STRUCTURAL STATE OF RAPIDLY QUENCHED Cu–Ti SYSTEM BRAZING FILLER METAL

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It has been established that the strip of a rapidly quenched brazing filler metal is in the amorphous state with a uniform distribution of alloying elements in its width. Temperature ranges of transition of the brazing alloy from the amorphous to crystalline state have been determined. X-ray examination of phase composition of the rapidly quenched strip in the initial state and after isothermal annealing has been conducted, the δ-CuTi and γ-CuTi crystalline structures being identified in the latter case.

Keywords: *brazing, brazing filler metal, Ti–Cu system, structure, phase composition, amorphous and crystalline state, super rapid quenching, isothermal annealing, X-ray diffraction analysis*

Amorphous metal alloys attract attention of many researchers owing to their unique properties, such as high mechanical characteristics, corrosion resistance, electromagnetic indicators, etc. [1].

Application of brazing filler metals in the amorphous state opens up new opportunities in the field of brazing. One of the key advantages of amorphous brazing filler metals is their chemical homogeneity. These brazing filler metals provide good wetting of the base metal surface, feature high capillary activity, diffusion activity of their components, and uniform distribution of the latter within the brazing zone, thus reducing the probability of formation of brittle phases and providing the optimal strength of brazed joints. The brazing filler metals are characterised by high viscosity, this making it possible to manufacture imbedded elements of the required size and dispense the brazing filler metal in fabrication of unique critical structures applied in different industrial sectors [2].

The purpose of this study was to conduct comparative investigations of structural peculiarities of rapidly quenched brazing filler metal $Ti_{57}Cu_{47}$ in the initial and annealed states, as well as evaluate thermal stability of its amorphous state in heating.

Alloys produced by rapid cooling of the melt (quenching) are classed with rapidly quenched alloys. Structure and properties of the rapidly quenched alloys are substantially different from those of the cast alloys produced by traditional melting methods. Depending upon the cooling rate, they may have a highly dispersed dendritic, microcrystalline, nanocrystalline or amorphous structure [3].

The method of rapid ($1\cdot10^4$–$1\cdot10^6$ °C/s) solidification of the melt on the external fast-rotating cooling disk is most widely applied to produce brazing filler metals in the amorphous state [4, 5]. Under the pressure of inert gas, the molten metal passes through the nozzle and gets to the external surface of the rotating disk, where it solidifies in the form of a thin strip, which is removed under the effect of centrifugal forces. Ductile thin amorphous foils (strips) can be produced even from brittle alloys (eutectic, intermetallic) by super rapid quenching. When cooled at a high rate, such systems tend to suppress formation of centres of the above phases and reach the amorphous state even in the absence of amorphising agents, such as boron, silicon, phosphorus, etc.

The rapidly quenched $Ti_{57}Cu_{43}$ strips, 30–50 μm thick and about 20 mm wide, were used for investigations. As shown by metallography, the typical structure of a free surface of the $Ti_{57}Cu_{43}$ amorphous strip in contact with air is smooth and mirrored (glassy), and features the absence of any depression or roughness (Figure 1, *a*).

The underside of the strip in contact with the disk surface has irregularities (Figure 1, *b*) caused by surface geometry of the disk material, its rotation velocity, etc. Important factors for production of rapidly quenched strips are temperature of overheating above the liquidus line of the melt, alloy viscosity, surface tension and wetting of the disk material with the melt.

It should be noted that rapid quenching of the melt is accompanied by formation of a temperature gradient in a direction normal to the strip plane, which leads to concentration heterogeneity in distribution of elements through thickness of the strip. As a result, surface layers adjoining the free side of the strip are enriched with lighter elements, whereas heavier elements prevail in surface layers on its contact side [6]. The rapidly quenched strip of the brazing filler metal under investigation was produced using no chemical amorphising elements. Investigation of chemical heterogeneity in a cross section of the strip showed that the brazing filler metal components are uniformly distributed along the scanning line (Figure 2).

