New technology for stainless steels brazing with copper based amorphous alloys

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Keywords

Stainless steel, brazing, brazing alloys, brazing technology, amorphous alloy, copper based amorphous alloy

1. Introduction

In the brazing process there are some problems, caused by:

- hard and stable oxides which are formed on the surface of brazed parts, because of the presence in composition of stainless steel of some alloying elements, such as: Cr, Mo, Mn, Si, Ti, Al;
- the separation of chromium in form of carbides, because of the high temperatures when brazing takes place (800 - 1000°C). The chromium carbides precipitate at the grain boundary, creating the possibility of intercrystalline corrosion.

Therefore, it is recommended that the brazing of stainless steel to be achieved by very fast brazing methods, which will ensure a larger cooling speed and in oxygen-free atmosphere to avoid the chromium carbide precipitation, and respectively the formation of hard and stable oxides on the surfaces of the brazed parts.

The alloys for stainless steel brazing must ensure to the brazed joint a proper strength and a good corrosion resistance. Consequently, in the case of stainless steel brazing two categories of brazing alloys have been developed: Ni-Cr based alloys and noble metals based alloy [1], [2].

The addition materials based on Ni are usually alloyed with B, Si and P. This is done in order to form some eutectics which diminishes the melting temperatures of Ni respectively Ni-Cr matrix and thus the flowing and moistening behaviour of these alloys is improved. The brazing alloys based on Ni are divided, depending on their chemical composition, in five families: Ni-B-Si, Ni-Cr-B-Si; Ni-Cr-Si; Ni-P, Ni-Cr-P [1].

A great disadvantage of all addition materials based on Ni, used at stainless steel and refractory steel brazing, is the stability of hard phases as borides or chemical combinations of phosphorus and silicon with Ni and Cr in the structure. In the Ni matrix, which is relatively ductile, hard phases such as: Ni3B, CrB and Ni3Si are included. Removing the hard phases from the braze area to increase the ductility and thus to improve mechanical properties has a great importance by usage of addition materials based on Ni and can be made by increasing the brazing times or applying a heat treatment for diffusion of the hard phases in the base material.

The addition materials based on Ni, because of their high brittleness, are supplied in powder form, with or without a connecting element (a substance that turns into paste). The role of the connection element is to make possible the easier handling, determining the precise dosage and a better fixation of the powder additive material. Chemical in-homogeneity and unevenness in geometric form are the main disadvantages of these bands.

Another important group of filler materials for high temperature brazing is made of fillers with noble metal materials added, based on Au, Pd and Pt. These addition materials are ductile, because of the structure consisting of a solid solution, formed from the mutual dissolution of alloy components. Due to their large ductility, added material based on noble metals can easily be obtained under the form of wire or strip. They usually have melting points lower than in alloys based on Ni. The range of base materials, that can be processed with filler materials based on noble metals, is greater than the filler material based on Ni because in addition to steel and superalloy based on Ni or cobalt it is possible to braze using noble materials special metals and metalized ceramics. Furthermore the tendency to brittleness because of the lack of B, and P is less than the addition material based on Ni. The brazing alloys based on noble metals show the disadvantage of an unsatisfactory corrosion resistance in some applications, and a very high price cost [1].

From the findings of Sexton and DeCristofaro [3], [4], regarding the applied potential of producing flexible ribbons for brazing, their numerous applications have been found over the past 20 years. The important advantage of these amorphous brazing ribbons is their ductility and flexibility. If the high temperature brazing alloys, because of there fragility, can be used only in form of powder, the brazing ribbons obtained by ultrarapid melt cooling can be easily placed within the joining area, presenting also superior moistening properties. Currently the alloys with amorphous or quasi amorphous structure are produced at industrial level in form of ductile ribbons which being used as filler material for stainless steel and superalloys brazing led to the increase of corrosion resistance of the brazed joint [4].

A few examples of brazing alloys with amorphous structure are presented in Table 1 [4], [5].

Table 1. Amorphous brazing alloys based on Ni

N-o.	Composition (balance Ni), percentage by weight	Crystallization Interval in °C	
1	13Cr-4.2Fe- 4.5Si-2.8B-1Co	965	1103
2	7Cr-3Fe- 4.5Si-3.2B	969	1024
3	19Cr- 7.3Si-1.5B	1052	1144
4	15Cr- 7.25Si-1.4B	1030	1126
5	5.3Cr- 7.3Si-1.4B	950	1040
6	15.2Cr- 4B	1048	1091
7	212Cr-4.2Si- 1.5B-4.5W-53.8Co	1078	1139

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A disadvantage of these alloys is high temperature melting, as current research focuses on obtaining amorphous brazing alloys with lower melting temperatures, such as for example those based on copper.

