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Brazing Behaviour of Ag-Cu Filler Materials

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Abstract

Ecological brazing rods (cadmium free) represent a technical solution particularly useful for joining metallic or non-metallic components, providing the required mechanical and functional characteristics obtained in reproducible manufacturing conditions and at reasonable costs. The new class of coated rods for brazing must provide high deposition efficiency, chemical compatibility in relation to a number of metals and alloys currently used in industry and high corrosion resistance in different media. Such diverse characteristics can be obtained by achieving a special coating that contains a mixture of materials having a role of chemical activation and catalyst effects, as well as contributing to increasing the adherence to unmolten interfaces. This chapter presents some results obtained by using experimental brazing filler materials for different types of materials and applications. There are briefly highlighted some aspects on the diffusion effects of chemical elements in the soldering interface, the bonding of ceramics and some issues related to the effects of chemical elements from the brazing material.

Keywords: brazing, filler material, coated rod, diffusion, ceramics

1. Introduction

Currently, there is a range of alloys available on the specialized market, with different chemical compositions, used as filler materials for brazing. Of these alloys, a Cu-Ag class is used to obtain similar or dissimilar joints, operating in moderate corrosive environments at low or high temperatures. The Cu-Ag class brazing alloys yield specific characteristics such as high fluidity and ability to spread fast in very narrow interstices, high ductility and mechanical resistance, chemical stability in different environments and temperatures, good adhesion and excellent wetting capacity, suitable for a wide variety of metal or metal-ceramic materials [1, 2]. To determine the optimal operating temperature (melting point and eutectic temperature), the mutual

solubility of chemical elements and the types of main phases formed (such as solid solutions, eutectic phases, compounds, etc.), see the phase diagrams of the alloying system (binary or ternary diagrams) in **Figure 1**.

In **Figure 1(a)**, the eutectic point is at about 780°C with the specific concentrations of 72 wt% Cu and 28 wt% Ag, whereas in **Figure 1(b)**, other values for temperature and chemical composition are shown. The differences between the values specified by different charts are determined by the different purity values of the elements and by the accuracy of determining the transformation temperatures. If other chemical elements are added in the metallic matrix of the filler material, in order to obtain some special characteristics (lower temperature of the eutectic point, narrower or wider solidification domain), it becomes difficult to determine the exact value of the eutectic point position. The temperature range for Cu-Ag class brazing alloys is between 500 and 1000°C [2]. These alloys are used for brazing parts made of carbon steel, galvanized steel or stainless steel, some copper alloys (Cu, Cu-Sn and Cu-Zn) or others. Since December 2011, the introduction of Cd in these brazing alloys has been banned, in accordance with the EU regulation 494/2011.

Besides Cu (22–40 wt%) and Ag (25–56 wt%), brazing alloys may contain elements such as Sn (2–2.5 wt%) and Zn (17–35 wt%). The melting domain is 620–790°C, depending on the chemical composition [2].

The advanced brazing filler materials contain some chemical elements added in the coating or in the brazing rods, which give them a great capacity for the wetting of metallic surfaces coated with oxide layers. At the lowest temperature value of the melting domain (650–700°C), the ceramic mixture from the coating starts to melt, resulting in deoxidation of the surface for the parent material. At higher temperatures, between 700 and 800°C, the second ceramic coating, containing a mixture of silver particles, starts to melt, completing the final chemical composition of the filler material. In this way, the filler metal can spread rapidly and it can completely fill the gap between the joined components [3–6]. The most used filler material brands are 244 Ag, 134 Ag and 145 Ag, which are designed to perform connections for drinkable water pipes

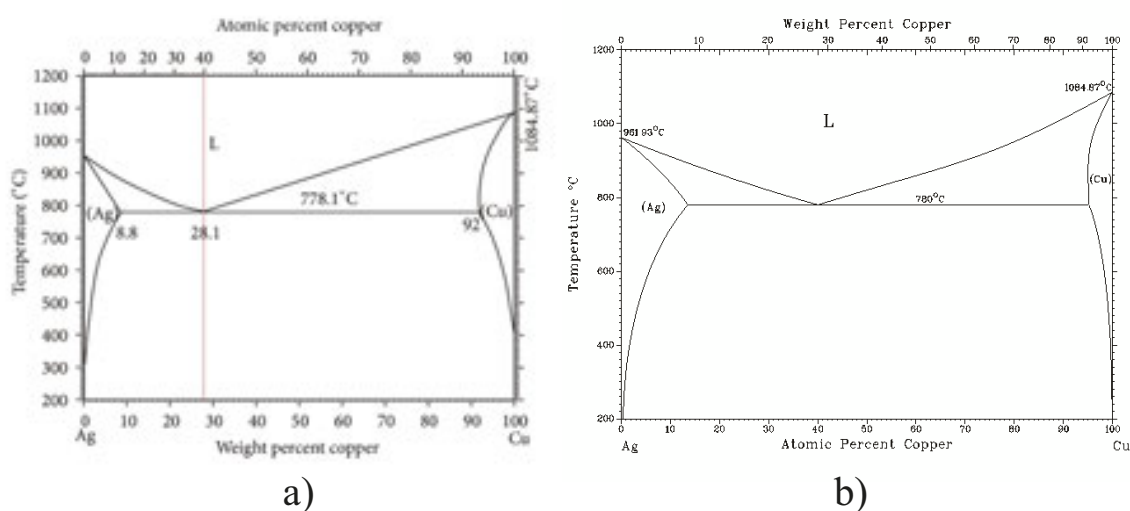


Figure 1. Phase diagram for the Cu-Ag alloying system. Cu: 71.9%wt, Ag: 28.1%wt [1, 2]; a) Melting Temperature: 778.1°C b) Melting Temperature: 780°C

with brazing temperatures of approximately 650–830°C, bundles or tubular exhaust systems. The operating conditions involve corrosive effects and oxidation at high temperatures (300°C), tensions and contractions in the joint. For these applications, the increase in the tin content can improve the wettability and mechanical properties of the joints. However, when the tin content exceeds 5% Sn, the shear strength of the joints decreases [7]. Lower temperatures desired for the diffusion brazing of stainless steels are not determined only by the melting point of the filler materials. In this case, the end product of the reaction between the filler material and parts is a solid solution, and residual interfacial tensions do not occur if the inter-metallic phases are not present. For that reason, the solubility limit of the minor metal constituents in the primary phase is crucially important [8].

Generally speaking, the stainless steel surface is wetted with difficulty by some brazing alloys, because the superficial oxide (chromium oxide) protects it against corrosion. Therefore, the chemical composition of the brazing flux is designed to ensure a rapid dissolution of oxides and to ease the wetting of the molten filler material on the base material. Due to the fact that additional surfaces of the brazing zone are affected by the dissolution effects favoured by the brazing fluxes, it is important to rapidly clean the surrounding surfaces after brazing [9]. The brazing flux preferred for this type of filler material is FB 10 [2, 3]. To ensure a good mechanical resistance of the joint, the brazing alloy must be sufficiently fluid, in order to penetrate the gaps between the components, on large distances. Especially in the case of dissimilar joints, the melting temperature of the brazing alloy that contains silver and copper must be well correlated with the type of base material. In the case of austenitic stainless steels, the holding in the 600–800°C temperature range is critical to avoid the inter-crystalline corrosion. In the case of very thin components, the effects of high temperatures are more critical [6].

This chapter presents some results obtained by using experimental brazing filler materials (ecological brazing rods, cadmium free, obtained under reproducible manufacturing conditions and at reasonable costs, metallic glass filler material and metallic foils) for different types of materials and applications.

The new class of coated rods for brazing can provide high deposition efficiency, chemical compatibility in relation to a number of metal and alloys currently used in industry and high corrosion resistance in different media. Such diverse characteristics were obtained by achieving a special coating that contains a mixture of materials having chemical activation role and catalyst effects, as well as contributing to increasing the adherence to unmolten interfaces. There are highlighted some aspects on the diffusion effects of chemical elements in the soldering interface of stainless steel 304 used for high temperature applications, dissimilar bonding of ceramics (tungsten carbide with steel), alumina bonding using metallic foil and some issues related to the effects of chemical elements from the brazing material. Some other results refer to the possibilities of joining ceramic materials using the various types of filler metal alloys.

2. Brazed joints

Several types of connections were made between different types of materials, such as 304 stainless steel, galvanized steel, carbon steel, tungsten carbide, ceramics pills (alumina) and copper.

As a general rule, before brazing, all the surfaces were cleaned with propane and then dried with hot air. After brazing, the joints were cleaned using hot water (90°C) and sampled for analysis. The samples were cut using a precision cutting machine that includes the Smartcut system to automatically adjust the feed rate and to prevent sample deformation.

2.1. Stainless steel brazing

To analyse the joint between very thin parts made of stainless steel, the spreading mode in the brazing gap and the diffusion of chemical elements in transition zones from the heat-affected zone (HAZ), two types of joints were analysed: corner joint (**Figure 2a**) and overlap joint (**Figure 2b**). The parts made of 304 stainless steel type have 0.5 mm thick, with a relative gap of 0.4 mm between them. Brazed joints were obtained using the oxy-flame process, with a

