Structure of Cu-Ti brazing filler metal in amorphous and crystalline states

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Abstract. Structure, chemical homogeneity and phase composition of rapidly quenched ribbons of brazing filler metal Ti₅₇Cu₄₃ were investigated. The ribbons were found to be amorphous. The alloy components are uniformly distributed along the thickness of the strip.

High-temperature differential thermal analysis was used to determine temperature ranges of the ribbons crystallization. X-ray diffraction analysis was performed to study phase composition of the rapidly quenched ribbons in the initial state and after their isothermal annealing. Two crystalline phases - γ-CuTi and CuTi₃ being identified in the latter case.

1. Introduction
Rapidly quenched binary or multi-component metal alloys in the amorphous state play an important role among new materials. For a long time they attract attention of researchers owing to their unique properties: high level of stress-strain properties, corrosion resistance, electromagnetic characteristics, etc. The most popular method for amorphous alloy production is rapid quenching of corresponding melt [1]. Application of amorphous ribbons of brazing filler metals gives some new opportunities in the field of brazing. In particular, even brittle alloys can form ductile thin amorphous foils after rapid quenching.

In this study we investigate microstructure, phase composition, chemical homogeneity, melting temperature range and topography of the surface of amorphous brazing filler alloy Ti₅₇Cu₄₃ in the as-quenched and annealed states.

2. Materials and experimental procedure
Rapidly quenched ribbons of brazing filler metal Ti₅₇Cu₄₃ with the thickness of 30-50 μm were used for the investigations. Thermal effects of transition from amorphous to crystalline state, as well as melting and crystallization temperature ranges were determined by high-temperature differential thermal analysis. Heating and cooling were carried out in the helium atmosphere at a rate of 80 °C/min.

The rapidly quenched ribbons were annealed at 510 °C for 1 h and investigated in the as-quenched state and after the heat treatment using metallographic and X-ray diffraction analysis. The last was performed using DRON-3 diffractometer with the MoKα - radiation in a point-by-point scanning mode. Graphite monochromator was placed in the primary beam. The recording equipment was selected to eliminate noises, fluorescent scattering from the specimen and radiation from the continuous spectrum with the wavelength λ/2 passed by the monochromator crystal. Procedures for
making corrections for incoherent scattering, polarization, absorption, fluorescent scattering from a specimen and normalizing of diffraction curves are standard [2, 3].

Topography of the surface and local distribution of components of the alloy were examined using the scanning electron microscope “Cam Scan” equipped with a micro analysis attachment.

3. Results and discussion

It was shown by metallography that in as-quenched state a typical structure of the exposed side of the Ti$_{57}$Cu$_{43}$ amorphous strip in contact with air is characterized by a smooth mirror-like (glassy) surface and absence of any depressions or roughness. The surface of the reverse side of the strip in contact with the disk has a specific relief caused by the disk surface, linear velocity of its rotation and other process parameters. Not less important factors are surface tension and temperature of overheating the melt above the liquidus, wetting of the disk material with the melt, toughness of the alloy etc.

It should be noted that at rapid quenching the melt a distinct temperature gradient in a direction normal to the ribbon plane exists. It promotes inhomogeneous distribution of elements along the ribbon thickness. As a result, surface layers adjoining the exposed side of the strip are, as a rule, enriched in lighter elements, whereas heavier elements are dominant in surface layers of the reverse side of the ribbon [1]. Nevertheless, in our case, according to results of local chemical analysis, concentrations of the main components of the brazing filler metal are uniform along the scanning line (fig. 1).

A typical thermogram of the initially amorphous ribbon of the Ti$_{57}$Cu$_{43}$ alloy (fig. 2) demonstrates one exothermic and one endothermic peaks while heating. The first effect in a temperature range of 480-500 °C corresponds to the alloy transition from an amorphous to a crystalline state, which is accompanied by a heat release. The wide endothermic peak is connected with melting the sample.

