

HYGIENIC CHARACTERISTICS OF WORKING ZONE AIR IN ARC WELDING OF COPPER AND ITS ALLOYS (Review)

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A literature review of harmful substances formed in arc welding of copper and its alloys is presented. Literature data on studying emissions of welding aerosols in welding of copper and copper alloys are considered. It is shown that to create new grades of welding materials that would satisfy not only their welding technology, but also sanitary and hygienic characteristics, it is necessary to continue the study of chemical composition and levels of emissions of welding aerosols using modern standardized international procedures. 13 Ref., 1 Table.

Key words: copper, copper alloys, welding, brass, bronzes, welding aerosol, harmful substances, toxicity

In terms of world production and consumption, copper and its alloys rank third after iron and aluminium. Such a wide demand is associated with the properties of this metal and its alloys [1]. Copper is a ductile metal with a high thermal conductivity and a low electrical resistance, copper alloys have high antifri-
ction properties, as well as high corrosion resistance, including in seawater. This determines a widespread use of copper and its alloys in electrical and chemical industries, in shipbuilding and cryogenic engineering, in instrument making, metallurgical and other industries. The most widely used methods of welding and surfacing of copper and its alloys are arc welding methods (manual arc welding with coated electrodes (MMA), TIG and MIG welding in shielding gases, submerged-arc welding (SAW). The use of these processes is associated with harmful and dangerous production factors affecting welder.

Despite the significantly lower emissions of harmful substances [2] during TIG, MIG and especially submerged-arc (SAW) welding in shielding gases, in industry most often the process of manual arc welding with coated electrodes (MMA) is used, which is accompanied by a considerable emission of welding aerosol (WA) into the zone of welder's breathing (in manual arc welding using electrodes coated with aluminium bronze, specific aerosol emissions are 2–4 times higher, and the content of manganese oxides is higher by 1.5–2.0 times than during mechanized

welding in argon [3]). In WA such chemical elements as copper, manganese oxides, fluorides, aluminium, zinc oxides, lead, phosphorus, ammonia and other may be present. WA has an irritating effect on human body and in some cases may cause oncology diseases. In particular, fluorides and oxides of manganese cause inflammation of mucous membrane and nervous disorders, lead provokes nausea, gastric, intestinal, nervous and kidney diseases, copper causes metal fume fever, aluminium oxides are accumulated in lungs, nickel oxides cause cancer of breathing passages [4].

The aim of the work is to analyze the existing data on harmful substances that contaminate air of industrial premises during arc welding and surfacing of copper and its alloys using coated electrodes.

The implementation of measures to improve the labor conditions of welding production workers is based on the analysis of data on chemical composition, emission levels and toxicity of WA. For this purpose, the primary sanitary and hygienic evaluation of welding materials applying the method of WA capture and determination of their quantity and chemical composition is carried out. At the same time, such sanitary and hygienic indices are used as intensity of formation (g/min) and specific emission of WA (g/kg of welding material). In addition, to evaluate the toxicity of WA or degree of impact on human body the following indices are used: threshold limit value (TLV) of harmful substances, the required volume of

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TLV of harmful gases and aerosols in the air of welding workshops in arc welding of copper and its alloys [7]

Number	Description of substance	TLV, mg/m ³	Predominant condition in the production environment	Hazard category	Peculiarities of effect on human body
1	Nitrogen dioxide	2	f	3	O
2	Nitrogen oxide	5	f	3	O
3	Ozone	0.1	f	1	O
4	Salts of hydrofluoric acid (according to F): fluorides of Al, Mg, Ca, Cu and Sr	2.5/0.5	a	3	
5	Manganese in WA at its content: a) up to 20 % b) from 20 %	0.2 0.1	a a	2 2	
6	Oxides of manganese (in terms of MnO ₂): a) disintegration of aerosol b) condensation of aerosol	0.3 0.05	a a	2 1	
7	Nickel, nickel oxides, sulfides and mixtures of nickel compounds	0.05	a	1	K, A
8	Hydrogen fluoride (in terms of F)	0.5/0.1	f	1	O
9	Copper	1/0.5	a	2	
10	Magnesium oxide	4	a	4	
11	Zinc oxide	0.5	a	2	
12	Aluminium and its alloys (in terms of Al)	2	0	3	F
13	Beryllium and its compounds (in terms of Be)	0.001	a	1	K, A
14	Lead and its inorganic compounds (in term of lead)	0.01/0.005	a	1	