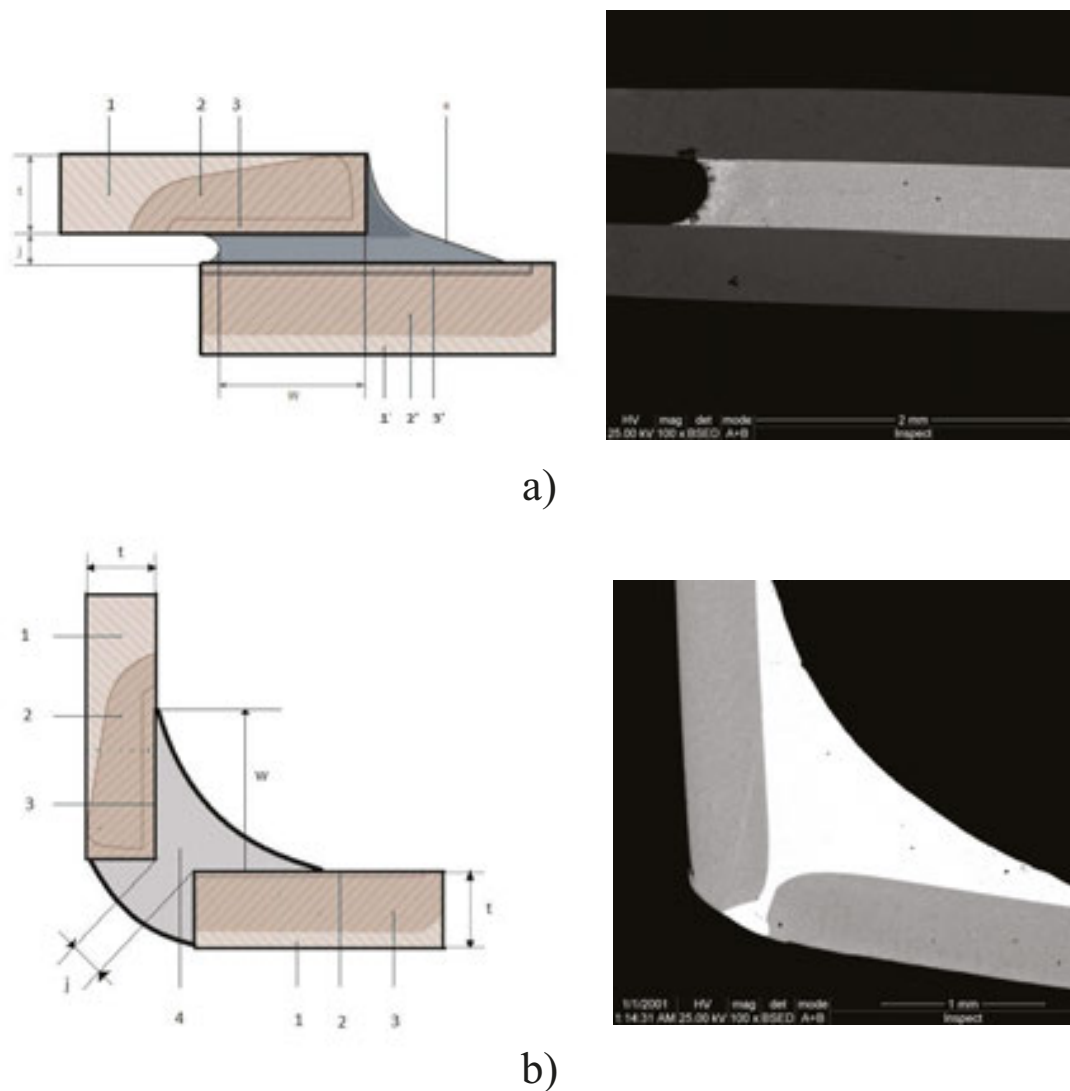


Figure 2. Schematic diagram and images for brazed joints: 1 and 1'—parent material unaffected by the brazing process; 2 and 2'—heat-affected zone; 3 and 3'—diffusion zone/transition zone; 4—braze metal; j —actual joint width; w —overlap/lap length; t —parent material thickness. (a) overlap brazed joint (100×) and (b) corner brazed joint (100×).

slightly oxidizing flame and VIAg22SnSiPR filler material (max. 22 wt% Ag; max. 43 wt% Cu, max. 35 wt% Zn, 0.5–1 wt% Sn and 0–0.2 wt% Si) [3].

The diffusion length for the chemical elements in the brazing zone was measured both in the base material and in the heat-affected zone using the EDX - Energy-dispersive X-ray spectroscopy analysis. The total duration of the brazing process was of 30 s, including the heating of components and the actual brazing, in order to avoid the deformation of the thin components and the corrosion effects. Cooling was carried out in cold water immediately after brazing. The samples were washed with hot water and dried in hot air. The representative areas from each brazed sample were cut using a cutting machine with a cooling agent to avoid the alteration of the microstructure [3]. The 'overlap' joint (**Figure 2a**) has the average size width (j) of 412 μm . The cross-section aspect of the brazing zone is correct, without molten material excess and with well-formed concavity, meeting the conditions imposed for this type of joint. The condition for the required maximum joint resistance is to have a minimum overlapping length of $5t$, where ' t ' is the thickness of the components. In the analysed case, the actual overlapping length (w) was of 4 mm, higher than the required minimum value of 2.5 mm. In the case of the 'corner' joint (**Figure 2b**), the geometrical dimensions of the brazed zone were actual joint width (j) of 42 μm in the root zone and maximum overlapping length (w) of 3.14 m. Individual measurements (EDX analysis) of the chemical composition were taken in 5 points at different distances from the brazing surface (**Figure 3a**).

The EDX measurements were afterwards performed in the molten filler material volume, by individual measurements taken in 5 points of the cross-section of the 'overlap' joint (**Figure 3b**). The results of each chemical composition measurement are shown in **Tables 1** and **2**.

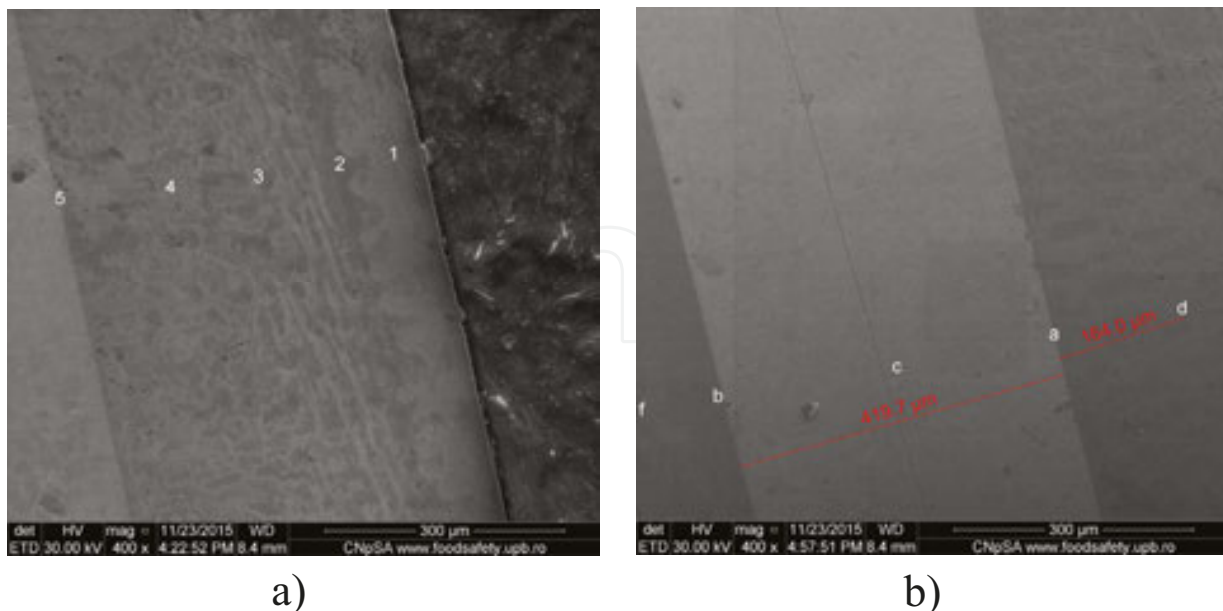


Figure 3. Location of the measurement points (overlap joint): (a) parent material; (b) filler material [3]; (a) 400 \times and (b) 400 \times .

Measurement zone	Chemical composition (wt%)									
	Si	Cr	Mn	Fe	Ni	Al	Ag	Zn	Sn	Cu
1. Base metal	0.23	18.82	2.5	70.94	7.5	–	–	–	–	–
2. HAZ	0.2	18.08	2.27	69.34	6.92	3.18	–	–	–	–
3. HAZ	0.19	18.16	2.46	69.53	7.59	2.06	–	–	–	–
4. HAZ	0.23	18.48	2.49	69.83	7.14	1.83	–	–	–	–
5. Near fusion line (at 20 μm)	0.3	13.45	1.56	49.43	4.63	–	3.95	10.97	0.43	15.28

Table 1. Chemical composition measured in 5 points in the cross-section of the parent material (**Figure 3a**) [3].

As shown by the chemical composition values in **Table 1**, diffusion effects are detected only at very small distances from the molten metal interface, at length of approximately 20 μm . There can be seen the significant diffusion effects of elements such as silver, zinc and copper, from the filler metal to the parent material (**Table 1**, point 5, **Figure 3a**) and the diffusion effects of chromium, iron and nickel starting from the parent material to the molten material.

To estimate the diffusion effects from the filler material to the base material, measurements were carried out outside the transition zones (**Figure 3b** and **Table 2**), at lengths of around 160 (point 'd') and 60 μm (point 'f'), respectively. The measurement points 'a' and 'b' were located in the transition zone, between the parent materials (overheated) and the molten filler material, approximately 20 μm away from the fusion line. Point 'c' corresponds to the chemical composition in the centre of molten filler material (around 200 μm from the interface with the parent material).

The most intensive diffusion effects were obtained in the case of copper (over 25%), zinc (over 21%) and silver (12%). To evaluate the global effects of diffusion (corner joint), the analysis of the chemical composition was made using scanning electron microscopy in 105 different points, located in the base material, root and seam zone from **Figure 4**. The measurements were carried out in straight line, from left to right, between points 1 and 105, at a distance between successive measurements of 10 μm .

The measurement distance in the first and second base material was of maximum 240 μm , on both sides of the fusion line. As it can be seen, the transition from the filler material to the

Measurement zone	Chemical composition (wt%)									
	Si	Cr	Mn	Fe	Ni	Ag	Zn	Sn	Cu	
a. Base metal	0.28	15.12	1.58	56.99	4.92	3.19	6.99	0.21	10.7	
b. Base metal	0.09	14.11	1.54	56.75	5.71	1.96	7.57	0.13	12.15	
c. Central zone of filler metal	–	–	–	–	–	21.36	34.5	1.16	42.98	
d. HAZ (164 μm)	0.23	18.43	2.74	70.33	8.1	–	–	–	–	
f. HAZ (60 μm)	0.22	18.45	2.33	69.24	7.28	–	–	–	–	

Table 2. Chemical composition measured in 5 points through filler material and HAZ (**Figure 3b**) [3].