Investigations of structural state of the rapidly quenched brazing filler metal in the initial and annealed states were performed by the radiography method using diffractometer DRON-3 in Mo_{K_α}-radia-

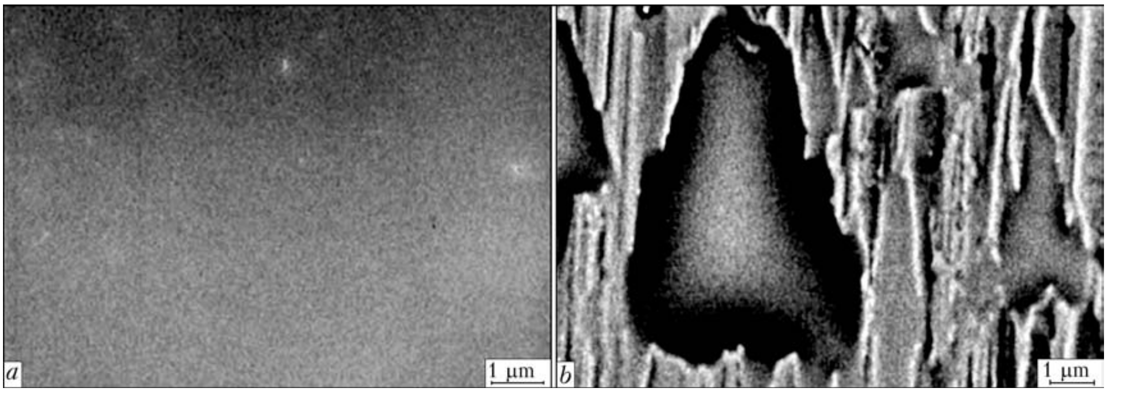

Figure 1. Surface of rapidly quenched strip in contact with air (*a*) and with disk surface (*b*)

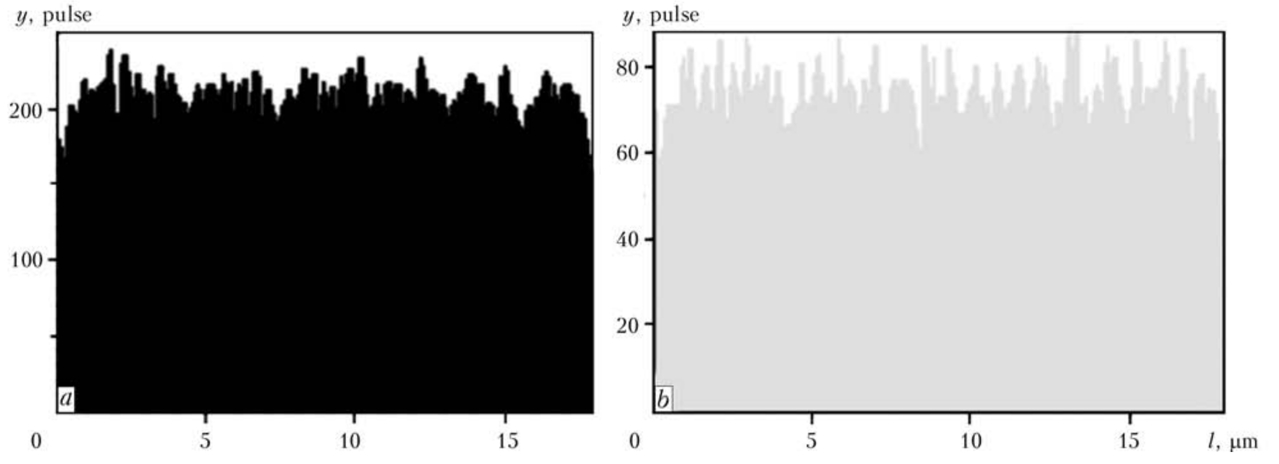

Figure 2. Distribution of titanium (*a*) and copper (*b*) in width of rapidly quenched strip (y — quantity of pulses)

tion in the scanning mode at a step of 0.1° in a range of the main maximum and 0.5° at other distances. Graphite monochromator was placed at the primary beam. Modes of the recording equipment were selected so that they eliminated noise, fluorescent scattering from a specimen, as well as radiation from the continuous spectrum with the $\lambda/2$ wavelength transmitted by the monochromator crystal.

