TECHNICAL ARTICLE

Microstructural Evaluation of Copper Brazed Joints Using Silver-Based Filler Metal

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Abstract

The oxy-acetylene torch brazing of copper tubes using silver-based filler metals (Ag-Cu-Zn-Cd) was investigated in this study. Filler metals containing silver content of 15% and 35%, designated by BR15 and BR35, were used to assess the influence of the silver content in the microstructure and mechanical performance of brazed joints. The brazed joints microstructure was analyzed by means of optical microscopy, scanning electron microscopy, and energy-dispersive spectroscopy. The microstructures of the BR15 and BR35 samples were composed mainly of Ag–Cd-rich phase, solid solution of Cu–Zn, and a eutectic structure of Ag and Cu. The increase in the Ag content changed the solidification mode from cellular to dendritic and caused an increase in the eutectic phase volume fraction. The tensile strength of the Ag–Cu–Zn–Cd filler and the phos–copper filler metals was compared. The tensile strength of silver-based filler metal was slightly higher than the phos–copper filler metal brazed joints.

Keywords Torch brazing · Copper · Silver-based filler metal · Microstructure evolution · Mechanical evaluation

Introduction

Copper is a material widely used in industrial piping, mainly in plumbing, heating, cooling, solar heating, air conditioning, and sprinkler systems because of its favorable properties, which include high thermal conductivity, high corrosion resistance, and easy processing [1]. The assembly process by the joining of components is a strategic solution that deserves attention in order to improve product performance.

Brazing is broadly used to join copper alloys and is a joining process with great development in research in several industrial sectors, such as aeronautics, petrochemicals, nuclear and composite materials [2–5]. Copper–phosphorus

brazing filler metals (BCuP) are the most recommended for joining copper and its alloys in various applications, being commonly used for joining copper/copper pipes, mainly in copper pipes for refrigeration and fluid transport systems [6, 7]. Moreover, silver-based filler metals (BAg) emerge as a good alternative for brazing copper pipes with strict mechanical requirements and in environments subject to corrosion and high service temperatures [2].

Silver-based filler metals are widely used in the aerospace, automotive, and construction industries, providing joints with good performance [8]. In addition, the Ag-based filler metal can be used to join a wide variety of ferrous and non-ferrous metals, with the exception of aluminum and magnesium [9, 10]. Filler metal alloys with compositions based on silver and cadmium are the most applied, as they favor the reduction of the brazing temperature and the greater fluidity of the consumable [11, 12]. However, the inherent toxicity of the cadmium, which is a heavy metal, means that restrictive measures have limited its use to applications in electronic and electrical equipments [13]. Moreover, new guidelines such as EU RoHs (European Union), RoHs 2 (China), J-Moss (Japan), and SB20 / SB50 (USA) have also limited the use of this alloy

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in their respective territories, which influences the alloy application in the Brazilian manufacturing chain [14, 15].

The Ag–Cu–Zn–Sn filler metal was created as a substitute for filler metals containing cadmium, having been developed over a long time and having its brazeability being the object of several studies [13, 16–18]. However, these filler metals are unable to achieve melting points as low and reach fluidity levels as good as those containing cadmium. There are several studies in the literature proposing the use of other elements to replace cadmium, such as Sn, Ga, In, Ni, and Ca [13, 19–22], aiming to improve the properties of the filler metal, with the choice of which replacing element depending on the application of the brazed component.

Despite the harmful aspects of the use of cadmium in silver-based filler metals, due to their advantages, they are still widely applied where there is no direct or indirect contact with humans, and there are studies about its use in the union of copper and their alloys [23, 24]. In this context, the high cost of silver is a limiting factor for its widespread use in filler metals, making them used where other types of filler metals cannot be well applied [2, 19]. Therefore, it is very relevant to conduct studies that propose the reduction of silver content in filler metals in order to offer the best performance and cost–benefit ratio, according to the application requirements [18, 19].

Given the above, the present work aims to evaluate the effects of silver content on the mechanical performance and microstructural characteristics of copper pipes joined by oxy-acetylene torch brazing using filler metals with 15% and 35% of silver content. The discussion is focused on how the performance of the joint correlates with the chemical composition of the filler metal. In addition, the mechanical

strength of the silver-based filler metals is compared to that of traditional BCuP filler metal (Phos-copper).

Materials and Methods

Equipment and Accessories

The brazing of the copper tubes was performed in the vertical downflow position using a manual system with a torch as the heat source, while the filler metal was manually added to the brazed joints. In addition, a spark gap was used to ignite the gas mixture, and a flange was used to produce the lap joints. The equipment used for the metallographic preparation of the samples and the mechanical tests will be described in Section "Methods" section. Figure 1 shows the schematic of the brazing process and the detail of the cross section of the tube joint.