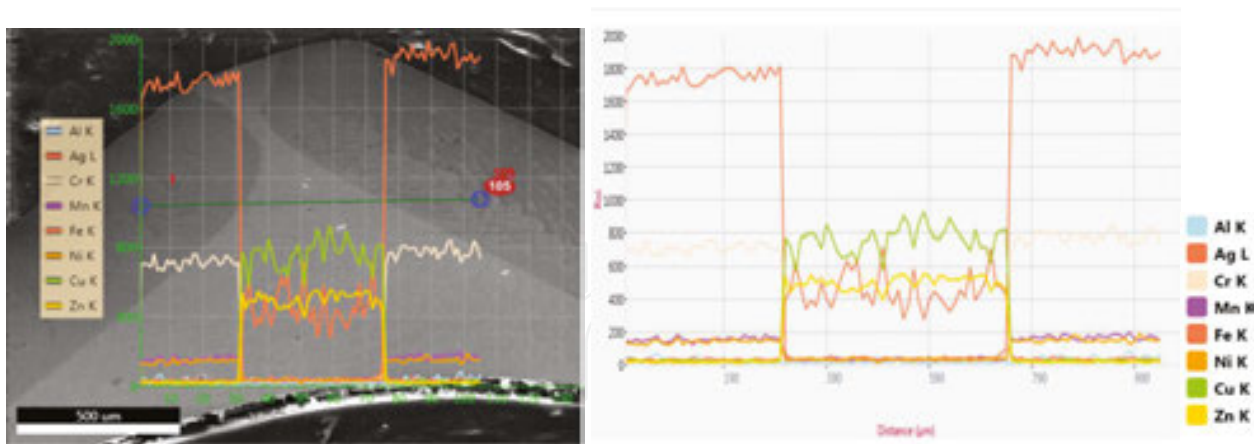


Figure 4. Evolution of the chemical composition in 105 different points for the corner joint [3].

base material is in a very narrow zone, the diffusion effects being visible only at 20 μm from the fusion line.

The metallographic analysis of the brazed samples targeted the visualisation of the molten alloy distribution in the joint's gap, the correctness of the molten filler material spreading and the absence of imperfections. The microstructural analysis was conducted using a scanning electron microscopy provided with electron gun with field emission—EGF with a resolution of 1.2 nm and an X-ray energy dispersive spectrometer (EDS) with a resolution of 133 eV at MnK.

In the case of the 'overlap' joint, a good adhesion between the brazing filler metal and the stainless steel surface was obtained (Figure 5a), despite a few pores located near the interface with the

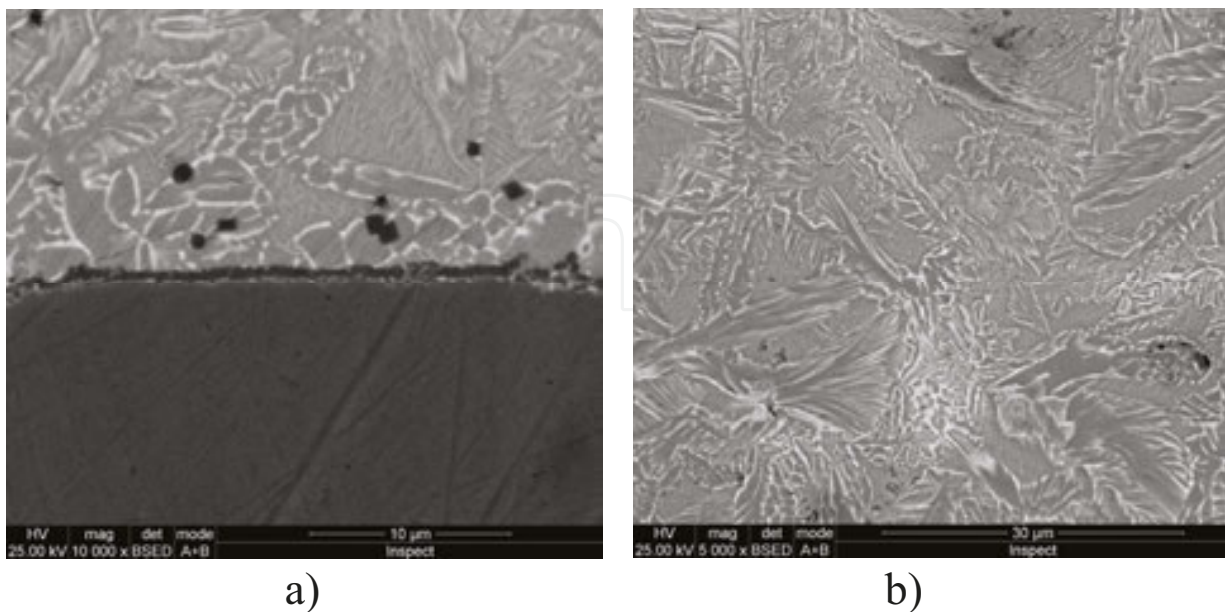


Figure 5. Microstructure appearance in the cross-section of the overlapped brazed joint: (a) interface between filler material and parent material; (b) filler material. (a) 10,000 \times and (b) 5000 \times .

parent material. The phases present in the molten metal have needle-like shape (**Figure 5b**), due to the cooling conditions. The expansion of the heat-affected zone (HAZ) was quite restricted (about 315 μm), given the very small thickness of the stainless steel components (0.5 mm).

In the case of the 'corner' joint, at higher magnification degrees (**Figure 6a**), there can also be seen a good adhesion between the molten material and the stainless steel surface. The correct geometry of the root and the absence of the secondary fragile phases are visible (**Figure 6b**).

Some pores with small diameters (about 1–2 μm) are located near the interface, with random spreading, but they do not endanger the bond strength (0.5 mm diameters are admitted for imperfections according to EN 12799-2002) (**Figure 6b**). During tensile tests, the overlapping samples were broken in the base material, thus highlighting a good behaviour of the filler metal.

The experimental alloy used in the study has a good spreading behaviour and does not produce any cracking tendency. The only types of imperfections observed in the brazed zone were unmolten flux inclusions and pores (gas) resulted from the coating of the filler material.

In the brazed joints made by stainless steel components, at the interface between the base material and the molten filler material, a diffusion phenomenon can occur due to the migration of some chemical elements through the interface and even the holding time at high temperatures is very short [3].

2.2. Dissimilar brazed joint

The cooling of a dissimilar joint after brazing (i.e. steel brazed with tungsten carbide) is very important due to the high expansion coefficient of the steel that tends to contract faster than

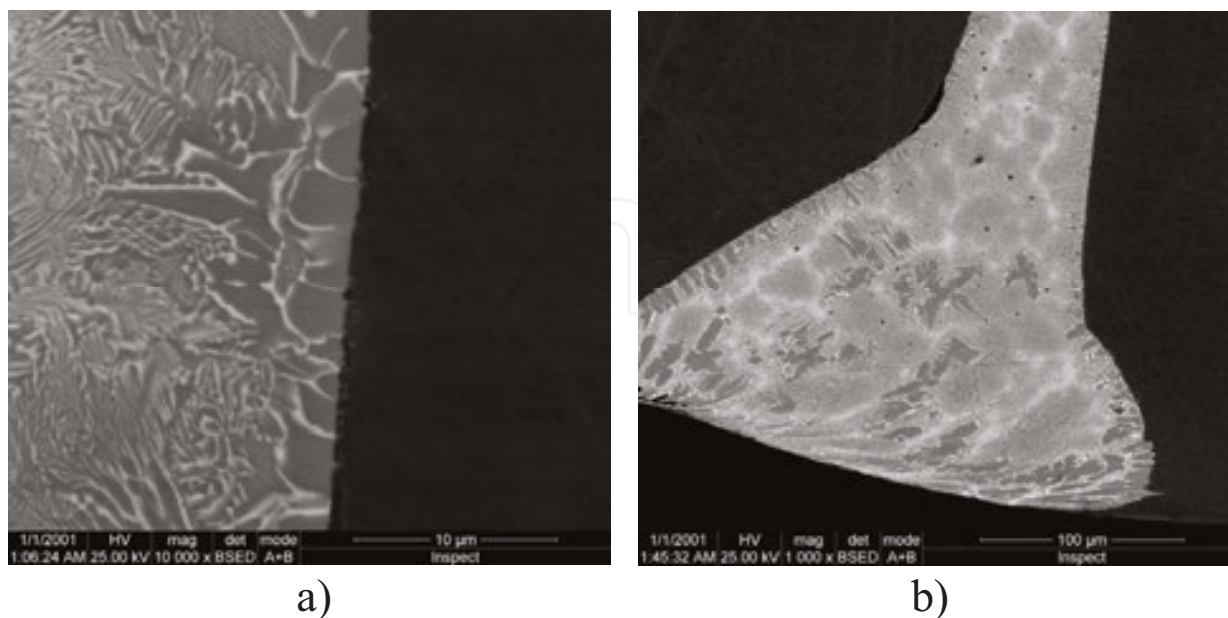


Figure 6. Microstructure aspects in the cross-section of the brazed corner joint: (a) interface between the filler material and the parent material; (b) brazed root zone. (a) 10,000 \times and (b) 1000 \times .

the part of tungsten carbide to which it is brazed. This mismatch develops shear stresses within the interfaces of the joint.

If a high-strength brazing filler material is used, these stresses will be directly transmitted to the brittle tungsten carbide and could cause its cracking (**Figure 7**) [7, 10]. For this reason, the filler metal must have a low yield point to be able to deform and to allow the dissipation of the shear stresses. If the dimension of the tungsten carbide does not exceed 10 mm, the best solution is to use a filler metal like EN 1044 AG102, 103 and 303, which is sufficiently ductile and provides a thin layer of brazing filler metal. Another advantage of these filler metals is their low-brazing temperatures, helping to minimise the amount of differential expansion developed between the tungsten carbide and steel [10].

To ensure good conditions for penetration by capillarity of the brazing alloy, a proper preparation of the surface of components is required. The brazing of different (i.e. low alloy steel and tungsten carbide) filler materials must provide a good wetting for both types of surfaces, at the same time, at similar operating temperatures.

Any substance in the brazing gap or in the filler material can cause a change in the wetting behaviour, preventing fluid flow [10, 11]. If the material surface is too smooth, there is obtained an inhibition of the metal flow and poor adhesion (tungsten carbide has low roughness, as it is obtained by pressing and sintering). A rough surface can increase wettability, but in the case of higher values, it can affect the spreading mode of the molten filler material and can favour mechanical stress on the micro-surface irregularities [12].