The method of correction for incoherent scattering, polarisation, absorption and fluorescent scattering by a specimen, as well as normalisation of diffraction curves were standard [7, 8].

It is a known fact that metal glasses give a diffraction pattern similar to that of metal liquids. Therefore, the experimental design and mathematical tool of Fourier transformation, which is used to investigate liquids, were employed to study their structure [7].

Structural factor $i(s)$ and radial atom distribution function (RADF) were calculated for brazing filler metal $Ti_{57}Cu_{43}$. Main structural characteristics, i.e. position s_1, height $i(s_1)$, width at half-height (half-width) $\Delta s_{1/2}$ of the first maximum of the structural factor, position r_1 and area A of the fist maximum of RADF were determined from $i(s)$ and RADF.

Results of X-ray diffraction analysis showed that the diffraction pattern of composition of the brazing filler metal was typical [9] of the amorphous state,

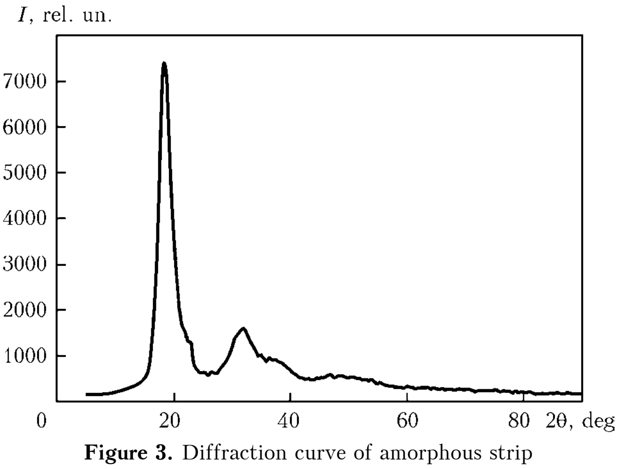

Figure 3. Diffraction curve of amorphous strip

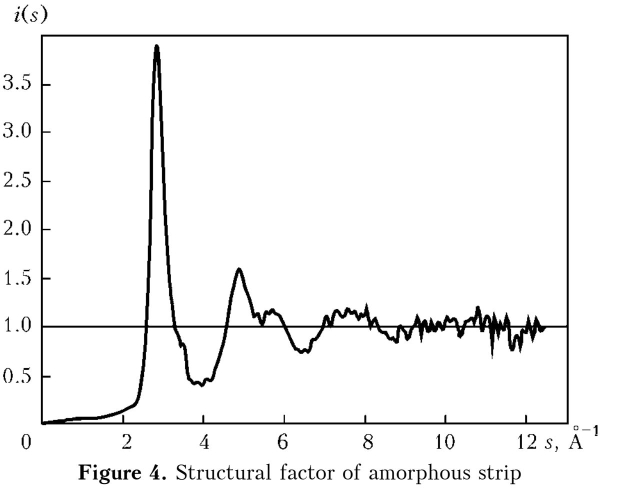

Figure 4. Structural factor of amorphous strip

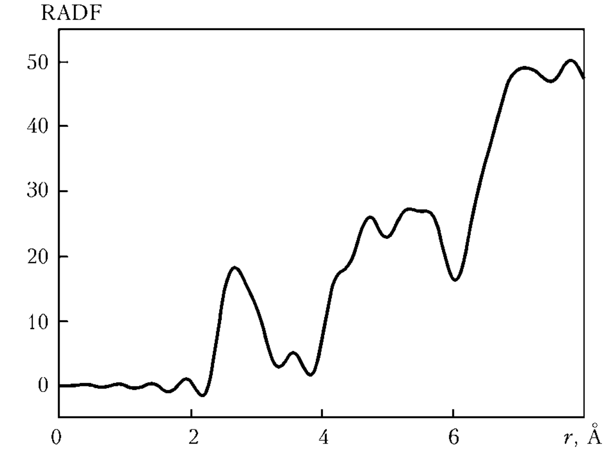

Figure 5. RADF curve

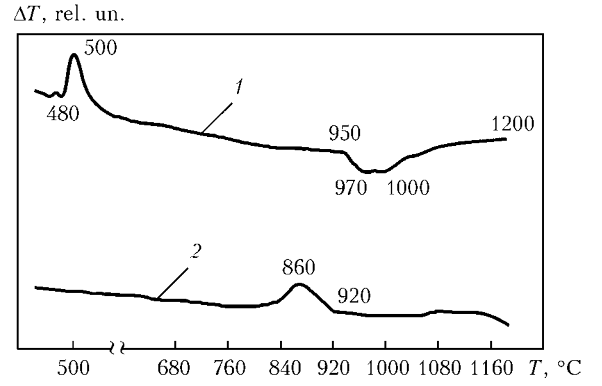

Figure 6. Thermogram of rapidly quenched strip of brazing filler metal $Ti_{57}Cu_{43}$ in heating (*1*) and cooling (*2*)

comprising diffusion maxima (Figure 3) with a clearly defined effect of bifurcation of the second maximum of $i(s)$ (Figure 4). A bulge can be seen on the right branch of the first maximum of structural factor $i(s)$ at $s \approx 3.5$ Å^{-1}. The RADF curve has asymmetry of the first maximum and additional maximum in a region of $r \approx 3.6$ Å (Figure 5). This is indicative of the fact that the first diffraction maximum and the first maximum of RADF, like in the case of atomic structure of the melts consisting of two or more components, can be considered a superposition of several maxima, which are caused by existence of several types of atomic groups differing in type of topological and compositional ordering of atoms [7].