Base Metal

Rigid copper tubes were used as the base metal in the brazing process. The class E copper tubes follow the ABNT NBR 13206 standard [25] and are seamless and drawn, with an outside diameter of 3/4" and a wall thickness of 0.035". The material of the tubes is composed exclusively of copper, and its melting point is approximately 1083.5 °C.

Filler Metals and Flux

Two commercial silver-based filler metals with different silver contents were used, one with 15wt.% Ag and the other with 35 wt.% Ag, classified as BR15 and BR35,

Fig. 1 Schematic of the oxy-acetylene torch brazing of tubes in the vertical downflow position
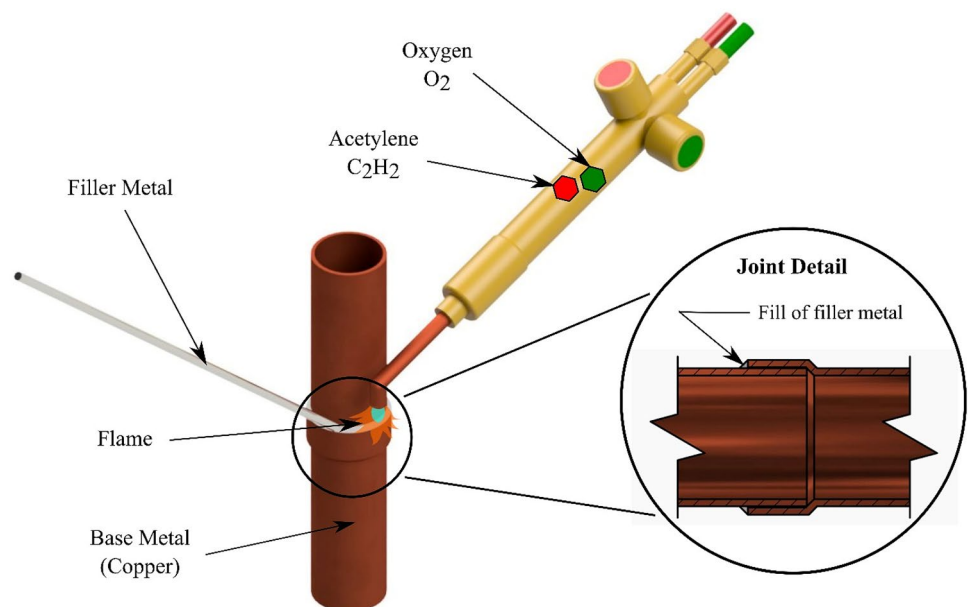
Table 1 Chemical composition and melting range of the silver-based filler metals [26]

Classification	Standard	Composition (wt.%)				Brazing temperature (°C)	Melting range (°C)
		Ag	Cu	Zn	Cd		
BR 15	…	15	43	30	12	702	607–702
BR 35	AWS A5.8 BAg2	35	26	21	18	770	700–780

Table 2 Chemical composition and melting range of the Cu–P-based filler metal [27]

Classification	Standard	Composition (wt.%)		Brazing temperature (°C)	Melting range (°C)
		Cu	P		
BR-FOS-3	DINEN1044CP201	Balanced	6.6–7.4	720	710–820

Table 3 Characteristics of the BR45 flux for brazing using silver-based filler metals

Classification	Standard	Form	Filler metal	Basic application	Acting range (°C)
BR45	…	Paste	Silver alloys	Special tools	550–950

respectively. The BR15 filler metal does not comply with any specific brazing standard, and the BR35 follows the brazing standard AWS A5.8 of the *American Welding Society* (AWS) [26], classified as AWS A5.8 BAg2. Table 1 shows the chemical composition, working temperature, and melting range of the filler metals.

In addition to the silver-based filler metals, the binary Cu–P alloy, known as phos–copper weld (BCuP), was used. A filler metal with 6.6–7.4%wt of phosphorus content was used, classified as BR-FOS-3 and following the brazing standard DINEN1044CP201 [27]. The phos–copper weld was used only to compare the mechanical performance of the brazed joints with the silver-based filler metals and, therefore, was not subjected to microstructural characterization. Table 2 shows the chemical composition, working temperature, and melting range of this filler metal.

A commercial flux specific for silver-based filler metals was used in the brazing process. The flux, referred to as BR45, was supplied in the form of a paste and is not covered by any specific brazing standard. Table 3 presents the temperature range, the filler metal, and the basic application indicated for this type of flux.

Methods

Firstly, the tubes were pre-cleaned using a steel brush and sandpaper to remove oxides and impurities that could affect the wettability of the filler metal. Then, one of the tubes was flanged to form the bell-and-spigot extremity and later fitted and fixed in the brazing position. The flux was applied in the joint region, which was heated using a torch with a gas mixture of oxygen and acetylene, where a neutral type flame was used. The joint was heated locally, and then, the filler metal was added.