Note. 1. If in the column «TLV» two values are given, it means that in the numerator TLV is the maximum and in the denominator it is the average variable. 2. Symbols: f — fumes and/or gases; a — aerosol; a + f — mixture of fumes and aerosols. 3. O — substances with a sharply directed mechanism of action that require automechanical control of their content in the air. A — substances that may cause allergic diseases in the working conditions. K — carcinogens. F — aerosols of mainly fibrogenic action.

air to dilute to TLV, expressed in m³/h (per a unit of time) according to the international procedure [5]. In domestic practice, the index of air exchange of general exchange ventilation (i.e. the volume of air that should be supplied to the production room to dilute harmful WA substances to TLV) is used, expressed in m³/kg of welding material.

The information on emissions of WA and gases in arc welding of copper, bronze, brass, and also copper-nickel alloys is very limited, and generalized data are absent. TLV of some harmful chemical elements, that may be in the composition of WA, formed during arc welding of copper and its alloys, are given in Table. These data are necessary for calculations of necessary air exchange of mechanical ventilation.

Coated electrodes for welding copper are manufactured of elongated (cold-deformed) wire or round elongated and pressed rods. The chemical composition of welding wire and rods of copper and copper-based alloys, regulated by the standard [6], depending on the grade may have a different amount of alloying el-

ements and impurities (Si, Mn, Ag, Cr, Bi, Sb, As, Fe, Ni, Pb, Sn, Zn, S, P, O₂). In welding copper, electrodes Komsomolets-100 are the most widely used. The main toxic component of WA, which determines the required air exchange, is manganese. According to the degree of impact on human body, manganese belongs to the 2nd hazard category, i.e. it is highly toxic. The content of manganese oxides (in terms of Mn) in WA during melting of electrodes Komsomolets-100 is 3.9 g/kg, and the threshold limit value in the air of the working zone is 0.3 mg/m³. According to the hygienic regulations of chemical substances in the air of the working zone [7], the threshold limit value of copper and its oxides in the air at the level of respiratory organs should not exceed 1 mg/m³. The amount of air required to dissolve the aerosol to TLV in welding using electrodes Komsomolets-100 should be at least 13000 m³/kg.

In industry the following bronzes are widely used: aluminium (4.0–11.5 % of Al), tin (2–10 % of Sn) [8, 9], manganese (4.5–5.5 % of Mn), silicon (0.5–3.5 %

of Si), beryllium (1.9–2.2 % of Be) and chromium (0.4–1 % of Cr).

In [3], the results of tests of electrodes for welding complexly-alloyed bronzes of the Cu–Al–Ni–Mn–Fe system are presented. Two grades of electrodes LKZ-AB and LKZ-ABN were tested. Electrodes of grades LKZ-AB and LKZ-ABN differ in the feature that the first are manufactured with the rods from the rolled bars of BrANMtsZh8-3-4-1 bronze and the second are with the rods from the wire BrAMts9-2. In this case, alloying of the deposited metal with nickel and iron is performed through the coating. The specific emissions of aerosol during alloying of the deposited metal through the coating (electrodes LKZ-ABN) are 2 times higher than without alloying (electrodes LKZ-AB). Therefore, in terms of sanitary and hygienic properties, the use of electrodes with alloying coatings in welding and surfacing of bronze is not rational. Two grades of electrodes such as Nicolium (BrANZhMts9-5-4-1.5) for welding bronze and Superston (BrAMtsZhN8-12-3-2) for welding bronze were also tested. The electrodes were manufactured of rods of the same composition as the base metal (respectively), and on the rods the coating of the base type was deposited. It should be noted that despite the differences in the composition of the electrode rods BrANMtsZh8-3-4-1 and BrANZhMts9-5-4-1,5 and the applied welding conditions, approximately the same average values of the total emission of WA (21.3 and 25.0 g/kg) were obtained.