Two exothermic thermal effects and one endothermic effect were fixed (Figure 6) in investigation of a melting temperature range by high-temperature differential thermal analysis (in helium atmosphere at a heating and cooling rate of 80 °C/min).

The presence of the first insignificant exothermic effect in a temperature range of 460–480 °C proves the fact of occurrence of structural relaxation, which decreases the level of quenching stresses in different microvolumes and precedes solidification. As the temperature is increased, maximal heat release takes place at 500 °C, this leading to volume solidification of the alloy and indicating to a relatively low thermal stability of the amorphous (metal-stable) state of the rapidly quenched strip. The exothermic effect is absent in a case of complete structural relaxation [6]. The endothermic effect takes place with further increase in temperature, this being indicative of complete melting of the brazing filler metal. The melt solidifies in cooling, and only one thermal effect is fixed in the thermogram. This character of distribution of thermal effects evidences the presence of the amorphous state in the rapidly quenched strip.

According to the data of high-temperature differential thermal analysis, low-temperature isothermal annealing was carried out in vacuum at a temperature of 510 °C (and at 400 °C, for comparison) for 1 h.

After annealing, the free surface of the strip had a wavy geometry (Figure 7, *a*), rather than a mirrored (glassy) one, which is characteristic of the initial state. The underside of the strip in contact with the disk surface remained almost unchanged (Figure 7).

Low-temperature annealing of amorphous alloys causes structural relaxation of residual stresses and leads to reorganisation of their local structure (change in arrangement of atoms, their ordering) [6]. For example, annealing at a low temperature (400 °C) hardly affects structure of the rapidly quenched strip (Figure 8, *a, b*). However, one should note formation of structural microregions with a blurred interface appearing between them.

At an annealing temperature increased to 510 °C, the contrast of microstructure aggravated, and structural changes became more clearly defined (Figure 8, *c, d*). The surface acquired a slightly pronounced cellular structure with broadened boundaries (Figure 8,