The metallography samples were prepared by cutting the brazed joint and exposing the interface between the walls of the two tubes and the filler metal. The samples were cold-mounted using epoxy resin in a mold for embedding to facilitate the handling of the samples in the sanding process, which involved the use of 100-, 180-, 320-, 400-, 600-, 1000-, and 1200-mesh sandpapers. The gritting step was carried out in a metallographic polishing machine, with the samples being rotated at 90° between each sandpaper. Figure 2 shows a schematic of the mounted sample and the cross section prepared for the metallographic analysis.

Then, two polishings were performed, with the first being coarser and performed with 3 μm diamond paste in alcohol-based lubricant. The second and final polishing was performed with 0.05 μm alumina suspended in distilled water. In addition, a chemical etching was carried out to reveal the microstructure of the material using the following solution: 5 ml of ammonium hydroxide (NH_4OH), 25 ml of deionized water (H_2O), and 25 ml of hydrogen peroxide (H_2O_2), using the immersion etching method. Finally, the brazed joint was observed using an optical microscope coupled with a digital camera and a SEM for the microstructural characterization of the material.

For the mechanical characterization, three specimens were produced for each filler metal, that is, three specimens for the BR15, three specimens for the BR35, and three specimens for the BR-FOS-3. Uniaxial tensile tests were performed using a universal mechanical testing machine (EMIC DL10000) following the dimensions and procedures recommended for mechanical tests on small diameter brazed pipes, according to item QB-462.1 (f) of the ASME BPVC. IX-2017 standard [28]. Finally, in the data processing step of the uniaxial tensile tests, the stress was calculated as the rupture load quotient by the cross-sectional area of the base

Fig. 2 Scheme for cutting and cold-mounted of the brazed joint cross-sectional sample for metallographic preparation
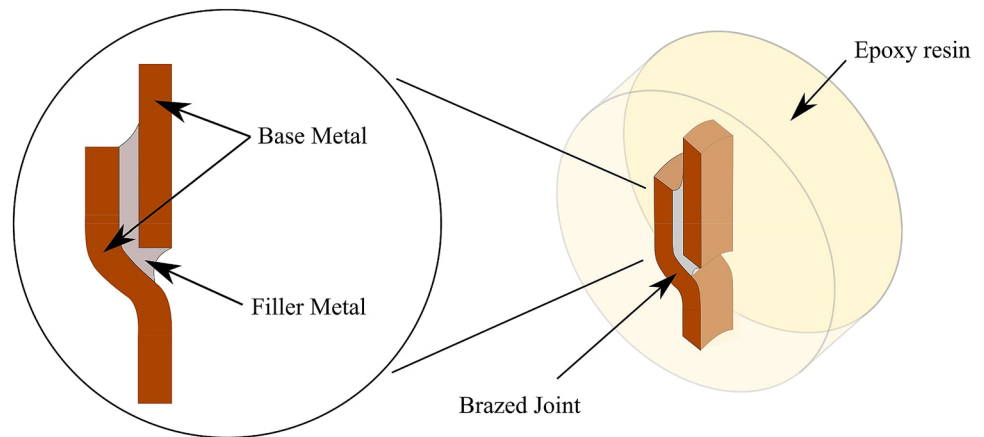
metal, as indicated in item 4.2.3.6. of the AWS B2.2/B2.2 M: 2010 standard [29].

Results and Discussion

### Microstructural Characterization by Optical Microscopy

Analyses were performed by optical microscopy of the brazed joints in the BR15 and BR35 filler metals. Figure 3 shows the microstructure of the brazed joint regions with 15% and 35% silver contents.

Optical microscopy tests on the brazed joints with both consumables indicate the formation of two microconstituents, one lighter and one darker. In the joints obtained with both filler metals, the light microconstituent shows a morphology that indicates that it is a product of primary solidification: In both conditions, the light microconstituent is oriented toward the normal direction of the base metal surface and is predominant at the interface between base and filler metals. However, there is a notable difference between the microstructures observed in the BR15 joint in relation to the BR35 joint.

In the BR15 microstructure, it is possible to notice a prominent predominance of the light microconstituent, with the dark constituent regions having a morphology that indicates it is a product of secondary solidification. Besides, it presents a morphology characteristic of the cellular solidification regime, with the direction of solidification