Investigations of sanitary and hygienic characteristics of the electrodes designed by the Saint-Petersburg State Institute of Technology, which are used for welding of aluminium complexly-alloyed bronzes (grades LPI-73, LPI-48-AB2, LPI-13, LPI-LKZ-ATs and LPI-LKZ-ATsK), were carried out by the Laboratory of Occupational Health and Ergonomics of the Research Institute for Labor Protection [3]. It should be noted that the specific emissions of WA during welding using all tested grades of electrodes are 18–25 g/kg, i.e. vary within relatively low limits despite significant differences in the composition and type of coatings, as well as used welding conditions. Exceptions are the electrodes of grade LKZ-ABN in which alloying of the deposited metal by nickel and iron is carried out through the coating. In this case, specific emissions of aerosol reach 40 g/kg, i.e. they increase by 1.5–2.0 times. In [3] the need in alloying metal of welds and deposits through the rods of electrodes instead of coatings is recommended to reduce the formation of welding aerosol and improve the sanitary characteristics of electrodes for manual arc welding of not only nonferrous but also ferrous metals.

The obtained results of hygienic evaluation of electrodes for welding of aluminium bronzes with unalloying coating allow concluding that the average value of specific emissions of aerosol is 20 g/kg of consumed electrodes. Large differences in the concentration of welding aerosol (WA) are predetermined by different sampling points (in front of the welder face shield and under the welder face shield), which makes them incompatible.

According to the results of hygienic evaluation of LPI-73 electrodes concerning justification of the hygienic certificate, the following data on the concentration of welding aerosol in the working zone are given (mg/m^3):

- during switched off ventilation in front of the welder face shield it is 111.1, and under the welder face shield it is 54.6;
- during operation of local exhaust ventilation in front of the welder face shield it is 15.7, and under the welder face shield it is 3.1.

Comparison of the results of the concentration of aerosol emitted during welding using bronze Superston and Nicolium electrodes, allows suggesting that the dust samples were taken under the welder face shield during the switched off exhaust ventilation. In this case the results are approximately the same (mg/m^3): 54.6 for LPI-73 electrodes; 39.0 for Superston electrodes; 41.0 for Nicolium electrodes.

Arc welding of bronzes using coated electrodes is characterized by particularly unfavorable sanitary and hygienic conditions because of evaporation of zinc. According to the degree of impact on human body, zinc oxide belongs to the 2nd category of hazard, i.e. it is a hazardous substance. According to the requirements, the threshold limit value of ZnO in the air of the working zone should not exceed $0.5 \text{ mg}/\text{m}^3$. At the same time, the specific emissions of aerosols and gases in arc welding of bronzes are much less studied than in welding of other nonferrous metals (for example, bronze and aluminium alloys) and such data are almost absent in the reference and technical literature. It was noted that a total emission of aerosol in welding using brass electrodes, the rods of which are made of brass LMtsZh55-3-1 reaches 211 g/kg of molten electrodes (coatings and welding conditions are not specified). This is 5 times higher than in welding of steels with the most toxic electrodes with acidic type coatings (up to 40 g/kg) and 10–20 times higher than in welding using electrodes with the coatings of basic, cellulose and rutile types (10–20 g/kg). It is quite obvious that this is mainly predetermined by evaporation of zinc, the boiling point of which (907 °C) is close to the melting point of brass.

A high fraction of zinc oxides in the composition of WA, which is formed during arc welding of brass, is confirmed by the data of [3]. Even in nitrogen-arc welding of L90 brass with M3r copper by a nonconsumable tungsten electrode using filler wire BrKMts3-1, the total amount of emitted aerosol was 48 g/kg, and the content of zinc oxide (ZnO) in it was 13.9 g/kg, i.e. 30 %. It should be taken into account that such a large amount of ZnO in the aerosol was formed in melting only the base metal. Based on the calculations of the authors, in order to bring the content of toxic elements to the threshold limit value, the specific air exchange in this case should be 27 200 m³/kg. During melting of brass electrodes and the base metal, the total amount of the formed aerosol and the content of ZnO in it grow by several times. Therefore, respectively, it is necessary to increase the required air exchange of supply and exhaust ventilation to provide TLV.

Studies of sanitary and hygienic characteristics of electrodes of grades LPI-LKZ-ATs and LPI-LKZ-ATsK, designed for welding bronze of the system Si-Al-Zn (BrATsKZh8-6-0.3-0.3) with a high damping capacity, were carried out. The rods of LPI-LKZ-ATs electrodes are manufactured of rods of the same composition with the base metal, which contains in average 6 % of zinc. The rods of LPI-LKZ-ATsK electrodes are manufactured of BrAMts9-2 bronze, on which a unalloyed coating is deposited, and zinc is introduced into the deposited metal through spiral or shell made of L63 or LK62-0.5 brass, put on the coated part of electrode. Hygienic evaluation of aerosols of both grades of electrodes was performed on the content of copper and zinc oxides (total dust level was not determined).