2. Obtaining of the amorphous brazing alloy

To obtain amorphous brazing alloys the "melt-spinning" method was chosen which requires ultra-fast cooling of the melted alloy on the outer surface of a rotating cylinder moving. This method involves two stages [6]:

- development of a primary alloy (master-alloy) with a chemically composition favourable for creating an amorphous state;
- remelting and continuous casting of the master-alloy on the outside surface of a rotating cylinder moving.

This study was performed for development of such types of brazing copper based alloy, from Cu-Ni-P-Zn family. The chemical composition of brazing alloy must be chosen to ensure both the amorphous structure and as good stretch and wetting as possible . These conditions are usually met in alloys with a composition close to the eutectics [6]. The presence of phosphorus is necessary because this component provides a good amorphous state catalyst and acts like a solvent during the brazing process. Nickel improves mechanical properties and corrosion resistance, and the presence of zinc reduces the melting temperature of the alloy.

Given these considerations and some preliminary research, for the brazing alloy the following chemical composition was chosen: Cu54Zn25Ni9P12. Thus ductile, continuous, uniform in terms of geometrical parameters ribbons were obtained, having thicknesses of 20 μm and 4 mm width. Macroscopic appearance of bands obtained is shown in Figure 1.

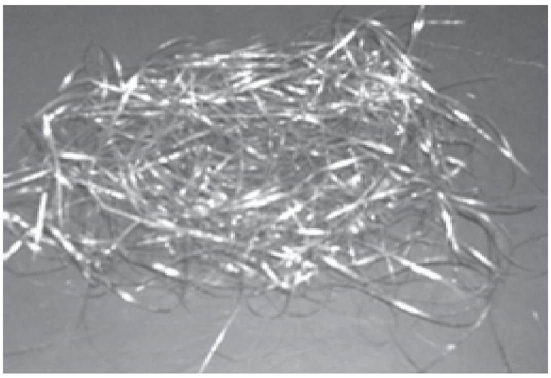

Figure 1. Solder alloy in form of ribbon

Certification of amorphous structure of the obtained ribbons was performed by X-ray diffraction analysis. This was carried out using DRON 3 diffractometer, from the endowment of Material Science and Welding Department, using the following parameters:

- voltage: U = 33 kV;
- current intensity: I = 35 mA;
- anticathode of Mo, λ_{kMo} = 0.71Å;
- X-ray tube speed: v_d = 1°/min.

The XRD patterns of the obtained ribbons (Figure 2) present a diffuse maximum and not an interference maximum at specific incidence angles. It can be said that the obtained ribbons have an amorphous structure.

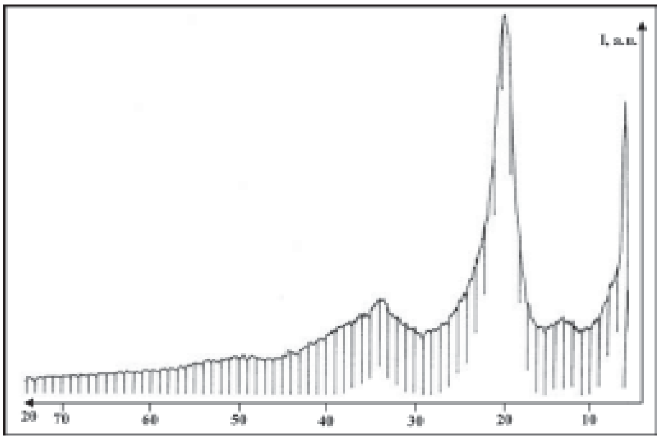

Figure 2. XRD pattern of the obtained ribbons

3. Brazing technology using copper based amorphous alloy

Taking into account the imposed conditions by stainless steel brazing, brazed joints were obtained by the resistance spot welding method, because it is a quick solder method, which provides higher heating and cooling rates, and avoids precipitation of intermetallic compounds in combination assembly. Brazing by resistance is a capillary process where the heat source is an electrical resistance. The basic principle consists in passing an electric current of high intensity and low voltage through a resistive circuit, so that the joint warms up to the soldering temperature. Directing heat at the joint is achieved by means of two electrodes, which are in contact with the base material near the joint [7].