Fig. 3 Micrographs of brazed joints obtained by optical microscopy of the BR15 and BR35 filler metals
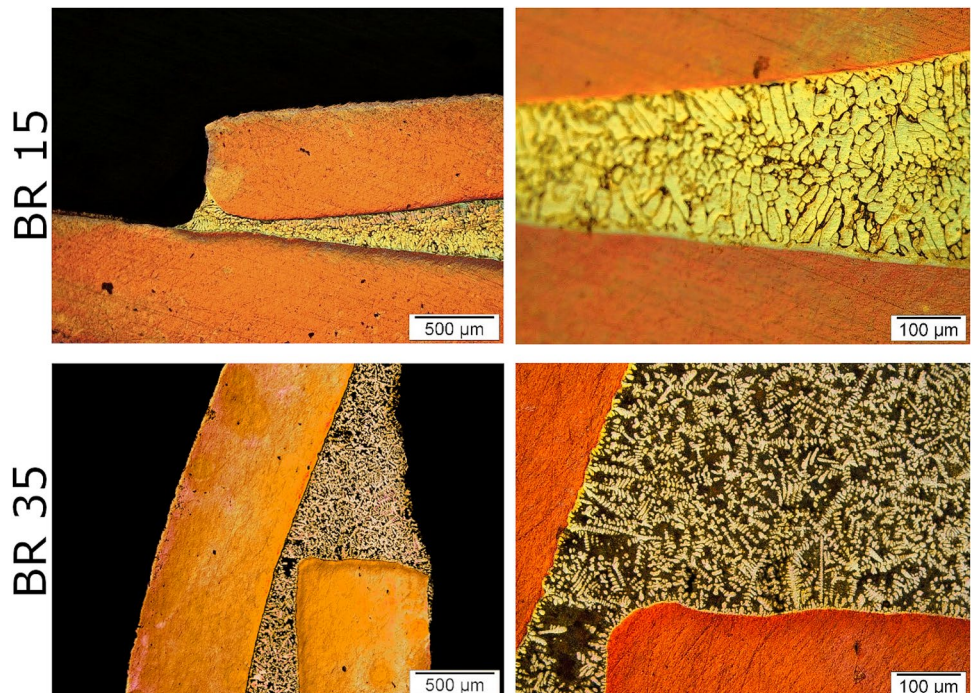
perpendicular to the tube surfaces. The microstructure of the joint with BR35 shows significantly different morphologies, with dendritic morphology and significantly higher content of the dark microconstituent. Microstructural homogeneity is observed throughout the BR35 joint. In the BR15 joint, however, the quantity and distribution of the dark microconstituent, which is a secondary solidification product, are not homogeneous throughout the entire joint.

SEM Microstructural Characterization

To obtain a better understanding of the microstructure developed by the filler metal during the brazing process, scanning electron microscopy tests were carried out using backscattered electron signals in non-etched samples to allow a more accurate identification of the constituents of the microstructure of the joint. The scanning electron microscopy–backscattered electron signal analysis allows distinguishing which phases are present in the brazed joint through the contrast between different chemical compositions. The images obtained with this technique show the phases with higher average atomic weight in lighter tones. In the microstructures resulting from the brazed joints, two distinct phases are visualized in both BR15 and BR35 filler metals.

EDS spectra were collected in the dark and light phases present in the brazed joints with the BR15 and BR35 filler metal. Figure 4 shows the points where the analysis was performed and the respective spectra for both filler metals. The EDS analysis indicates that the observed phases are a solution rich in Ag and Cd, and a solid solution rich in Cu and Zn, as observed in the literature [23, 24]. Table 4 presents the results obtained in the chemical composition quantification of the EDS spectra. In the BR15 weld, the highest intensities of the peaks corresponding to Ag and Cd constituents are in the light phase, indicating that this point has a microstructure rich in these two elements. In addition, in the light phase, a slightly higher concentration of Cd than of Ag and a considerable Cu content in solid solution are found. In the dark phase, a higher concentration of the Cu element is observed with lower concentrations of Zn, Ag, and Cd, indicating the presence of a Cu-rich phase. Table 4 shows that this phase has predominantly the element Cu, followed by Zn, indicating the presence of a solid solution of Cu–Zn containing a low content of Ag and Cd.

The same behavior of the BR15 filler metal is observed in the BR35, where the light phase shows peaks in the Ag and Cd elements and the dark phase shows the highest peaks in the Cu and Zn phases (Fig. 4). However, for the light phase, the amount of Ag and Cd is much more significant. Also, there is a predominance of the element Ag, indicating the presence of a solid solution based on Ag, as can be seen in Table 4. This increase in the Ag content in relation to the Cd element is related to the increase in its quantity in the filler metal. In addition, in the dark phase, the peaks of the Cu and Zn elements were predominant, most notably the copper element, as can be seen in Table 4, indicating the presence of a solid Cu–Zn solution containing Ag.

In addition to the EDS analysis carried out at the light and dark phases of the sample, EDS mappings were performed at the interface of the base and filler metals. Figure 5 shows an EDS mapping obtained at the brazed joint with BR15 filler metal. The region for map acquisition includes the base metal, the reaction layer, and the filler metal, where it is seen that the reaction layer already has a contrast similar to the Cu-rich phase of the filler metal. The results obtained in the analysis carried out for each element confirm what was observed in the point analysis, that the light phase predominantly presents the elements Ag and Cd and the dark phase presents mostly the elements of Cu and Zn. In addition, Ag and Cd are present in lower content in the composition of the dark phase, which corroborates with the quantitative result of spectrum 1, presenting a phase of a solid solution of Cu–Zn containing Ag and Cd. The reaction layer presents a greater quantity of Cu and Zn, indicating that among the elements in the filler metal, only Zn has a more intense diffusional effect in this region. The same occurs with the base metal containing only Cu, indicating that there are no harmful phases that might affect the mechanical properties.