![Figure 1. Distribution of copper and titanium along the ribbon thickness.](image1)

![Figure 2. Thermogram of rapidly quenched ribbon of brazing filler metal Ti$_{57}$Cu$_{43}$ (the upper curve corresponds to heating and the lower curve corresponds to cooling).](image2)

Cooling results in crystallization of the melt, and only one exothermic effect takes place here. The distribution of the thermal effects shown in fig.2 confirms the amorphous state of the rapidly quenched ribbon.

An isothermal annealing of the amorphous ribbon at 510 °C led to some changes in their surface geometry. Thus, the wavy relief replaces the smooth (glassy) one (fig. 3a), whereas no substantial changes were revealed on the reverse side of the ribbon. Microstructure of cross section of the ribbon consists of two phases (fig. 3 c), which is in good agreement with the results of X-ray diffraction analysis.

Structural factor $i(s)$ and function of radial distribution of atoms (FRDA) were calculated for the amorphous brazing filler metal Ti$_{57}$Cu$_{43}$ and their main structural characteristics (position $s_1$, height $i(s_1)$), half-height width (half-width) $\Delta s_1/2$ of the first maximum of the structural factor, position $r_1$ and
area $A$ of the first maximum of FRDA) were determined from them. The results of the X-ray diffraction analysis of the Ti$_{57}$Cu$_{43}$ rapidly quenched ribbons prove that their diffraction patterns $i(s)$ are typical for amorphous state [4] and consist of two diffusion maxima with a clearly defined splitting of the second one (fig. 4a). At $s \approx 3.5$ Å$^{-1}$, there is a zoom on the right branch of the first maximum of structural factor $i(s)$ (Fig. 4b). The first maximum of the FRDA curve is asymmetric and there is an extra maximum near $r \approx 3.6$ Å (fig. 5a).

![Figure 3](image1.png)
![Figure 4](image2.png)

**Figure 3.** Surface of the amorphous ribbons in contact with air (a) and drum (b) and its microstructure (c) after the isothermal annealing.

**Figure 4.** Diffraction curve (a) and structural factor (b) of the amorphous ribbons.
These facts evidence that the first diffraction maximum and the first FRDA maximum consisting of two or more components can be considered a superposition of several maxima caused by existence of several types of atomic groups differing in type of topological and compositional ordering of atoms [2].

Taking into account that the brazing filler metal under investigation was produced from the melt with the eutectic composition we used structures corresponding to the phase diagram of the Cu-Ti system for amorphous ribbons modeling. It was discovered that atomic groups with the short range orders of $\gamma$-CuTi and CuTi$_3$ turned out to be the most probable for its description. This is in a good agreement with the results of X-ray diffraction analysis of the Ti$_{57}$Cu$_{43}$ alloy obtained after the isothermal annealing the ribbons in vacuum. Really, the crystalline structures of $\gamma$-CuTi and CuTi$_3$ were identified after their crystallization (fig. 5 b).

4. Conclusions

1. Rapidly quenched ribbons of brazing filler metal Ti$_{57}$Cu$_{43}$ are X-ray amorphous.
2. Isothermal annealing at 510 °C leads to transition of the alloy from the amorphous to a crystalline state.
3. Crystalline structures of $\gamma$-CuTi and CuTi$_3$ were identified in the crystalline state.

References

[1] A.P. Shpak, Yu.A. Kunitsky, V.I. Lysov, Cluster and nanosrtructural materials. Volume 2. Kiev: Akademperiodiodika, 2002. 540
[2] Yu.K. Kovneristyj, Volume-amorphizing metal alloys. M.: Nauka, 1999
[3] V.V. Nemoshkalenko et al., Amorphous metal alloys. Kiev: Naukova Dumka, 1987
[4] A.V. Romanova, Metal Physics, Noveishie Tekhnologii. 1995, No. 8, V.17, 17.