, the liquid phase melted and flowed away under the action of the flux; if the remaining solid phase with a higher melting point did not melt when the filler metals were continually heated, the tumor was formed. When 6% of Sn was added, the melting range became narrower, the melting temperature was compatible with the active temperature of the flux, and the spreading property of the filler metals was superior and suitable for brazing of Cu-steel dissimilar metals.

At present, there have only been a few studies on the influence of Sn on wettability of Cu-Zn filler metals. From the known studies, it was found that the Sn element played a positive role in the wettability of Cu-Zn filler metals, and the mechanism was similar to the influence of Sn on Ag-Cu-Sn filler metals [51].

3.3. Influences of Sn on the Microstructure of Cu-Based Brazing Filler Metals

Crystalline Cu-P filler metals generally consist of the α-Cu solid solution matrix and the Cu_3P compound, as shown in Figure 13 [19], and the amount of the matrix determines the property of the filler metals [14]. Figure 14 shows the microstructure of as-cast Cu-6.5P-xSn filler metals [52]. When the content of Sn in the filler metals increased from 0% to 0.8%, the microstructure of the filler metals gradually changed from a flake eutectic structure (Cu_3P + α-Cu solid solution) into a lamellar structure, and then transformed into equiaxed grains. Then, when the Sn content was increased to 1%, the eutectic structure of the filler metals was elongated and transformed toward the lamellar structure, because the Sn element could form a low-melting eutectic with the Cu and P elements. The low-melting eutectic segregated at the grain boundary, which hindered the growth of the lamellar eutectic structure, and promoted the fragmentation and spheroidization of the solid solution dendrites, causing the filler metals to transform into equiaxed grains. This is the reason why an appropriate addition of Sn can improve the mechanical properties of filler metals.

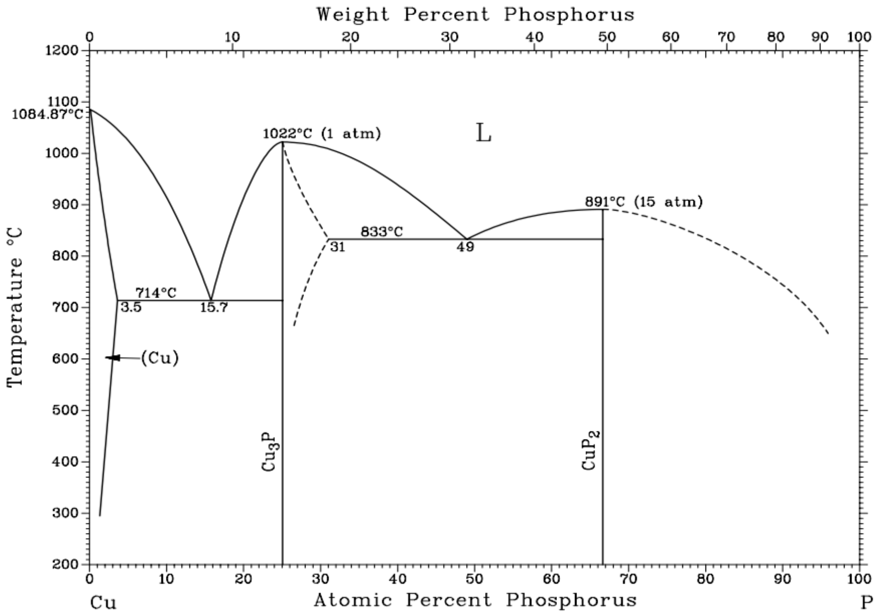

Figure 13. Cu-P phase diagram [19].