Figure 6 shows the scanning electron microscopy–backscattered electron signal micrographs of the brazed joints in both studied conditions. The results of the microstructural analysis by scanning electron microscopy–backscattered electron signal and EDS indicate that the dark microconstituent seen in the optical microscope is the phase rich in silver and cadmium, and the light microconstituent in the optical microscopy is the phase rich in copper, for both alloys. In contrast, in the scanning electron microscopy–backscattered electron signal technique, a silver-rich phase is seen as a light microconstituent and a copper-rich phase is seen as a dark microconstituent. The scanning electron microscopy–backscattered electron signal results of the BR35 joint point to the primary solidification of the Cu phase with subsequent formation of a eutectic background, indicating that this alloy is hypoeutectic in relation to Cu. The high concentration of eutectic microconstituent indicates that this alloy is close to the eutectic composition, which favors the possibility of its application for brazing with less energy addition and faster and more homogeneous solidification of the filler metal. Besides, as verified in the optical microscopy analysis, a dendritic structure in the BR35 filler metal is observed, with the dendrites constituted by the Cu-rich phase. In the BR15 joint, there is a cell-like structure—more evident in the optical microscopy analyses—with Cu-phase cells, presenting primary solidification of the Cu phase with secondary formation of the Ag phase. In none of the brazed joints, the presence of secondary phases was found during
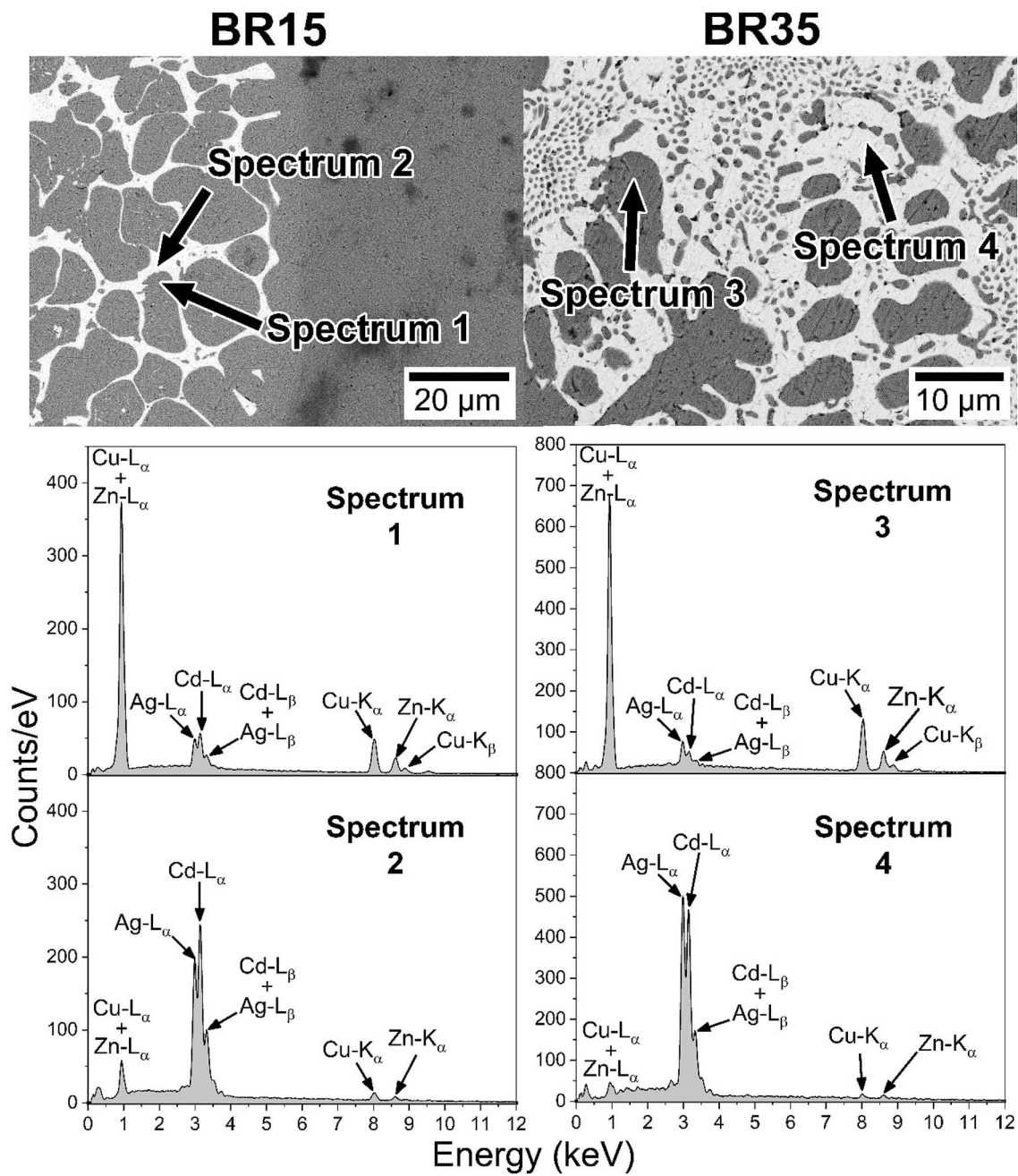
Fig. 4 Micrographs indicating the points analyzed by EDS and their respective spectra in brazed joints with BR15 and BR35 filler metals