Another problem that can occur during heating is the oxidation of the tungsten carbide component. The oxidation can occur on both surfaces causing superficial damage and the emergence of micro-cracks. The brazing surface must be completely protected against oxidation by the coating provided by paste or flux. When brazing tungsten carbide with steel component, the heat

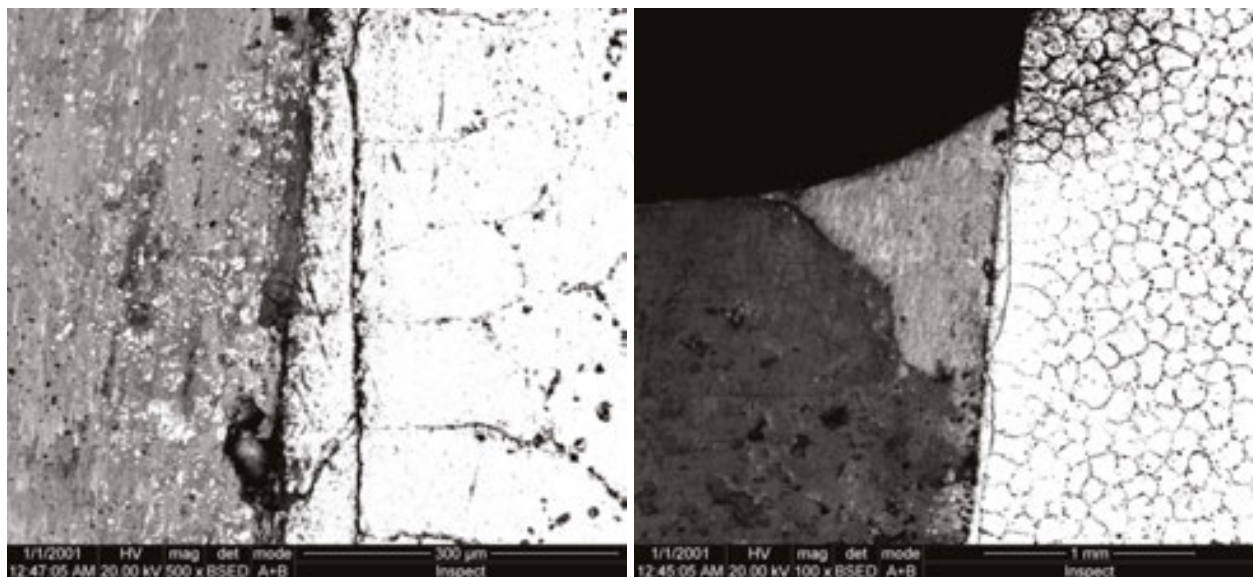


Figure 7. Crack formation in tungsten carbide brazed with steel components (500×, 100×) [7].

flow is more effective on the sides and less at the bottom of the joint, as the complete penetration of the brazing alloy in these zones is prevented. Therefore, to balance the heat flow, a few pieces of solder wire can be placed under the tungsten carbide to contribute to better warming and heat dispersion into the gap, by wetting the entire surface of the parts, from the bottom up (**Figure 8**).

Currently, there are several types of fillers for brazing tungsten carbide with steel, classified into two main groups.

The first group contains copper and copper alloys, including Cu-Zn (special brazing alloys) and Cu-Zn-Ni alloys. The first types of brazing alloys for tungsten carbide were those containing 100% Cu or 60% Cu + 40% Zn. Subsequently, other copper alloys have been developed by adding chemical elements such as Cd, Ag and Si. Copper is used not only because it is very malleable and can be processed as a sheet or a rod in different dimensions, close to those required (under 0.08 mm), but also because it allows the accommodation and dissipation of internal stresses during cooling. Note that 0.4-mm thick Cu-based sandwich sheets for brazing contain a middle sheet of 0.2 mm, covered by two 0.1-mm thick sheets.

The second group contains alloys with low melting point, containing silver in different proportions. The first brazing alloys based on silver have been developed since 1944 and they are mainly used for brazing tungsten carbide. Subsequently, 3% Ni or Cd was added in these alloys for low temperature applications. Adding Ni led to increase the carbide wetting capacity, as well as increase the capacity to accommodate tensions in very thin interstices of the joint. Nowadays, nickel is a common element added in filler materials for brazing WC.

Of the two main groups, Ag alloys are most commonly used because they have melting points below 750°C and exhibit an excellent brazing behaviour. Such brazing alloys are suitable for both induction and flame gas (**Figures 9 and 10**), applicable both for WC and steel, since their



Figure 8. Assemblies prepared for brazing: (a) as-cast steel body and tungsten carbide tip; (b) solder wire placed in the brazing gap; (c) brazed assemblies [3, 7].

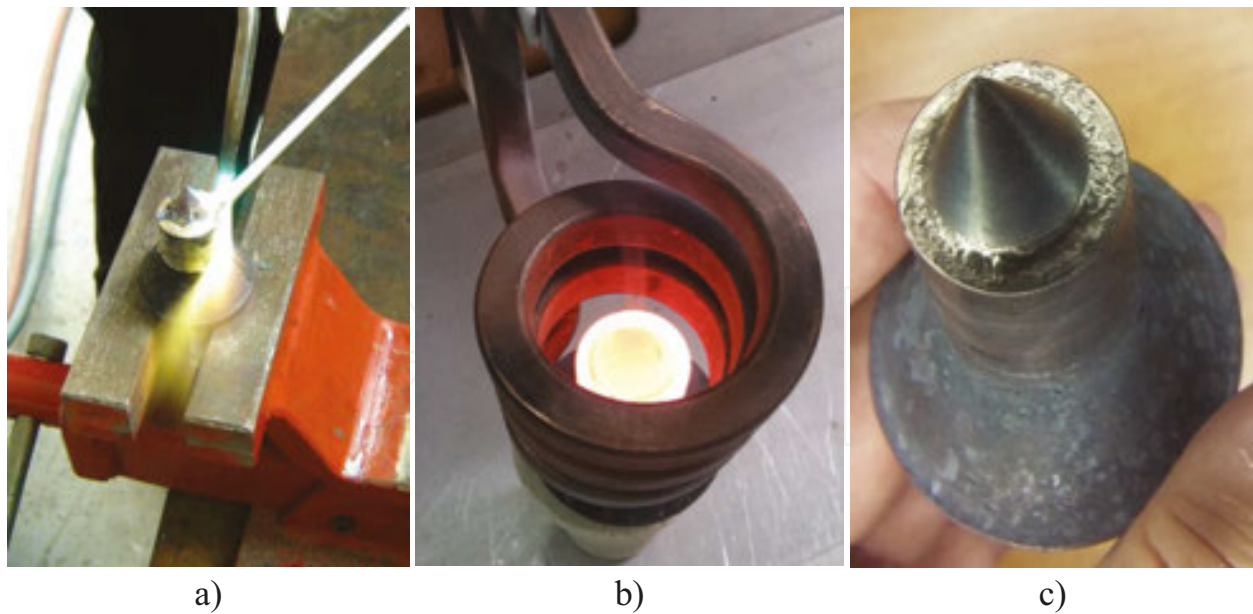


Figure 9. Procedures for brazing dissimilar joints between steel and tungsten carbide: (a) oxy-flame brazing; (b) induction brazing; (c) brazed assembly [7].

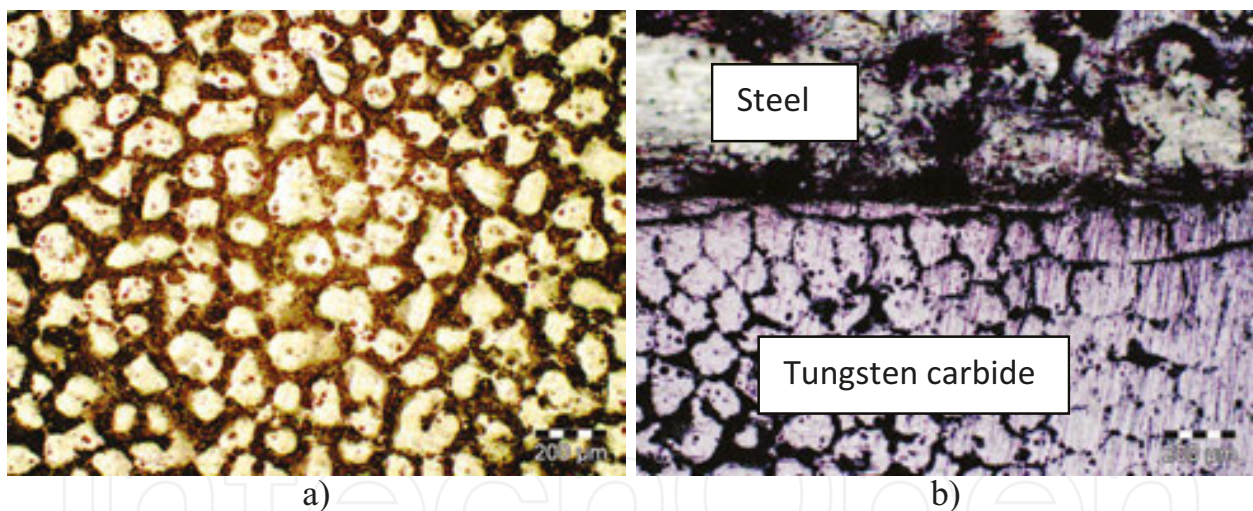


Figure 10. Optical microscopy images of the joining zone obtained by brazing between tungsten carbide and steel: (a) tungsten carbide microstructure and (b) joint between tungsten carbide and steel [7]. (a) 200× and (b) 200×.

melting point is below the Curie point of steel. This characteristic is very important during brazing by induction, due to the fact that on reaching the Curie point, the steel becomes paramagnetic and changes the effectiveness of the inductive heating effect (it requires a larger amount of energy for the soldering process). For manual, the oxy-flame brazing process has been used as an experimental filler material Ag₁₅CuP₆ (cadmium free) (max. 15 wt% Ag, max. 82 wt% Cu, max. 3 wt% P) having 2 mm diameter and 450 mm length [7]. The stages of brazing process (**Figure 9a**) were as follows:

- positioning of the tungsten carbide tip into the brazing gap;
- protecting the free surface of the ceramic body using refractory slurry (dip coating, leak and drying in furnace at 150°C for 1 h);
- application of flux into the brazing gap;
- heating the assembly with flame, by moving the flame around the steel body until reaching a prescribed preheating temperature, without exceeding the melting temperature of the brazing alloy;
- continuing the heating by positioning the flame on the ceramic tip and adding filler material (**Figure 10**) until a slow refluxing in the brazing gap can be seen;
- slow cooling of the assembly in air;
- removal of the flow excess using hot water (40°C) and alcohol, followed by drying in hot air.

FH10 flux is generally used for brazing and soldering, according to EN 1045. The operating temperature range of this flux is 550–800°C, coupled with filler materials that have a melting point below 800°C (typically below 750°C). The condition required is for the selected flux to be active at minimum 50°C over the liquidus temperature of the brazing alloy. The flux is recommended for homogenous or heterogeneous joints, for components made of carbon or stainless steel, copper, brass, ceramic materials but not aluminium. It is recommended especially for the brazing of aluminium bronzes, steels, tungsten or molybdenum carbide or whenever protection is needed for components during heating [7, 9, 11].