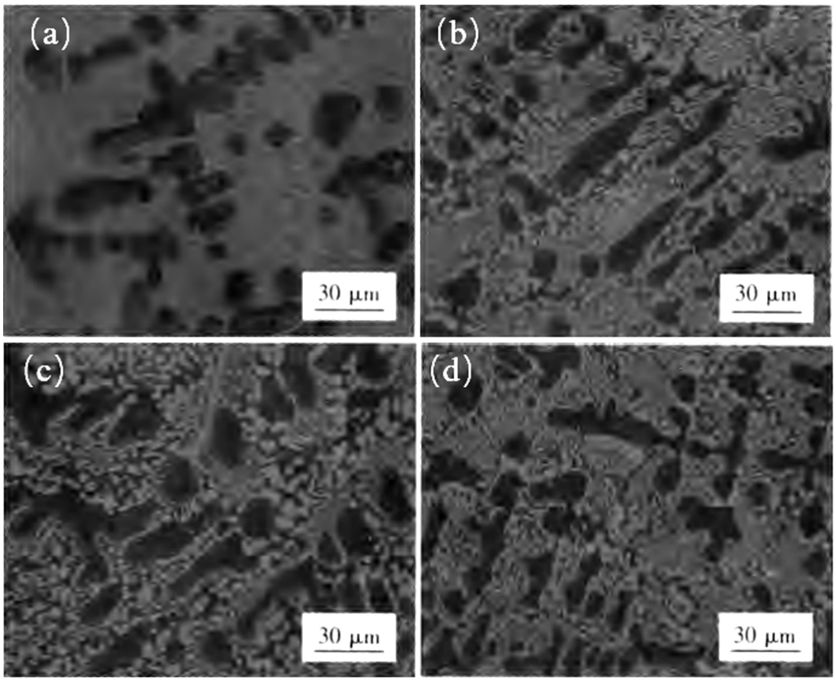

Figure 14. Microstructures of as-cast Cu-6.5P-xSn filler metals with different contents of Sn: (**a**) Sn 0%; (**b**) Sn 0.5%; (**c**) Sn 0.8%; (**d**) Sn 1% [52].

To solve the high brittleness and poor formability problems of the Cu-P-Sn filler metals with a relative high content of Sn, Pashkov et al. prepared amorphous Cu-P-Sn (P14 filler metals) by the rapid condensation method, and found that the influences of Sn on properties of amorphous and crystalline Cu-P-Sn filler metals were basically the same [53]. The amorphous Cu-P-Sn filler metal was composed of a saturated solid solution with a uniformly distributed Cu_3P phase.

Figure 15 shows the optical micrographs of the 60Cu-Zn-0.6Si and the 60Cu-Zn-0.6Si -0.6Sn filler metals. In Figure 15a, huge equiaxed grains of the α + β phases can be seen, while additions of 0.6 wt % Sn enlarged the volume fraction of the β phase in the α + β structures, as shown in Figure 15b. It is clear that the α phase in the 60Cu-Zn-0.6Si-0.6Sn filler metal was smaller than that in the 60Cu-Zn-0.6Si filler metal, which demonstrated that the Sn addition decreased the size of the α phase [54].

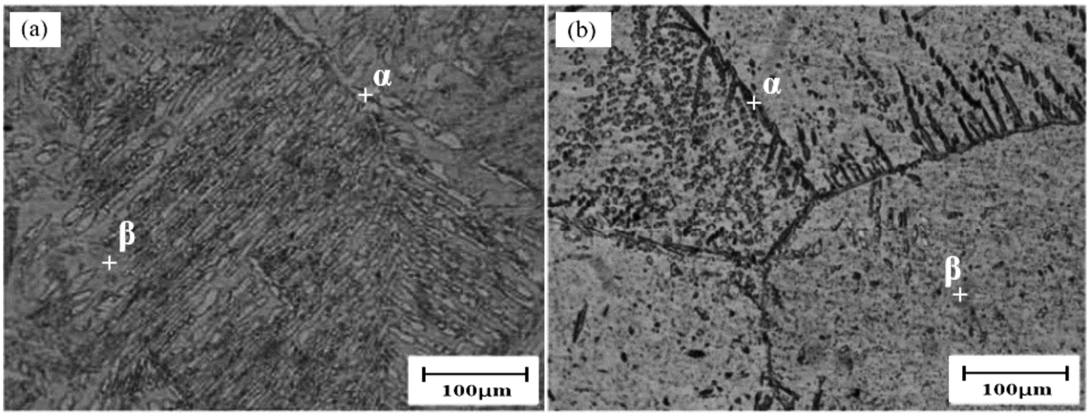

Figure 15. Optical micrographs of (**a**) the 60Cu-Zn-0.6Si and (**b**) the 60Cu-Zn-0.6Si -0.6Sn filler metals [54].

3.4. Influences of Sn on the Mechanical Properties of Joints Brazed by Cu-Based Filler Metals

The tensile strength of the Cu/Cu joints brazed by using crystalline Cu-6.5P filler metals with different Sn contents is shown in Figure 16 [55]. When the content of Sn was lower than 6%, the strength of the brazed joints increased gradually with the increasing Sn content. When the content of Sn was higher than 6%, the tensile strength of the joints decreased with the increasing Sn content. The strength of the brazed joints depended mainly on the metallurgical bonding degree between the diffusion layer and the base metal, as well as the distribution and size of the brittle structure in the residual layer formed at the center of the brazing seam. When the content of Sn was 6%, the thickness of the diffusion layer was moderate, and the brittle phase was uniformly distributed. The Sn-containing Cu-based solid solution that wrapped the brittle phase had good plasticity and could hinder the crack propagation, which showed the dispersion strengthening effect and gave the joints the highest strength. When the content of Sn was higher, the diffusion of Sn into the base material during the brazing process was stronger, while the solid solubility of P in Cu was limited, and P could easily react with Cu. There was a large amount of Cu in the brazing seam, and the P element concentrated at the center of the brazing seam through uphill diffusion, forming a small amount of α solid solution and a large amount of Cu_3P hypoeutectic brittle phase, making the microstructure become coarse again, and the coarse brittle structure at the center of the brazing seam was detrimental to the mechanical properties of the joints. Based on this, it can be predicted that an appropriate amount of Sn element can improve the brazing performance of brazing filler metals.