Table 4 Quantitative chemical analysis obtained from the spectra of the BR15 and BR35 filler metals

| Spectrum	Composition (wt.%)				Possible phase
	Ag	Cu	Zn	Cd	
1	17.8	38.6	25.1	18.5	Cu–Zn solid solution
2	35.0	17.4	8.1	39.5	Ag–Cd rich
3	7.5	62.2	28.9	1.4	Cu–Zn solid solution
4	59.0	3.5	3.5	34.0	Ag-based solid solution

the microstructural analysis. The microstructural analysis also confirms that the microstructure resulting from the BR35 filler metal shows homogeneity throughout the entire joint, while in the BR15 joint a gradient in the content of Ag- and Cd-rich phase is found along the joint.

Figure 7 shows the micrographs of the joint with the BR15 filler metal in several regions of its extension to show the difference in the distribution of the phase rich in Ag and Cd content. It is observed that in the upper region of the brazed joint—in which the process of solidification occurs
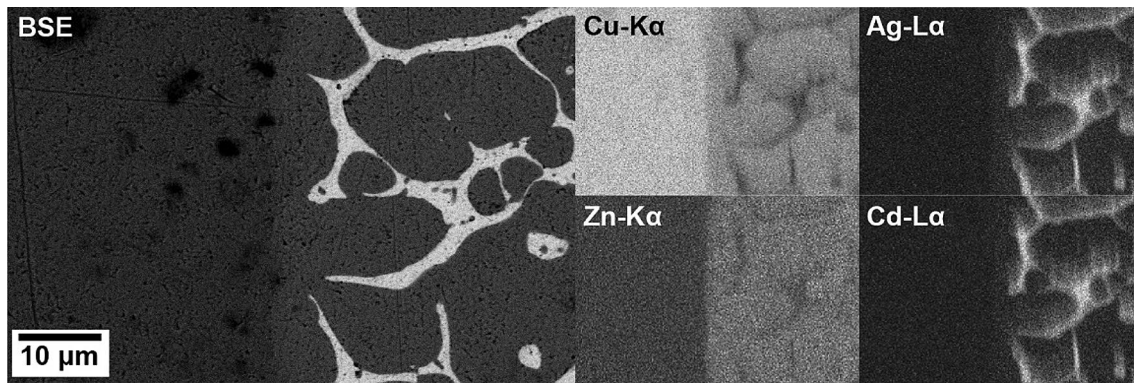
Fig. 5 Micrographs of the brazed joint with BR15 filler metal showing EDS maps with the distribution of the chemical elements Cu, Ag, Zn, and Cd in the interface between base and filler metal

Fig. 6 Micrographs obtained by scanning electron microscopy showing the microstructures formed in the brazed joints with the BR15 and BR35 filler metals
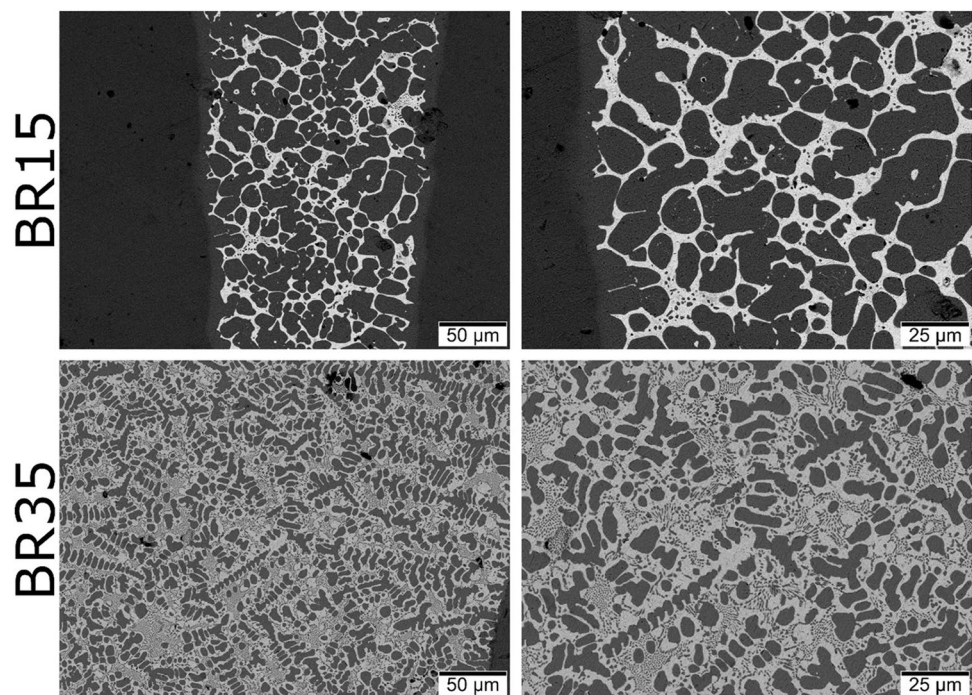