The preheating stage during induction brazing (**Figure 9b**) must be carried out gradually (40–60 s) until reaching the melting temperature for brazing, using the following parameter values: 60 s brazing time, 7–8 A current, 60–175 V voltage and 30 kHz frequency. Otherwise, unwanted effects may occur, as brazing alloy boiling. If the assembly is overheated, it may cause the boiling of the brazing alloy, which can generate its expulsions outside the bonding zone or pores formation.

The heating process can be monitored using a thermal infrared camera in order to establish the exact temperature achieved during brazing. After brazing, cross-section of joining area can be evaluated using optical and SEM microscopy (**Figure 11**).

Recent filler materials used for the brazing of tungsten carbide are those alloyed with Ag and Zn (Cd-free), whose disadvantage is the high potential of evaporation during soldering.

For this reason, in the most recent filler materials, Zn is replaced by Sn, Cu, Ni, P and Mn (**Figure 12**), sometimes accompanied by small amounts of indium or tin, to decrease the melting temperature [13–17].

2.3. Ceramic joining

According to Schwartz [18] and Klomp [19], the continuous diffusion joint between ceramics and metal is greatly influenced by the surface quality of the filler material because it involves

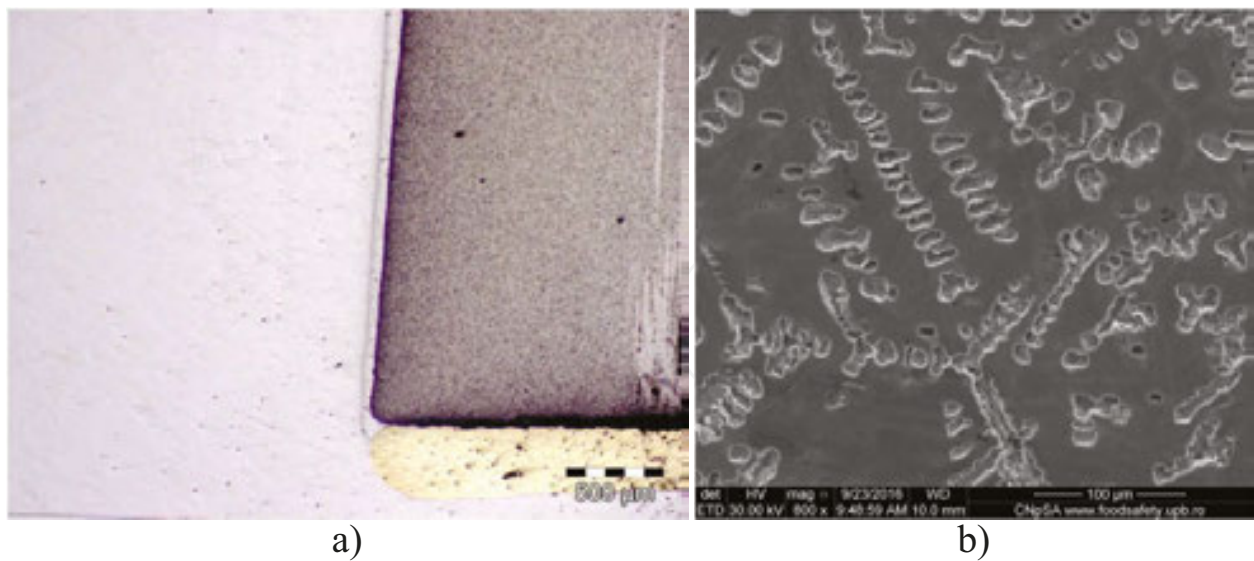


Figure 11. Optical microstructure in cross-sections of brazed joint (a) and SEM microstructure of filler material (b). (a) 500× and (b) 800×.

the ability to get into very close contact with the entire free ceramic surface. If the ceramic surface is smooth, the time required for bond formation at the atomic level is determined by the deformation of the metal. Surface filler material irregularities can prevent the formation of a continuous interface, even by applying a pressure, as superficial energy can change during plastic deformation [13]. The ceramic surface quality depends on the processing method. Therefore, in the experiments, alumina pills were polished using sandpaper with different grits, until a smooth surface was obtained (a roughness of about $0.8 \mu\text{m}$) [20, 21].

The researcher analysed the joint between two components of Al_2O_3 using a metallic inter-layer placed between the contact surfaces of ceramic. There were used several types of filler materials, including Co-Nb-Si-B (0.1 mm), FeNiB (0.1 mm), Cu 99% (0.2 mm), Al 99.99%

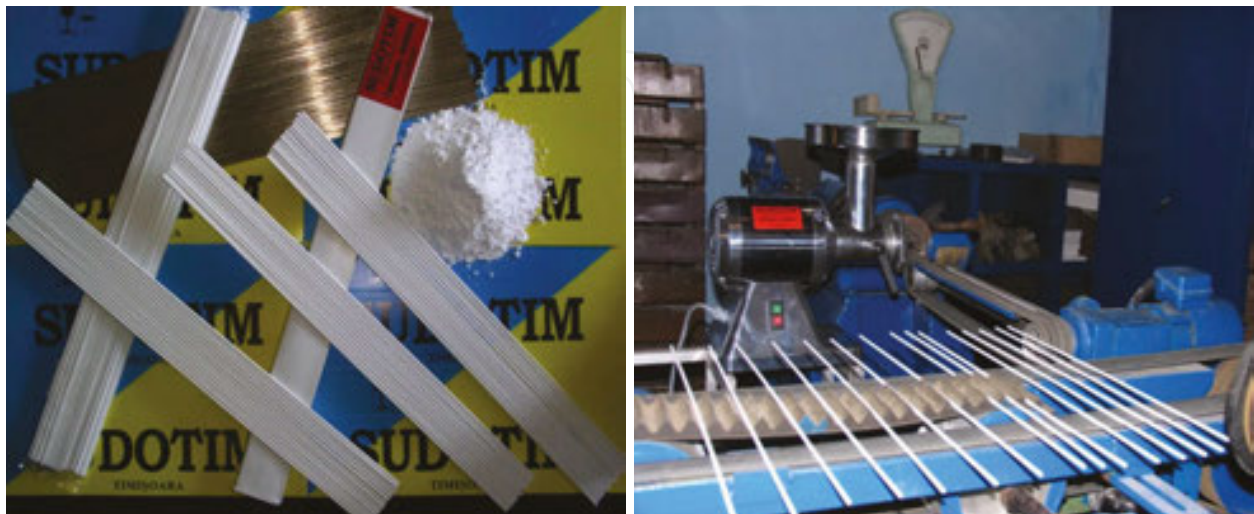


Figure 12. Experimental filler material (B Ag 40CuSnP, Cd-free) and manufacturing factory [21].

(1 mm), $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}$ metallic glass (0.01 mm), CoNbSiB (0.15 mm) and $\text{Cu}_{50}\text{Ag}_{40}\text{Zn}_{10}$ (0.8 mm). Brazing was performed using an electric furnace in a controlled atmosphere. The brazing parameter values used for the experiments were as follows: the maximum temperature of 1100°C, 60-min holding time at maximum temperature, 5°C/min heating and cooling velocity in an argon atmosphere.

After joining, the assembled parts were mechanically tested (shear test) and the microstructure of both fracture surfaces and cross-sections was analysed in order to evaluate the integrity of the joint, the diffusion of the chemical elements and the nature of the compounds formed into the interface between the ceramic and metallic materials [20].

The values of the chemical composition were measured in different points located in each zone of interest by X-ray microanalysis. A common feature of all ceramic samples combined using various metal foils is that there can be seen, in their interface zone, the appearance of a semi-vitreous material with complex chemical composition, which tends to expand to the metallic material (filler material). In zones where the semi-vitreous material is formed in sufficient quantity, the adhesion of the ceramic parts is good and this material is behaving like a binder. This new type of material is probably the result of chemical reactions that took place between the filler material, ceramics and the pickling solution because it contains chemical elements of all three. Adhesion is poor in zones where this semi-vitreous material is missing or is insufficient.

During experiments, it was found that, in the case of very soft metals (1000 μm -thick Al foil), poor adherence was obtained during soldering due to excessive deformation of the metal foil between the surfaces to be joined. When 0.2-mm thick foil was used, there were obtained better results (a breaking shear of about 85 N/mm^2). The use of 0.1-mm thick FeNiB alloy sheets yielded poor shear resistance (around 70.3 N/mm^2) while 0.01-mm thick $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{15.5}$ metallic glass strips yielded a much higher value of shear resistance (267 N/mm^2) [21]. The analysis by electron microscopy and X-ray diffraction showed that an intermediate metallic layer was obtained at the interface, leading to the conclusion that the diffusion bonding mechanism occurred most likely during brazing.

The microstructural appearance seen in the case of the sample joined using the CoNbSiB metallic glass was as follows: the pores of the ceramic material were filled with semi-vitreous materials in the zones with complete adhesion, evidencing a transition zone with own chemical composition, similar to a mixture between ceramic and filler materials (containing elements such as Co, B, Si and Nb).

Fine cracks are visible in the metallic filler material, separating volumes of materials by a few hundred nanometres. The transition zone has compact appearance, free of pores or cracks (**Figure 13b**). The results of the chemical composition (**Table 3** and **Figure 14**) show a transition zone between the ceramic material (points 1 and 2) and the metallic material (points 5 and 6) like a new semi-vitreous material, containing elements that diffuse both from the ceramic (Al and O) and from the filler material (Co, Nb, Si and B). Ancillary elements coming from surface preparation solutions are also present in the vitreous materials (Na, Mg, K and Ca).