Figure 17 shows the shear strength of Cu/304 stainless steel joints brazed by using amorphous Cu-5P-2Ni filler metals with different contents of Sn [49]; the strength of the joints brazed by using amorphous Cu-5P-2Ni filler metals was low, only about 65 MPa. When the Sn was added into the filler metals, the strength of the brazed joints was improved, and the strength increased gradually with the increasing Sn content. When the Sn content was 8%, the shear strength of the joints could reach 122.5 MPa, but a further increase of Sn alloying would decrease the strength of the brazed joints. Therefore, proper addition of Sn into amorphous Cu-5P-2Ni filler metals had an obvious effect of improving the strength of the brazed joints, and the action mechanism was similar to that of the Sn element on crystalline Cu-based filler metals.

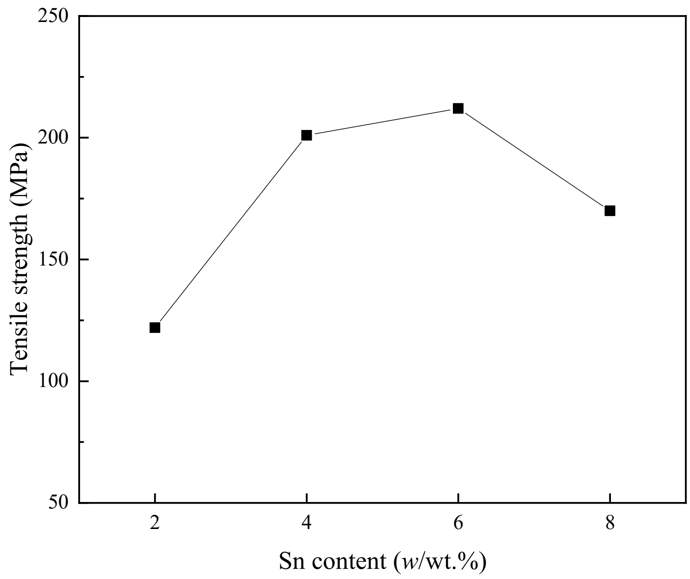

Figure 16. Effects of Sn content on the tensile strengths of Cu/Cu joints brazed by using crystalline Cu-6.5P filler metals [55].

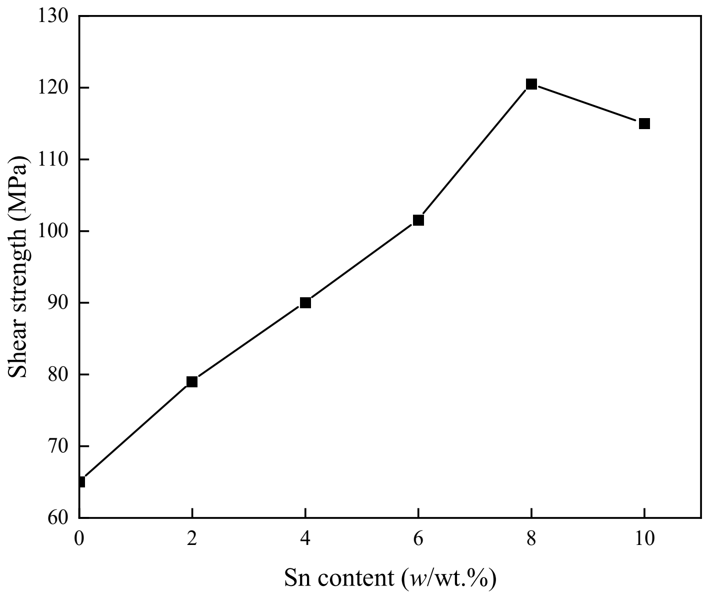

Figure 17. Relationship between the shear strength of Cu/304 stainless steel brazed joints and the content of Sn in the applied amorphous Cu-5P-2Ni brazing filler metals [49].