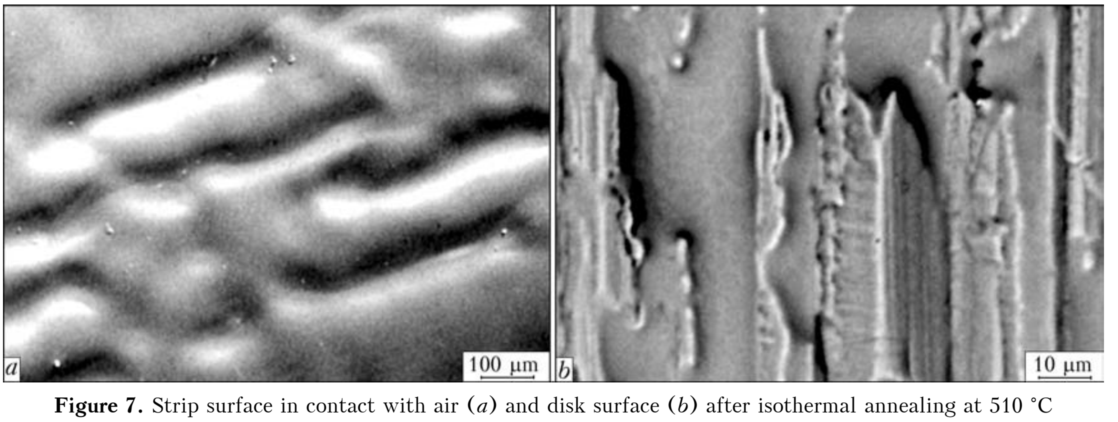

Figure 7. Strip surface in contact with air (*a*) and disk surface (*b*) after isothermal annealing at 510 °C

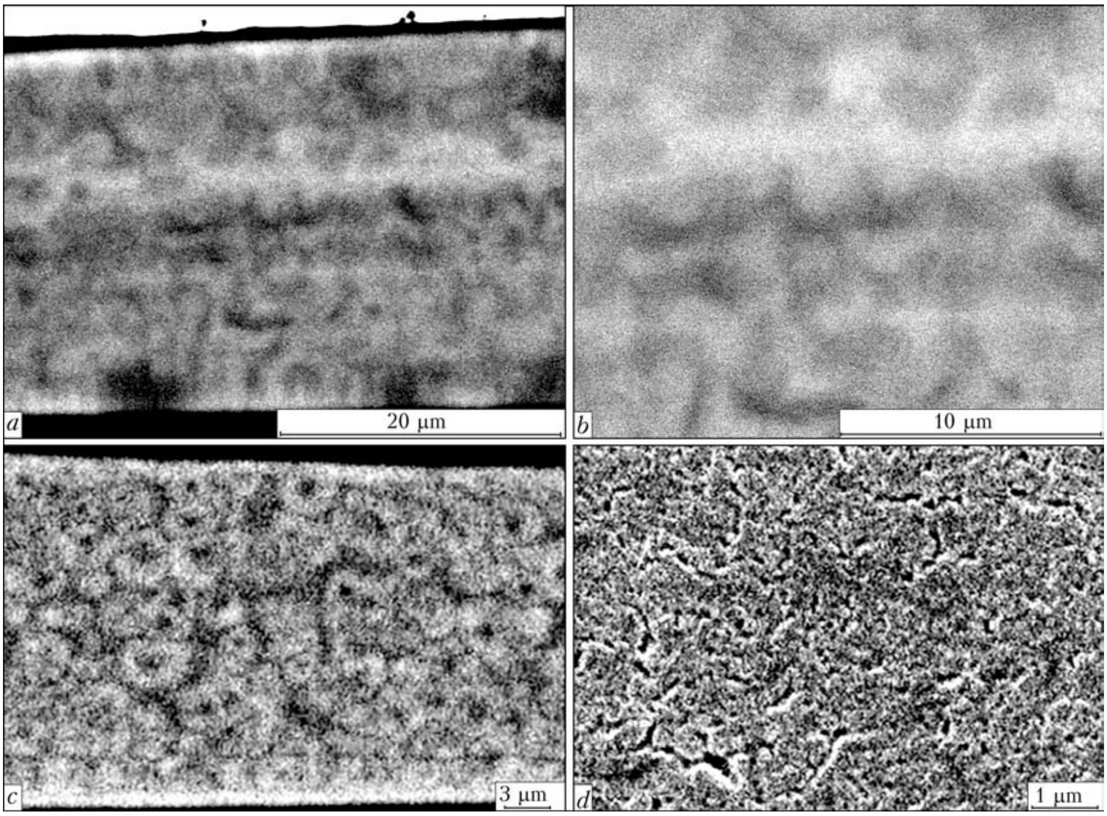

Figure 8. Strip microstructures after isothermal annealing at 400 (*a, b*) and 510 (*c, d*) °C

c), which is characteristic of the initial stage of decomposition of the amorphous state. Chemical etching of the annealed specimen revealed appearance of interfaces between individual microvolumes (Figure 8, *d*).