Part of the metallic material was spun off during the shear test, due to its weak adherence during brazing. Breaking was located mainly at the level of the semi-vitreous material, which

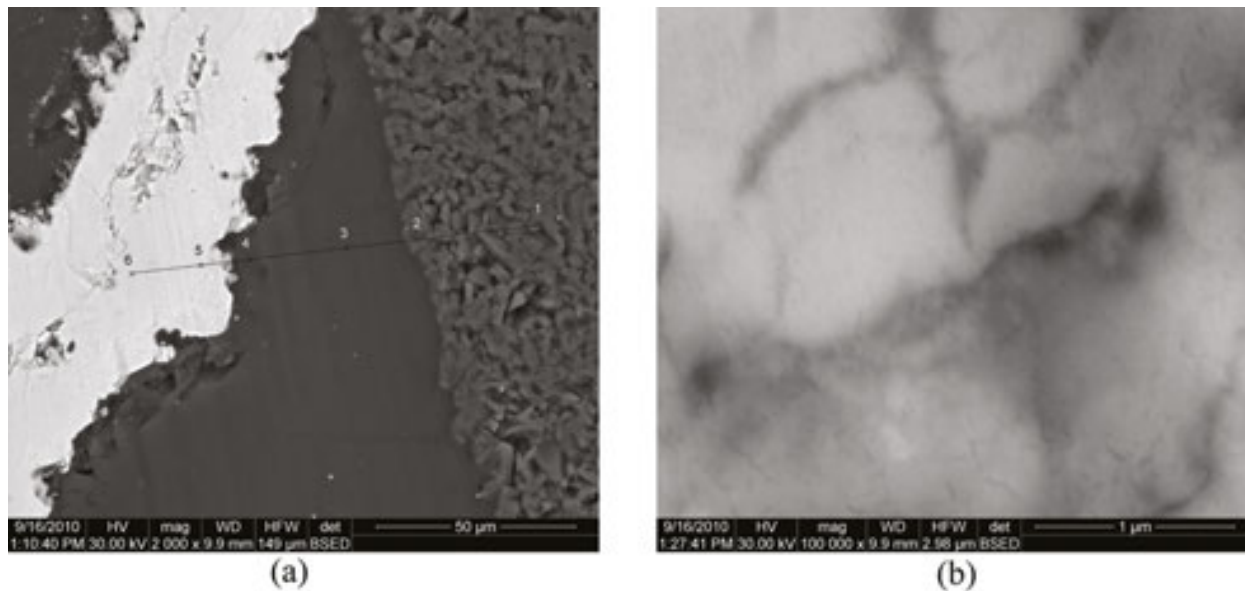


Figure 13. The melting temperature is situated in range of 778–780°C, depending on the chemical composition and accuracy of chemical composition method [1, 2]. (a) overall cross-section (ceramic, transition zone and metallic filler); (b) appearance of filler material (very fine cracks). (a) 2000× and (b) 100,000×.

shows a low deformation capacity compared with the metallic material and a lower mechanical strength compared to ceramics.

Bonding zones occur in the cross-section of the sample joined using FeNiB (**Figure 15a**), containing metallic material embedded in the semi-vitreous zones, forming a continuous belt and being deformed towards the interface with the ceramic materials. The diffusion of chemical elements forms some Fe-rich micro-crystals, ‘surrounded’ by thin films of semi-vitreous materials. In the case of the sample joined using the FeNiB metallic glass, the fracture surfaces obtained after shear tests are 40% covered by metallic materials. On the fracture surface, there were observed, in addition to the metallic material with a dendritic structure, some semi-vitreous zones in which very fine metallic polyhedral crystals were increased, having dimensions of 5–6 μm.

Point	Chemical composition (wt%)										
	Al	O	Si	Na	Mg	B	K	Ca	Fe	Nb	Co
1	60.77	31.29	5.02	2.04	0.23	–	–	0.65	–	–	–
2	25.46	39.12	8.51	9.46	0.62	5.7	0.40	3.17	–	6.89	–
3	24.82	39.7	8.92	9.12	0.61	6.57	0.25	3.31	0.24	5.46	0.73
4	25.22	40.39	9.85	8.87	0.65	5.45	0.39	3.27	0.13	3.69	2.10
5	2.53	–	0.92	2.61	–	3.3	–	–	0.70	5.18	84.76
6	2.73	–	1.16	3.12	–	3.0	–	–	0.37	15.43	74.20

Table 3. Chemical composition measured in 6 points through the cross-section (**Figure 13a**) [16].

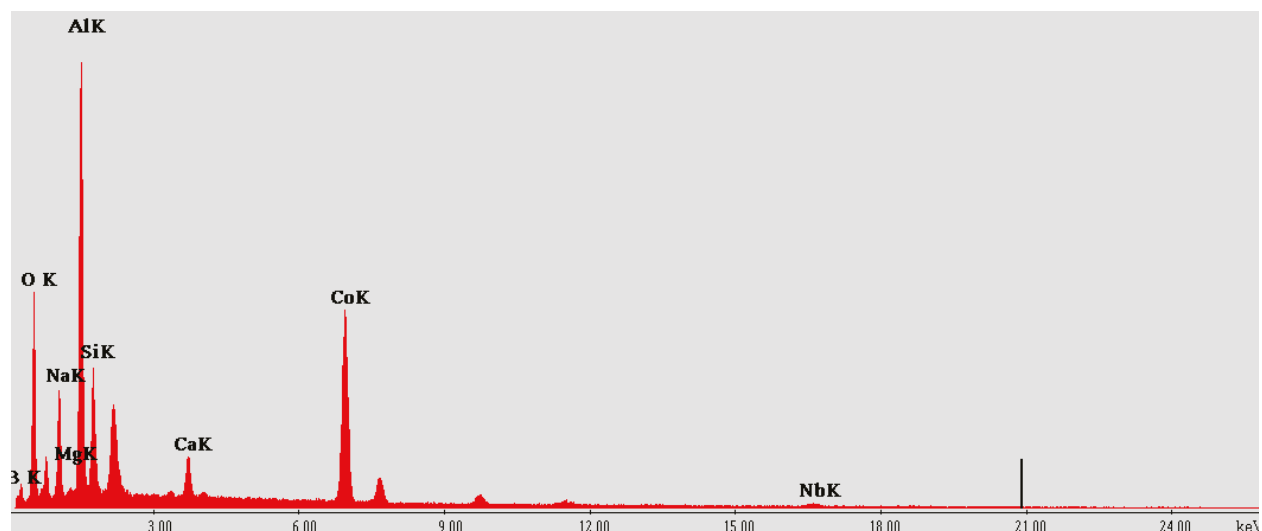


Figure 14. Energy spectrum for micro-zones from Figure 13.

Nanosized crystallites, which keep the nanostructured feature of the filler material, occur in zones covered by metallic material fragments (Figure 15b). Very fine cracks were observed both in the metallic and vitreous materials. Good adhesion to ceramic material is being provided by forming a semi-vitreous zone, with high iron content and Ni-free.

The main chemical elements present in this layer are as follows: Al, Fe, O, Na, Mg, Si and Ca (Figure 16).

The sample brazed with FeNbB alloy showed an asymmetry of the diffusion path in the ceramic layers, one of them containing large quantities of metal and polyhedral crystalline particles virtually several hundred microns deep (Figure 17).

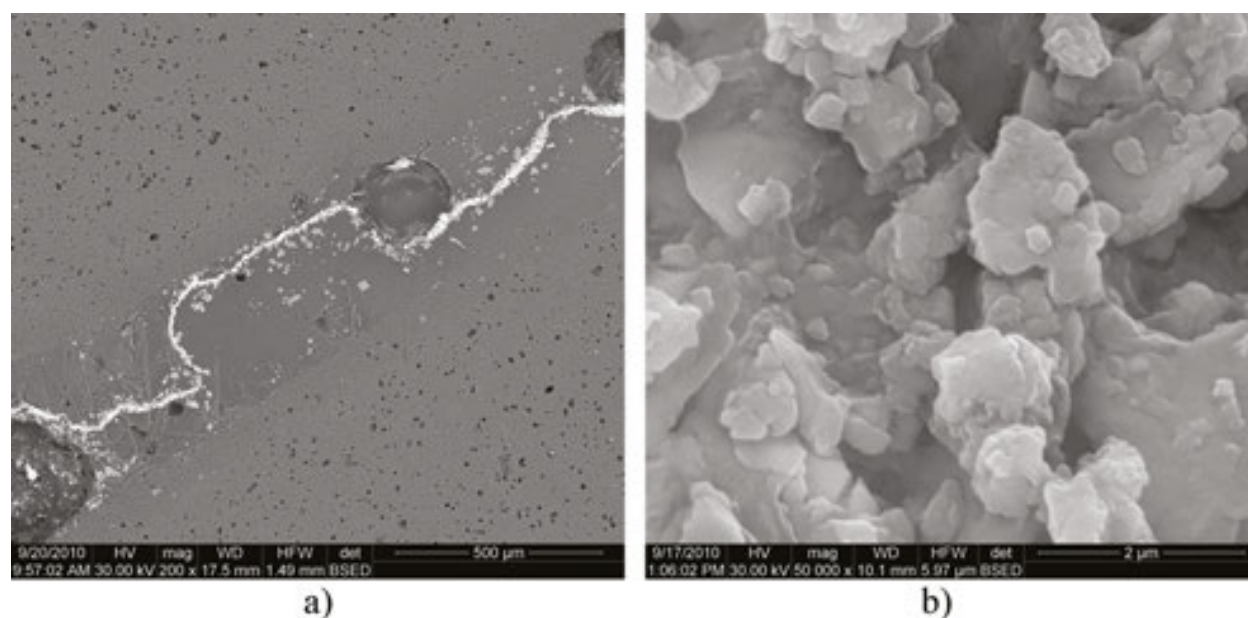


Figure 15. The melting temperature is situated in range of 778–780°C, depending on the chemical composition and accuracy of chemical composition method [1, 2]. (a) overall cross-section (ceramic, transition zone and metallic filler); (b) appearance of filler material in fracture surface (nanosized crystallites). (a) 200× and (b) 50,000×.

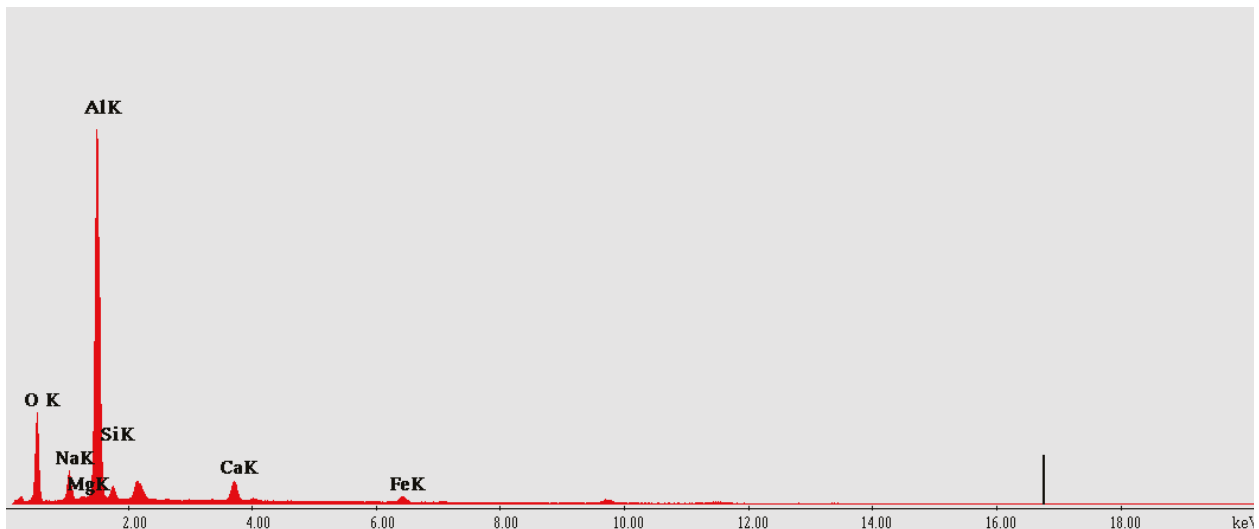


Figure 16. Energy spectrum for micro-zones from Figure 17.