For electrical resistance brazing the following solder alloy in amorphous state was used: Cu54Zn25Ni9P12, with a melting temperature of 640 °C, which has the following advantages:

- it has a melting temperature lower than 800 °C, which theoretically makes the heating of the base material not leading to precipitation of chromium carbides;
- having an amorphous structure it has a high electrical resistivity, and therefore, its electrical resistance heating is very rapid.

Joints were made by overlapping of two austenitic stainless steel parts, X10CrNi18-8/EN 10088, with thickness of 1 mm and 15 mm wide, free-flow soldering, using the installation PPU-125. Two constructive solutions for electrodes were used: electrode from the welding machine equipment, with the active part circular section with diameter of 10 mm and one electrode which has prismatic form in the active side, rectangular section, size 5x15 mm (Figure 3).

Figure 3. Electrode with prismatic working head

Drawings of the brazed joints are shown in Figure 4.

The experiments were performed using multiple pulsed current, so that for a brazed point one ensures more pulses of an appropriate current for different periods.

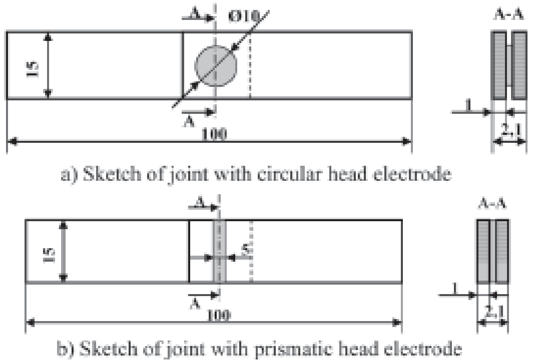

Figure 4. Sketches of brazed joints

The main technological parameters that influence the brazing process are the current intensity and brazing time. The setting of these parameters was experimentally done in order to avoid the base material welding. Thus, the following optimal technological parameters were established: Is = 400 A current, time ts = 16 s, force on 500 N.

4. Characterization of the brazed joint

To characterize the brazed joints, these were subjected to metallographic analysis and shear-breaking test.

Given that the joining is realized by combining different materials, in order to reveal the microscopic structure the metallographic etching was performed being different for the base metal and brazed area.

Metallographic analysis of the base material showed in both cases an austenitic structure with twins, being unaffected by heat during the brazing process (Figure 5). Thus, because the electrical resistance of the joint is higher, because of high electrical resistivity of the amorphous alloy, the brazing current values may be lower. This fact and the relatively small time passed during the brazing process make that the temperature, from the base material, does not reach values which affect the structure and properties.

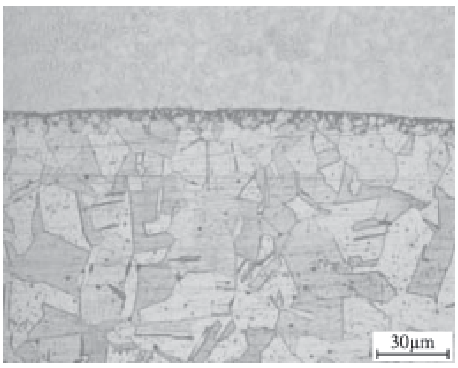

Figure 5. Microstructure of base material

Metallographic analysis of brazed joints was performed in transverse sections of the ribbons.

In case of brazing using an electrode with an active circular area it has been found that at the edge of brazed joint the filler material did not melt (Figure 6). This is because the electrode does not fully cover the entire width of the ribbon that is to be brazed.

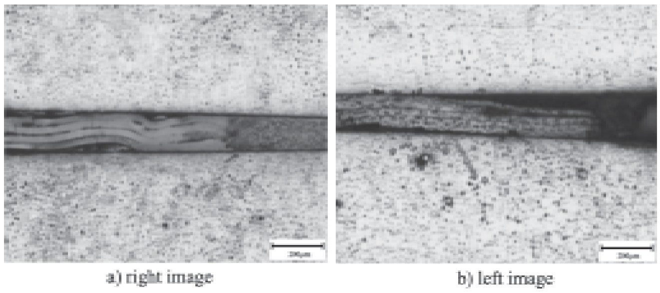

Figure 6. Marginal areas of the joint brazed with a circular electrode

Moving us to the joint centre one noticed that the brazing alloy is melting obtaining the brazed joint (Figure 7).

This is due to the fact that this part of the joint came under the electrodes action. At the same time it can be seen that the brazed area size is not uniform, being reduced as we approach to the joint axis.