Relatively low melting and boiling points of zinc during arc welding using coated electrodes (420 and 907 °C, respectively) lead to its losses on WA and spattering at the drop stage from 30 to 60 %. This is predetermined by a high content of formed zinc oxide in WA (9–11 g/kg). In this case, the content of copper oxides in WA during welding using electrodes of grades LPI-LKZ-ATs and LPI-LKZ-ATsK is 6.1–6.5 g/kg, i.e. it is at the level of the content of copper oxides in the emitted aerosol during welding using electrodes of grades LKZ-AB and LKZ-ABN (5.25–7.55 g/kg).

In the technical literature, not enough information is available concerning sanitary and hygienic characteristics of arc welding of tin bronzes. At the PWI, the electrodes of grade ANBO were designed [10–12]. Their coating has a specific composition, associated with the presence of chemically active components of sodium salts (hexafluorosilicate, hexafluoroaluminate and fluorides) relative to the binder (liquid glass), as well as nontraditional metal components (tin, cop-

per-phosphorus powders). For the study, standard (sodium, potassium and mixed sodium and potassium) experimental lithium-containing samples of liquid glass were prepared, which provide unique properties to some types of electrodes [10, 13]. Sanitary and hygienic characteristics of the electrodes were evaluated according to the intensity of V_a formation and the specific emission of G_a WA. Determination of the intensity of formation and specific emission of WA was performed applying gravimetric method. The lowest levels of WA emission are achieved in welding with electrodes manufactured using sodium-lithium glass ($V_a = 0.393$ g/min, $G_a = 8.71$ g/kg). The electrodes close to them in terms of WA emission are manufactured of sodium-potassium and lithium binders. In terms of sanitary-hygienic indices, electrodes on potassium and potassium-lithium binder are the most favorable. Thus, for example, the intensity of formation and specific emissions in electrodes manufactured on potassium binder are, respectively, 22.0 and 23.6 % higher than in the electrodes on sodium-potassium glass. In terms of sanitary and hygienic properties, the electrodes manufactured on K-Na and Na binders, occupy intermediate positions between two extreme groups of electrodes [4].

Sanitary and hygienic characteristics of electrodes for welding copper-nickel alloys are absent in the technical literature.

In beryllium bronze the most toxic element is beryllium: its TLV amounts to 0.001 mg/m³, and its hazard category is –1. Therefore, it can be welded only in closed chambers with exhaust ventilation at an air velocity in the working hole of the chamber not lower than 1 m/s, and the outlets of vacuum pumps should be connected to local ventilation. After welding of beryllium bronze, the chamber is cleaned with a 5 % hydrochloric acid solution with a switched on local exhaust ventilation and with the use of Lepestok respirator.

To reduce the concentration of WA in the zone of welder's breathing, local dust and gas receivers should be placed directly at the workplace, and the capacity of stationary or mobile ventilation devices should be at least 1000 m³/h [2].

As the literature review showed, arc welding of copper and its alloys is accompanied by a significant emission of welding aerosol into the working zone of welder. The data on investigation of WA toxicity for arc welding methods are almost absent.

Comparative hygienic evaluation of welding methods was performed according to the value of ventilation air exchange (m³/kg). But this value is not objective and does not provide us a complete picture of WA toxicity.

According to the international standards DSTU ISO 15011, welding consumables should be constantly inspected for compliance with the indices of labor safety (chemical composition, level of emissions, toxicity and hygienic class of welding aerosols). Therefore, to create new grades of welding consumables, that would satisfy not only their welding technological, but also sanitary and hygienic characteristics, it is necessary to continue the study of chemical composition and levels of emissions of welding aerosols with the use of modern standardized international procedures DSTU ISO 10882-1:2008, DSTU ISO 10882-2:2008, DSTU ISO 15011-1:2008, DSTU ISO 15011-2:2008 and DSTU ISO 15011-4:2008.

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Received 03.12.2021

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