In the case of the sample joined using the FeNbB metallic glass, the fracture surface resulted from the shearing test shows around 60% of the zone covered by metal (Figure 18a).

In the semi-vitreous mass (Figure 18b), there were observed metallic crystals containing mainly iron and silicon 'embedded' in a thin film of binder.

The microstructural appearances observed by scanning electron microscopy in samples joined using a copper foil as a filler material revealed melting-solidification effects in the metallic layer and a significant infiltration of liquid material through the porous ceramic materials. The entire surface of the ceramic layer is covered by a compact oxide layer. In the vicinity of

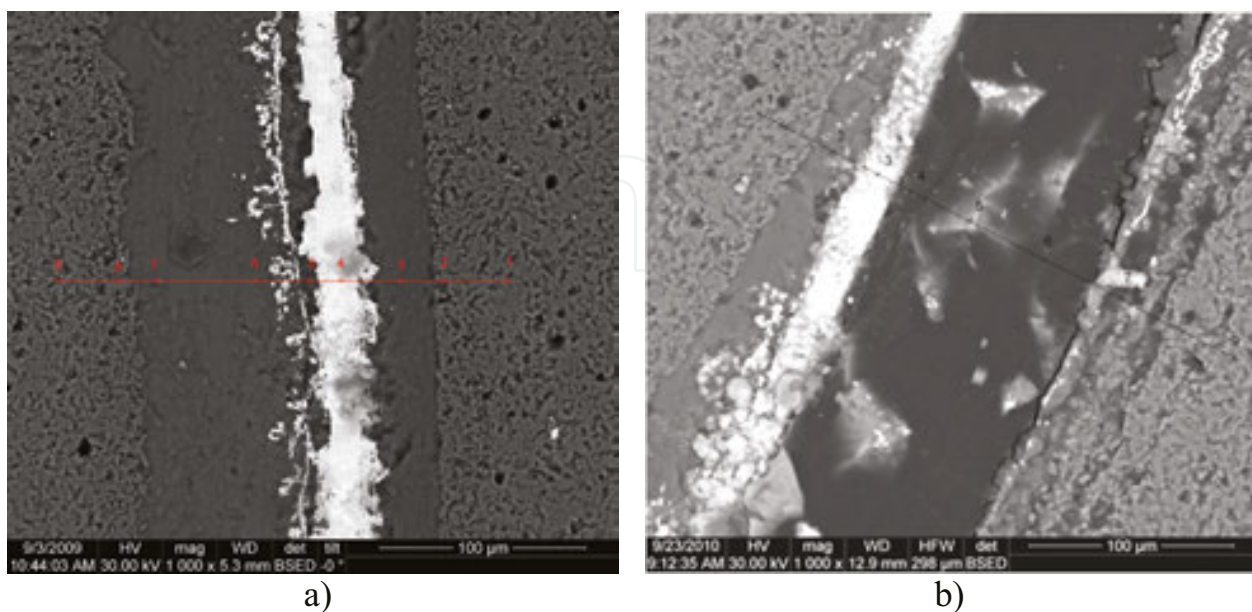


Figure 17. Cross-section of Al_2O_3 joint using FeNbB foil: (a) the joint appearance of the zone between two parts of aluminium oxide, containing a metallic layer in the central zone, bordered by two metal-ceramic zones; (b) vitreous zone containing metallic precipitates and having a porous structure. (a) 1000 \times and (b) 1000 \times .

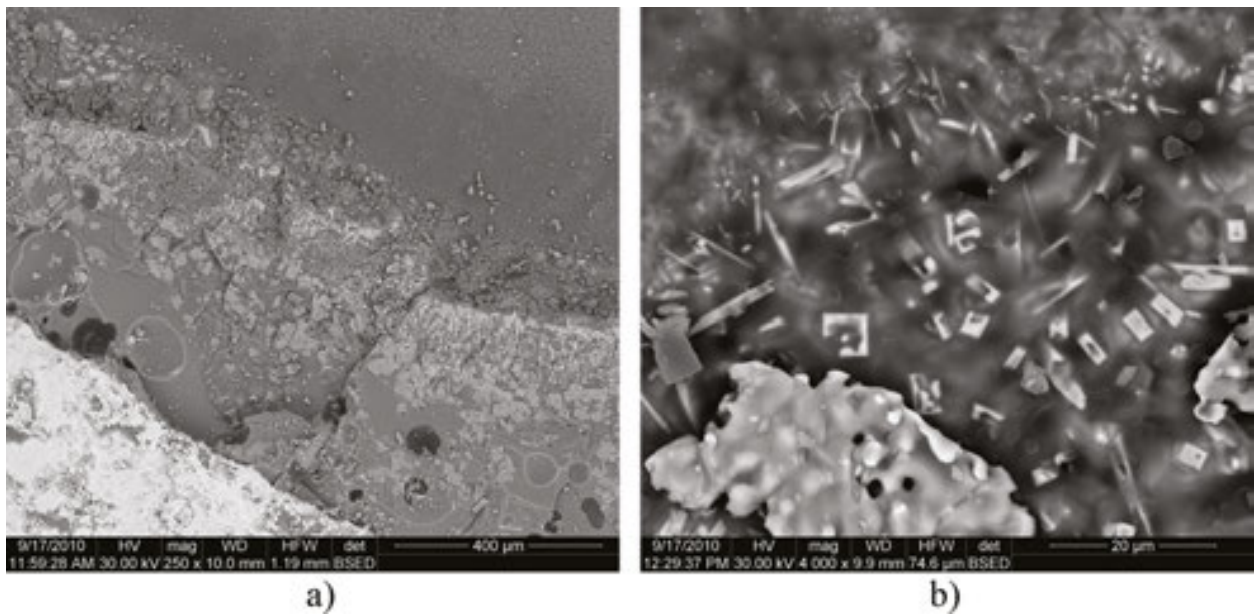


Figure 18. Fracture surface resulted from the shearing test in the case of the sample joined using FeNbB metallic glass. (a) 250× and (b) 4000×.

the metallic foil, layers with multiple cracks are visible, rich in O, Al, Na, Ca and Si and containing lower amounts of Mg, C, K and Cl.

Their appearance suggests a mixture of oxides whose continuity is interrupted by Cu-rich and Si-rich compounds with polygonal morphology (probably separated from the liquid during solidification) (**Figures 19 and 20**).

Unlike the samples previously analysed, the use of copper as a filler material allows obtaining better adherence to ceramic, without discontinuity. Copper infiltrated the alumina pores

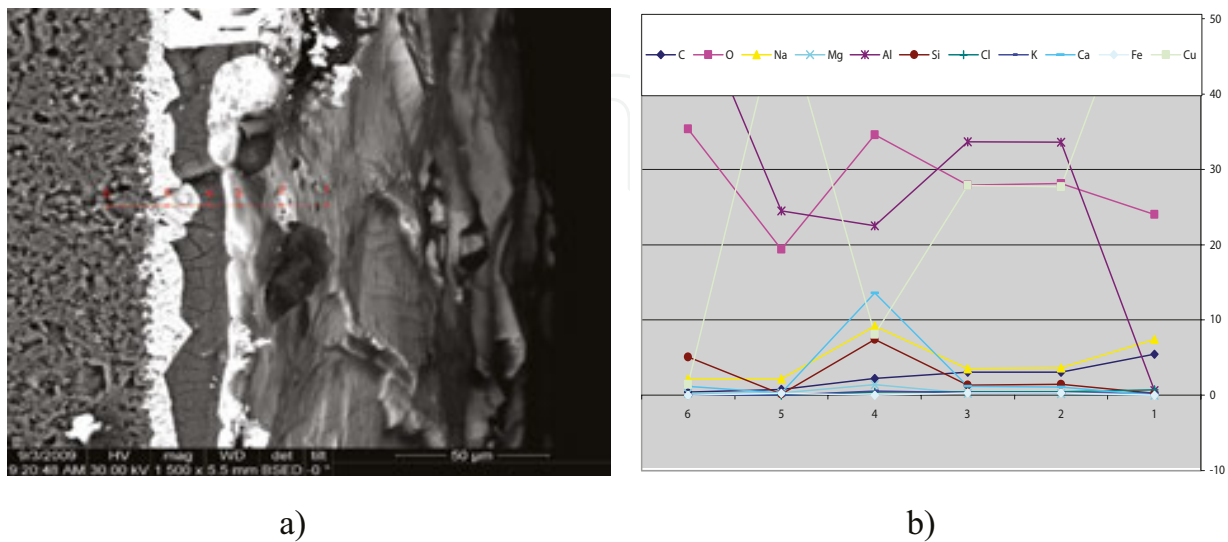


Figure 19. Cross-section of Al_2O_3 joint using Cu foil (1000×) (a) and the evolution of chemical elements concentration in six different points from the cross-section of the Al_2O_3 joint using Cu foil (b) Distribution of chemical elements in the brazing interface, %wt: 24–34 wt% O; 0.63–53.96 wt% Al; 1.45–61.21 wt% Cu; 0.27–7.40 wt% Si. (a) 1500×; (b).