The tensile strengths of Q235 carbon steel joints brazed using BCu68Zn filler metals with different contents of Sn are shown in Figure 18 [56]. When using BCu68Sn with no Sn, the tensile strength was 318.24 MPa. With increasing Sn content, the strength increased gradually, and reached the maximum value when the content of Sn was 1.6%. Then, it decreased with increasing Sn content. The reason was that the atomic radius of Sn is large, and when the content of Sn was low, it could dissolve in the α phase matrix, and played the role of solid solution strengthening. In contrast, the solubility of Sn in the α phase was relatively low. With increasing Sn content, the Sn and Cu formed brittle compounds, which distributed in the β phase with relatively poor plasticity or the γ phase with extremely poor plasticity, resulting in the decrease in tensile strength of the brazed joint.

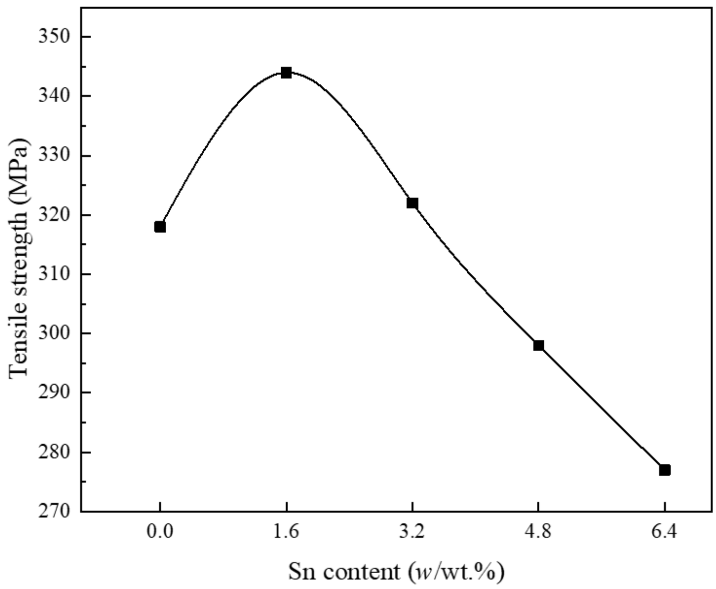

Figure 18. Tensile strengths of the Q235 carbon steel joints brazed using BCu68Zn filler metals with different contents of Sn [56].

4. Conclusions and Prospects

In conclusion, both Ag-based and Cu-based brazing filler metals containing Sn have been widely applied in many engineering fields. By summarizing the effects of Sn on the melting temperature and wettability of the filler metals, we found that the Sn element can significantly decrease the melting point and improve the wettability. In terms of the microstructure and the mechanical properties, proper addition of Sn can optimize the microstructure and improve the comprehensive properties of the filler metals, while excessive addition of Sn will form brittle IMCs and decrease the mechanical properties of the filler metals.

At present, the high price of Ag restricts the research and promotion of high-Ag brazing filler metals, while regulating the properties of Ag-based filler metals through a low addition of Sn is not ideal for Ag saving and property modifications. There is a brittle phase in Ag-based filler metals with high Sn content that decreases the tensile strength and greatly limits the application. For Sn-containing Cu-based filler metals, a lower melting temperature can be obtained, while Cu-based filler metals with high Sn are too brittle to be formed into brazing wire. Therefore, there is still a long way to go in the research and development of Ag-based and Cu-based brazing filler metals with high Sn content.

In general, the development direction of Sn-containing Ag-based and Cu-based brazing filler metals can be summarized as follows:

(1) Improvement of the mechanical properties: although Sn-containing brazing filler metals have good melting characteristics and wettability, their mechanical properties are still lower compared with the Cd-containing filler metals. Improving the properties of Sn-containing brazing filler metals through multialloying and the addition of nanoparticles is still the research focus in the future. For instance, the mechanical properties and reliability of lead-free solder with nanoparticles could be significantly improved [57].

(2) Innovation of the processing technologies: the preparation of Sn-containing filler metals can be conducted with new processing technologies such as in situ synthesis, plating diffusion combination, and powder electromagnetic compaction. These processing technologies for brazing filler metals will become a new research hotspot. Long [58] and Hu [59] et al. have made some progress in preparing Sn-containing brazing filler metals by in situ synthesis and electromagnetic compaction, respectively.

(3) Optimization of the brazing technology: the evolution in the phase structure of the seam brazed by using Sn-containing filler metals under different conditions, especially the evolution of the IMCs, needs to be tracked, as well as how the Sn element migrates during the brazing process, and how the existence of Sn in the phases is conducive to the optimization of the brazing technology.
(4) Full-scene application aspect: the service environment of brazing filler metals is usually complex, and will face a multiple-field coupling effect in practical applications. Therefore, it is also necessary to study the reliability of the joints brazed by using Sn-containing filler metals under the multifield coupling condition.

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