last in relation to the rest of the joint extension—there is a silver phase content significantly lower than that observed in the rest of the joint. In addition, in the lower region of the BR15 joint, where there is a higher concentration of the Ag phase, small regions with the formation of eutectic morphology are present. The Ag phase is found to be present among the Cu phase cells throughout the entire joint. However, this intercellular phase shows greater thickness and homogeneity in the lower region of the joint. The morphology of the Ag phase is characteristic of a diffusional transformation product, so that temperature and time become factors that control the transformation. Taking this into account, the results suggest that a significant content of the Ag phase must have been a product of a solid-state phase transformation that took

place after solidification. In the case of torch brazing in the vertical configuration, the upper region of the brazed joint is the last one in which the solidification process is completed and it is the region with the least exposure to high temperature after the solidification process, as there is an immediate interruption of the heat added by the torch. Therefore, this region of the joint has a shorter exposure time to high temperatures after solidification, thus limiting the occurrence of phase transformations controlled by diffusion at higher temperatures. On the other hand, the lower portion of the brazed joint is exposed to high temperatures for longer times after the solidification of the filler metal, due to the thermal accumulation occurred, while the rest of the joint receives the filler metal. These factors make the BR15 composition

Fig. 7 Micrographs of different regions (upper, central, and lower) along the length of the brazed joint with the BR15 filler metal
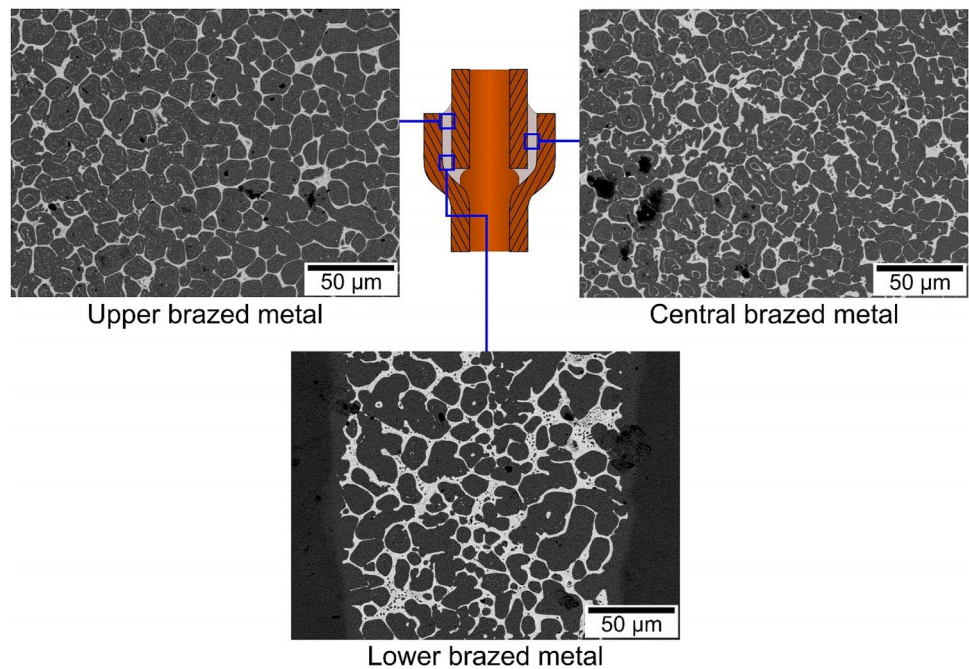
Upper brazed metal

Central brazed metal

Lower brazed metal

Mechanical Characterization of the Brazed Joints

Uniaxial tensile tests were performed to characterize the mechanical performance of the brazed joints. Figure 8 shows the specimens after the uniaxial tensile test for the brazed joints with BR15, BR35, and BR-FOS-3. In all tensile tests, the rupture of the specimens occurred in the base metal, which indicates that all filler metals provide higher tensile strength to the brazed joint.