A typical diffraction pattern of the amorphous state was observed after annealing of the $Ti_{57}Cu_{43}$ strip at 400 °C.

On the one hand, this system is characterised by a complete absence of amorphising non-metals, such as boron, silicon, etc. But, on the other hand, it belongs to the eutectic type with the presence of intermetallic compounds.

It is a known fact that the presence of intermetallic compounds with a complex type of the crystalline lattice in a system is a key factor of the glass-forming ability of alloys, which allows achieving the amorphous state.

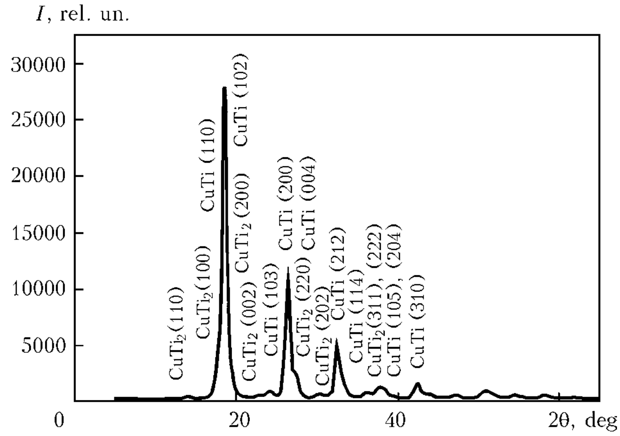

Figure 9. X-ray pattern obtained after isothermal annealing of the brazing filler metal

For instance, the glass-forming ability in the Cu–Ti system is caused by the eutectic character of interaction of glass-forming intermetallic phases, such as CuTi and $CuTi_2$ [1]. An important feature evidencing that a given chemical compound of a particular type has a glass-forming ability is its formation in solidification from the amorphous state during heating.

These data are in good agreement with the results of X-ray diffraction analysis of alloy $Ti_{57}Cu_{43}$, obtained in isothermal annealing in vacuum. For example, the δ-CuTi and γ-$CuTi_2$ crystalline structures were identified in alloy $Ti_{57}Cu_{43}$ after its transition from the amorphous state to the crystalline one (Figure 9).

Therefore, when using amorphous brazing filler metals to produce permanent joints by brazing with a long heating, its initial stages are characterised by structural relaxation of the amorphous state with further transition into the crystalline one. Brazing is performed with a brazing filler metal in the microcrystalline state. Finer investigation methods, including high-temperature metallography, are required to study this process in more detail.

Amorphous state of the used brazing filler metal has a positive effect, first of all, on its practicability. Owing to high viscosity, small thickness and chemical homogeneity, the brazing filler metal provides the high quality of brazing, absence of defects (in the form of lacks of penetration) and high strength of the brazed joints. Application of the investigated brazing filler metal in the amorphous state for brazing of precipitation-hardened copper alloy of the Glidcop Al–25 grade provided the brazed joints with a tensile strength of 80–90 % of that of the base metal [10].

It can be concluded from the above-said that rapidly quenched brazing filler metal $Ti_{57}Cu_{43}$ in the form of a strip is X-ray amorphous. Isothermal annealing at 510 °C leads to transformation of the alloy from the amorphous state to the crystalline one, in which the δ-CuTi and γ-$CuTi_2$ crystalline structures are identified.