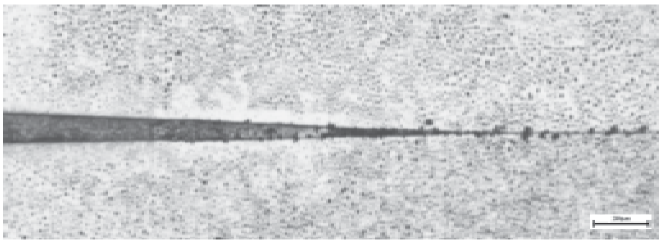

Figure 7. Microscopic image of the centre of brazed joint

In the joint centre is has been found that the brazing alloy is expelled due to the higher pressure exerted by the electrodes in this area (Figure 8).

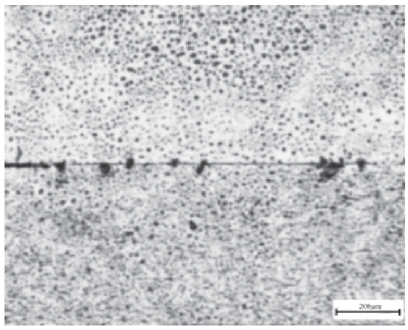

Figure 8. Microscopic image in the central brazed joint

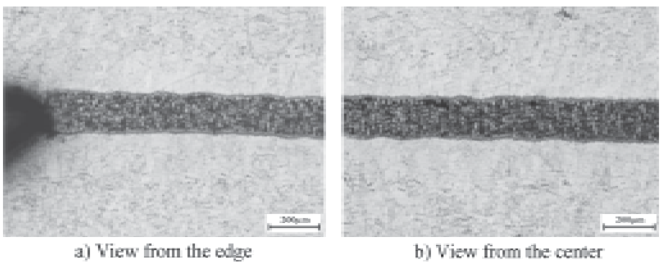

Figure 9. Microstructure of brazed joint with prismatic electrode head

In case of the electrode with the prismatic active side it was observed that the brazing alloy was melted on the entire section and the brazed joint is uniform in terms of geometry (Figure 9).

Also one shows a single-phase dendritic structure of brazed joint and also the presence of a small diffusion zone in the base material, which contribute to the increase of mechanical strength joint.

Taking into account the geometry of the bonded joints, realized by overlapping of stainless steel bands, they were tested for shear fracture behaviour. The experiments were performed on an Instron 5584 equipment. The tensile curves of the tested samples are presented in figure 10.

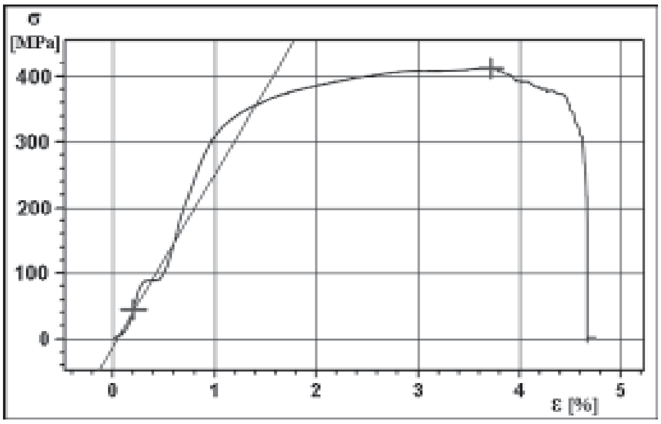

Figure 10. The tensile curve for joining with prismatic electrode

Analysing the obtained results one can say that in all cases the shear breaking resistance of the brazed joint is over the yield strength of the base material (260 MPa).

5. Conclusions

Researches regarding the stainless steel brazing with copper-based brazing alloys, from the Cu-Ni-Zn-P family having an amorphous structure, led to the following conclusions:

Electrical joining method by pressure in points is a viable method of stainless steel brazing, ensuring high heating and cooling speed. This avoids precipitation of Cr carbides and formation of hard oxides on the surface pieces.

Structural analysis of welded joints show that the brazing process heat did not affect the base material, and the very low time brazing and very fast cooling speeds led to avoiding of intermetallic compounds precipitation and the appearance of a monophasic dendritic structure in the brazed area.

Using a prismatic head electrode provides by bands brazing a uniform joining on its whole section.

In conclusion it can be said that the brazing alloy from Cu-Ni-P-Zn family with amorphous structure can be used successfully with resistance spot welding method at stainless steel joining .

Optimization of process parameters (brazing current, especially brazing time) led to a uniform brazed joint section with a single phase structure.

6. Acknowledgement

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