Figure 9 presents the graph with the tensile strength values obtained in the uniaxial tensile tests of brazed joints performed with the BR15, BR35, and BR-FOS-3 filler metals. The BR35-brazed joint shows the highest tensile strength (211 MPa), even with the fracture occurring in the base metal. In contrast, the BCuP brazed joint had the lowest tensile strength (200 MPa). Looking at the standard deviation

of the filler metals, it is noted that the tensile strength values are statistically near one each other, mainly between BR15 and BR-FOS-3 filler metals. In fact, tensile strengths cannot be directly compared, because the specimens have broken in the base metal. Nevertheless, it is important to highlight that the mechanical testing represents all the composite brazed joint (base metal + brazed zone), and its values depend on the resistance improvement of the brazed zone, and it can point out the slightly higher strength for brazed joint with silver-based filler metals.

For brazing procedure qualification standards [28], the acceptance criterion for the tensile test when rupture occurs in the base metal is that the resistance obtained in the tensile test should not be less than 95% of the tensile strength of the base metal. For copper, the value found in the literature for tensile strength is on average 207 MPa [29]. As shown in Fig. 9, the joints produced with BR15, BR35, and BR-FOS-3 filler metal meet this criterion, since the minimum value of 196 MPa, which is 95% of the tensile strength value, is

Fig. 8 Specimens for uniaxial tensile testing after fracture using the BR15, BR35 and BR-FOS-3 filler metals

Fig. 9 Tensile strength of copper brazed joints using BR15, BR35, and BR-FOS-3 filler metals
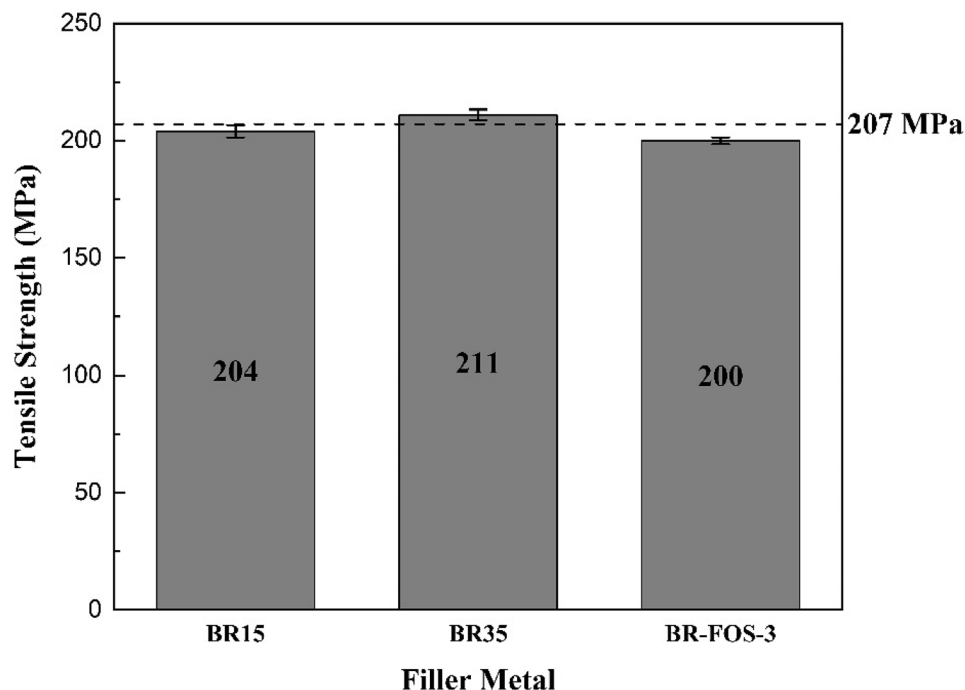
met in the tensile specimen for all filler metals. The tensile results could not exactly determine the effect of adding silver to the filler metal, only to the brazed joint. The tests previously discussed demonstrate that all the filler metals perform better than the base metal because in all cases the specimens break in the base metal.

Conclusions

Microstructural aspects and the mechanical performance of copper brazed joints were evaluated using silver-based filler metals, with silver contents of 15% and 35%. The brazed joint using the BR35 filler metal shows good microstructural uniformity, with dendritic morphology. On the other hand, when using the BR15 filler metal, it presents a morphology characteristic of the cellular solidification regime. In addition, upper, central, and lower regions of the brazed joint have shown microstructural differences, which must be related to the thermal accumulation by the torch in lower regions of the joint, as the lower region solidifies first, near the heat source, resulting more heat in the lower region favoring solid-state Ag-rich phase transformation.

All tensile tests of the brazed joint failed in the base metal. Furthermore, the brazed tubes tensile strength overcame the acceptance criterion for brazing qualification standard. Although the brazed zone cannot be compared between them, it is important to point out the improvement of the brazed joint, making the silver-based filler metal performance slightly higher than the phos–copper filler metal brazed joints.

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