1. Kovneristy, Yu.K. (1999) *Volume-amorphising metal alloys*. Moscow: Nauka.
2. Khorunov, V.F., Maksymova, S.V. (2005) Amorphous filler alloys — promising material for advanced brazing processes (Review). *The Paton Welding J.*, **10**, 33–38.
3. Fatkhullin, O.Kh. (2005) State-of-the-art in metal science of rapidly quenched heat-resistant alloys. *Tekhnologiya Lyog. Splavov*, **1–4**, 24–31.
4. Kalin, B.A., Fedotov, V.T., Sevryukov, O.N. et al. (1996) Amorphous brazing filler metal strips. Experience of development of the manufacturing technology and application. *Svarochn. Proizvodstvo*, **1**, 15–19.
5. Kalin, B.A., Plyushchev, A.N., Fedotov, V.T. et al. (2001) Effect of structural state of brazing filler metal on physical-mechanical properties of brazed joints. *Ibid.*, **8**, 38–41.
6. Shpak, A.P., Kunitsky, Yu.A., Lysov, V.I. (2002) *Cluster and nanostructural materials*. Kiev: Akademperiodika.
7. Nemoshkalenko, V.V., Romanova, A.V., Iliinsky, F.G. (1987) *Amorphous metal alloys*. Kiev: Naukova Dumka.
8. Romanova, A.V. (1995) Some historical facts and memories about development of notions of atomic structure of liquid and metal glasses. *Metallofizika, Novejshie Tekhnologii*, **8**, 3–29.
9. Golder, Yu.G. (1978) Metal glasses. *Tekhnologiya Lyog. Splavov*, **6**, 74–93.
10. Maksimova, S.V., Khorunov, V.F., Shonin, V. A. et al. (2002) Vacuum brazing of dispersion-strengthened copper alloy Glidcop Al–25. *The Paton Welding J.*, **10**, 13–17.

INFLUENCE OF WORKING DISTANCE OF WELDING ELECTRON GUN ON WELD GEOMETRY

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Geometry of electron beam penetrations in a wide range of gun to workpiece distances was experimentally studied. A weak correlation was established between the gun to workpiece distance and penetration depth in thick metals. The possibility of substantially increasing of working distance without a marked change in the penetration parameters is attributable to a corresponding decrease of the convergence angle of the beam within the workpiece region.

Keywords: *electron beam gun, welding gun, working distance, weld depth, focal point, angle of beam convergence*

No international standard on spatial characteristics of welding electron beam has been introduced so far, despite a high interest to the issue of interaction of beam parameters and weld geometry [1, 2]. Focal spot dimensions, i.e. beam minimum section in the welded workpiece plane, are quite often specified in the requirements to welding electron gun. It is believed that a small spot is the main condition for formation of deep welds with minimum transverse dimensions of the cast zone and with simultaneous improvement of secondary electron image of the welding zone. As the focal spot dimensions are directly proportional to the welding gun working distance, many operators are trying to place it as close as possible to the workpiece, despite a concurrent increase of the probability of electric breakdowns in the accelerating gap of the gun, because of metal vapour and gas penetration from the weld pool.

At electron beam welding of thin metal (up to several millimetres), when surface supply of thermal energy is performed and there is practically no crater in the weld pool, dimensions of minimum beam section on the workpiece surface indeed determine the dimensions of the cast zone at other conditions being equal.

However, when the weld forms in the metal of the thickness of tens and even hundreds of millimetres, focal spot dimensions proper no longer determine the cast zone dimensions, and spatial characteristics of the so-called focal depth of the beam, or, in other words, its isthmus, along the length of which the averaged specific energy density in the beam is practically constant, have a much greater role. The longer the isthmus, the easier it is to form a weld of maximum depth with practically parallel side walls. Therefore, it is correct to state that the angle of inclination of side walls of the cast zone is largely determined by the overall configuration of the beam in the isthmus region.

Experimental study of the geometry of electron beam penetrations in a broad range of welding gun working distances, the results of which are discussed below, has been performed as a stage of preparation of normative materials on equipment and technology of electron beam welding.

Experimental procedure and obtained results. Experiments were performed using ELA-60 power unit with 60 kV accelerating voltage. Schematic of electron-optic system is given in Figure 1. The gun is fitted with tablet LaB_6-cathode with radius r_{cath} = = 1.5 mm, working temperature T_{cath} = 2000 K. Middle of non-magnetic gap of the focusing electromagnetic lens is located at distance a = 120 mm from beam