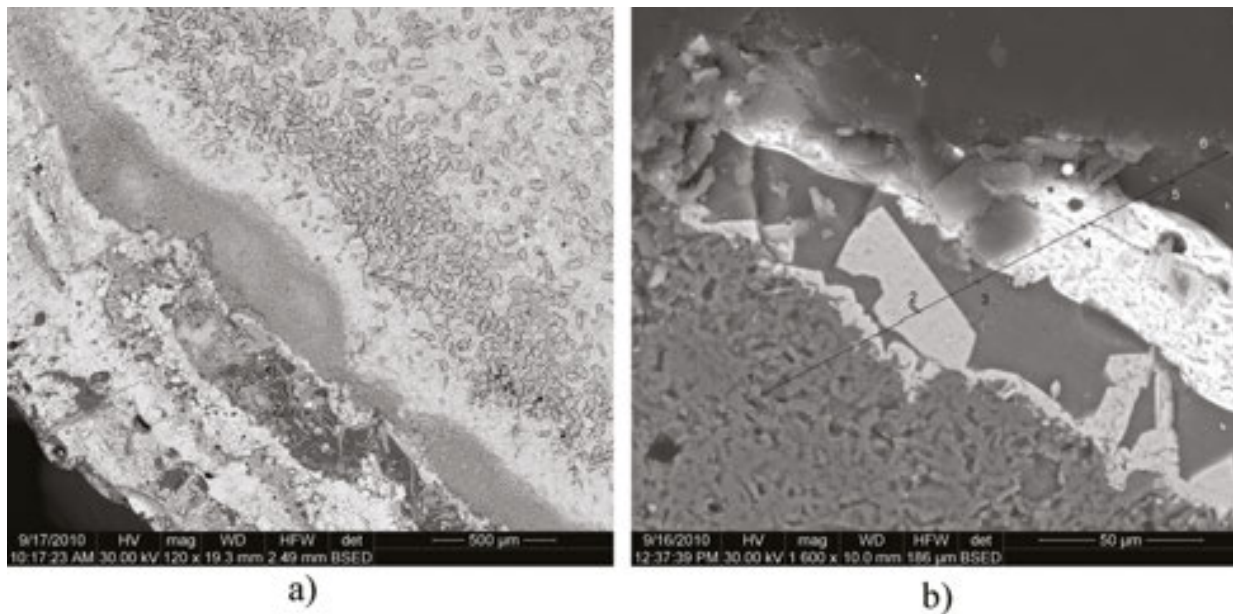


Figure 20. Fracture surface resulted from the shearing test in the case of the sample joined using copper foil. (a) 120 \times and (b) 1600 \times .

(about 2 mm deep), giving good mechanical resistance. The metallic material from the joining zone shows a dendritic structure, with very fine crystallites (tens of nanometres) (**Figure 20**).

Fracture mode resulted as peeling or pulling-out of the metallic layer from the ceramic material. An estimated 50–60% of the fracture zone is located in the metallic materials and some rare and adherent ceramic crystals that are visible. Some micro-cracks are also present on the fracture surface, generated by shear stress or by thermal contraction during the solidification of the filler materials. The metallic material was solidified in dendritic mode and contains polyhedral crystals of different sizes and geometries, influenced by the cooling rate. The microstructure also contains coarse crystals (several hundred microns in size) and very fine crystals (a few hundred nanometres in size), quickly solidified (**Figure 21**).

The shear strength of the joint is given primarily by the vitreous layer strength. The good adherence between the vitreous layer and the polygonal nanoparticles is provided by the good chemical compatibility and by the size of the particles. If the particle size is reduced, the resistance of the vitreous layer is increased. The metallic material is mechanically anchored on the porous ceramic layer and it adheres to the semi-vitreous material that contains some chemical elements diffused during brazing.

The influence of the reactive nature of the braze material on the joint integrity and strength was evaluated using shear tests. Cylindrical samples were used to conduct a shear test. A simple device and the LLOYD Instruments testing machine were used in the shear test. The normal force applied in the centre of the sample was balanced by the shear force, so the shear stress can be located at the level of the metallic material. The peak stress in the plot corresponds to the peak load at which shear failure occurred in the joint.

Shear failure occurred entirely in the braze material. As shown by the shear test (**Figure 22**), the best values for mechanical resistance are provided by a very thin layer of semi-vitreous material (ferrous-based metallic glass) [20].

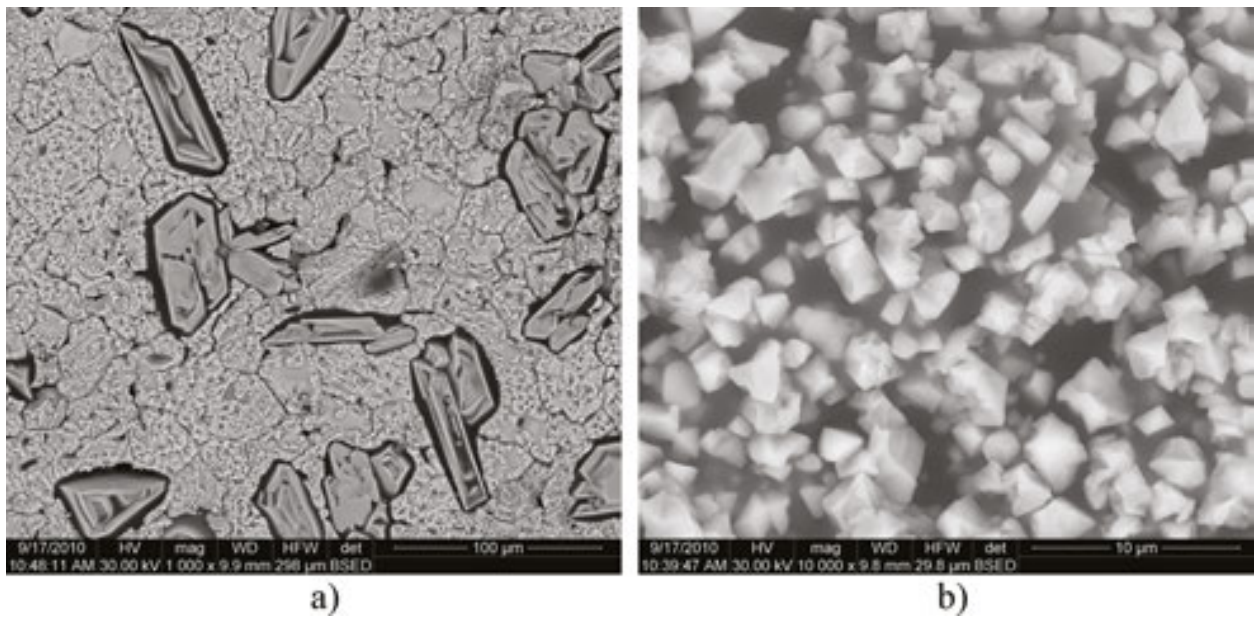


Figure 21. Polyhedral crystals of different sizes and geometries in the sample joined using copper foil. (a) 1000× and (b) 10,000×.

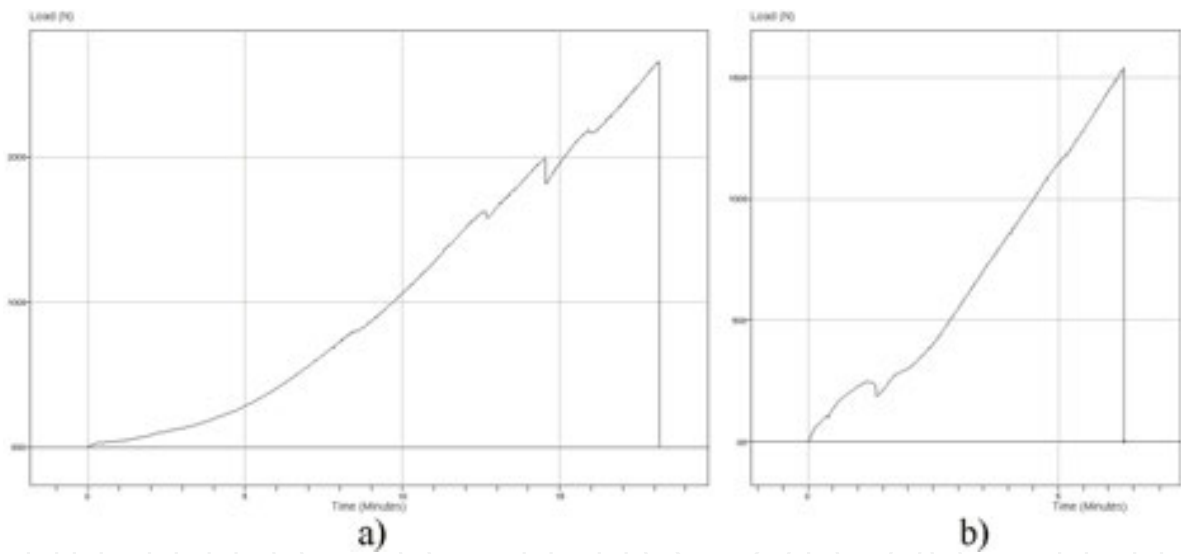


Figure 22. Schematic shear test diagrams: (a) ferrous-based metallic glass. $F_{max}=2670$ N, testing speed $v=0.2$ mm/min and (b) copper [14]. $F_{max}=1534$ N, testing speed $v=0.1$ mm/min.

3. Conclusions

The brazing of parts made up of stainless steels using fillers containing Cu and Ag requires specific operating conditions in order to avoid contamination with chemical elements that can cause embrittlement or hot cracking. It is therefore necessary to apply brazing procedures with very short operating times, utilizing filler materials with narrow domain of melting and solidification.

Furthermore, the fluxes used for this application must ensure the pickling effect on the brazed surfaces at temperature 50°C above the melting temperature of the filler material.

The elements with greater participation in the filler material (copper, zinc and silver) migrate by diffusion towards the base material, the biggest rate of diffusion being for copper (25%). These diffusion effects are extending only in a small area, of 20 to 60 microns from the interface, and do not affect the mechanical resistance or corrosion resistance of the base material.

During the brazing of tungsten carbide with steel parts, there must be ensured a good penetration of the molten filler material into the brazing gap, given that the wettability of the two types of material is different and problems related to the bond strength can occur. Recent filler materials used for the brazing of tungsten carbide are those alloyed with Ag and Zn (Cd-free), whose disadvantage is the high potential of evaporation during soldering. For this reason, in the most recent filler materials, Zn is replaced by Cu, Ni and Mn, sometimes accompanied by small amounts of indium or tin to decrease the melting temperature.

The brazing of Al_2O_3 components using metallic filler metal can be performed with satisfactory results by using the furnace brazing technique. If the filler materials for brazing and ceramic surfaces are not properly cleaned and processed (degreasing, etching, polishing), there can appear oxide layers that diminish the resistance to shear.

In the case of Al_2O_3 components, the combinations of filler materials that provide satisfactory results are $Ni_{59}Cr_{13.5}Zr_{4.3}Fe_{4.2}Nb_{2.9}Si_{15.3}B$ and $Fe_{73.5}Cu_1Nb_3Si_{15.5}B$. Metallographic examinations revealed the occurrence of oxide layers at the interface between the ceramic and filler materials, containing intermetallic compounds that ensure connection continuity but do not provide sufficient mechanical strength. For this reason, a protective atmosphere must be used during the brazing of reactive ceramic materials.

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