Amorphous alloys for brazing copper based alloys

VA Şerban, C Codrean, D Uțu and C Opriş
Politehnica University of Timisoara, Dept. for Materials Science and Welding, 1, M. Viteazu Bvd., 300222, Timisoara, Romania
serban@mec.upt.ro

Abstract. Silver based alloys are used widely when brazing copper based alloys. Due to its high cost, researchers try to obtain silver free brazing alloys, in the shape of amorphous structure ribbons, avoiding thus the formation of intermetallic compounds that diminish its ductility and plasticity. In this paper, the authors present their results in trying to obtain brazing alloys from the Cu-Zn-Ni-P family, ribbon shaped with amorphous structure, using the melt spinning method. The amorphous character of the processed alloy is emphasized by X-Ray diffraction, and the brazed joints made with the alloy were submitted to metallographic analysis and shearing tests.

1. Introduction
Until not long ago, brazing was used just to make joints performed to low loadings, the brazing alloy was used just as an adhesive; the present technique, based on the knowledge of phenomena taking place during the brazing process, having modern equipments (furnaces with reducing atmosphere or vacuum, quenching using high frequency current) allows the manufacturing of different parts from metallic alloys with high strength.

In the case of brazing copper based alloys, the majority of brazing alloys contain silver (25...70%). Silver reduces the melting temperature of the alloy, it increases its wettability, and also it ensures good mechanical and corrosion resistance to the brazed joint. Since silver is an expensive metal, the trend is to produce silver free brazing alloys, that present adequate technological properties and ensure optimal exploitation characteristics to the brazed joint [3].

Starting form the discoveries concerning the applicative potential of the manufacturing of brazing alloys in the shape of amorphous ribbons [4], using the ultra-rapid cooling of the melt technique, in the last 20 years numerous applications for these alloys were found. The advantages which these amorphous ribbons brazing alloys present are structural and geometrical homogeneity as well as providing good mechanical and corrosion resistance to the brazed joint.

2. Obtaining of the brazing alloy
The “melt-spinning” method was used for the processing of the amorphous brazing alloys, which involves the ultra-rapidly cooling of the melt on the exterior surface of a rotating cylinder. This method has two steps [1]:

- Processing of the master alloy with a chemical composition favorable to amorphization;
- Re-melting and continuous casting of the master alloy on a rotating cylinder.
The experiments performed in this paper followed the manufacturing of a copper based brazing alloy from the Cu-Ni-P-Zn family. The chemical composition of the brazing alloy must be chosen so that it ensures both the amorphization of the alloy and a good spreading and wettability. These conditions are accomplished usually by compositions situated around the eutectics [1], [3]. The presence of phosphorus is necessary because this element acts as a dissolvent, and in the case of brazing copper the tendency in not to use any fluxes. Also, phosphorus has positive influence on the formation of amorphous structures. Nickel improves mechanical properties and corrosion resistance, and the presence of zinc decreases the melting temperature of the alloy.

Having in mind these considerations, as well as some preliminary researches, the following chemical composition was chosen for the brazing alloy: Cu$_{54}$ Zn$_{25}$ Ni$_9$P$_{12}$.

The primary alloy was elaborated by introducing the raw material (CuP7, metallic Ni, metallic Zn) in an induction heated graphite crucible, using an induction melting equipment, having as main component a compact converter with transistors type CTC 100K12. The resulting melt was cast in a mould; 13 mm diameter rods were obtained.

The microscopic structure of the primary alloy is a dendritic structure, specific to the cast state of the metals (figure 1).

The ribbons were obtained by the melt-Spinning method using the installation from figure 2. The processing technology of the ribbons involves the following steps: cutting the primary alloy rods into 20 mm pieces, inserting the primary alloy in the crucible and fixing the quartz crucible, inductive heating and melting of the primary alloy, bringing the cooling roll to the optimal rotative speed, relative positioning of the crucible towards the cooling roll, applying the over-pressure to the melt using inert gas and ejecting the melt through the orifice of the ejecting nozzle on the surface of the cooling roll (figure 2).

Having in mind the anterior experience in elaborating such ribbons by ultra-rapidly melt cooling, in a first stage the following parameters were used for experiments: melt temperature: 800 °C, rotative speed of the cooling roll: 2100 rot/min, ejecting nozzle dimensions: 0.7x4 mm, distance nozzle-surface of the cooling roll: h = 0.8 mm, overpressure applied to the melt: 0.20 Bar.

The above conditions lead to obtaining ductile, continuous, geometrically uniform ribbons, with 20 µm thickness and 4 mm width. The macroscopic aspect of the ribbons is presented in figure 3.

The amorphous structure authentication of the obtained ribbons was done using X-Ray diffraction analysis. This was conducted on the DRON 3 diffractometer, using a Mo-Kα-radiation. The diffraction pattern of the obtained ribbon reveals typical halos with no evidence of crystalline Bragg peaks (figure 4). One can affirm thus that the ribbons that were obtained have amorphous structure.
3. Producing of the brazed joints using the processed alloy

In order to test the brazing behavior of the processed alloy, brazed joints were made using resistance spot brazing, because it is a rapid brazing method that ensures high heating and cooling speeds, avoiding the precipitation of intermetallic compounds in the joint. Brazing resistance is a capillary adhesion process which uses as heating source an electric resistance. The principle consists by passing of a high intensity and low voltage electric current through a resistive circuit, so that the joining place heats up to the brazing temperature. The heating process in the joining place was assured with two electrodes that were brought in contact with the base material near the joint [2], [5].

The joints were made on the PPU-125 equipment. The brazing parameters (current $I_s = 400$ A, time $t_s = 16$ s, pressing force 500 N) were optimized after a set of preliminary experimentations (figure 5).

Brazing by overlapping was made on two copper tie plates, 1 mm thickness and 15 mm width, without any brazing flux. The brazed joint is shown in figure 6.

In order to characterize the brazed joint, metallographic analysis and shearing tests were performed. Metallographic analysis supposes making metallographic samples. Etching of the brazed joint was done by immersion at 20°C, for 10 seconds using a solution of cupric ammoniacal chloride. Microscopic analysis revealed a geometrically uniform brazed joint without any precipitations of intermetallic compounds (figure 7).

Shearing tests were conducted on an Instron type equipment (figure 8).
In the case of the tested samples, it was found out the fact that the brazed joint presented no deterioration, the breaking being produced in the base material (figure 8-right image), which leads to the conclusion that the brazed joints present a higher shearing strength than the copper.

**Figure 7. Microstructure of the brazed joint**

**Figure 8. Shearing test**

### 4. Conclusions

Studies and researches conducted reveal the possibility to obtain brazing alloy for the copper based silver free alloys, directly from the melt, in the shape of ductile ribbons, with amorphous structure. The processed brazing alloy is characterized by a good brazing behavior, and because there is phosphorus in the chemical composition, the presence of fluxes is not necessary to produce the brazed joint. This may lead to the easy automation of the technological process.

The microscopic analysis showed that the structure of the brazed joint presented no precipitations of intermetallic compounds, and ensures good ductility to the joint.

Following the shearing tests, it was found out that the shearing strength of the brazed joint is superior to the fracture strength of the base material.

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