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Hardfacing of Copper

Abstract: The article discusses the primary issues of the hardfacing of copper elements exposed to intense abrasive wear, gas-abrasive wear at high temperature and in contact with liquid metal. In addition, the article presents test results concerning the surfacing of copper grade M1 performed using a self-shielded flux-cored wire providing weld deposit Fe14 and plasma powder surfacing performed using powder providing weld deposit Ni₃ ((in accordance with EN 14700)).

Keywords: copper surfacing, hardfacing, self-shielded tubular cored arc surfacing, plasma powder surfacing, fusion zone

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Introduction

The low abrasive wear resistance of copper combined with its low high-temperature creep resistance are responsible for the quick wear entailing the exchange of copper elements exposed to hot metal, high-temperature gas streams and abrasive materials of various hardness (blast furnace nozzles, crystallisers etc.). The fact that costs of repair greatly contribute to costs of production necessitates increasing the service life of copper elements exposed to high temperature, mechanical loads, various types of wear and corrosion as well as to other adverse conditions. One of solutions enabling the extension of the service life of copper elements involves providing the latter with layers characterised by high operational properties. Presently, the use of copper and

its alloys in the welding and surfacing of steels (aimed to save non-ferrous metals) is relatively well examined and discussed [1–9]. However, the opposite issue, i.e. the surfacing of copper with wear resistant alloys of various metals (including iron, nickel and cobalt-based alloys) is little known and nearly unsolved. The above-named problem results from significant difficulties which accompany surfacing processes involving the use of alloys characterised by higher melting points and significantly lower thermal conductivity than copper.

Methods of depositing wear resistant layers onto copper surfaces

The analysis of reference publications revealed that the deposition of wear resistant layers onto

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copper surfaces is usually performed using the flame spraying of coatings containing refractory metals, e.g. tungsten and molybdenum, nickel and cobalt-based alloys, zirconium oxide-based ceramics etc. [10–14].

One of the reference publications was concerned with the possibility of applying flame spraying to increase the service life of copper elements being in contact with liquid metal [10]. The test discussed in the publication involved the deposition of a coating containing aluminium (having a thickness restricted within the range of 0.1 mm to 0.5 mm) on a copper surface. However, although the average service life of elements was extended by between 1.5 and 2.0 times, it was also possible to notice the delamination of the coating during operation. The aforesaid defect resulted from the low strength of the joint between the layers and the significant difference between the thermal expansion coefficient of the coating and that of copper (Fig. 1).

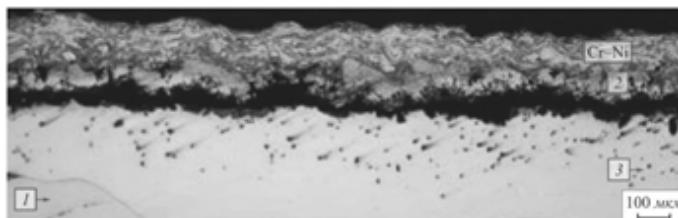


Fig. 1. Microstructure of a copper specimen thermally sprayed with an aluminium prime coat and a Cr-Ni layer:
1 – base material; 2 – porous layer; 3 – phase α [10]

To eliminate the above-presented defect, the Author [8] recommended the performance of additional heat treatment, where aluminium diffuses in the surface layer of copper. Such a solution should increase the adhesion of the coating to the base material and enable the obtainment of a layer characterised by higher high-temperature creep resistance and higher resistance to wear. However, the application of heat treatment not always translates into the increased adhesion of a coating to the surface of elements made of copper [10]. The foregoing results from the fact that, during the diffusion of the chemical elements of the coating into

copper, the concentration of the former in the intermediate layer of the coating decreases significantly [5]. This, in turn, leads to increased amounts of brittle oxides in the layer, possibly contributing to the delamination of a part of the layer on the coating side. The phenomenon is discussed in more detail in publication [15]. During long-lasting operation, microscopic cracks present between the coating and the base (Fig. 2a) eventually lead to the spalling and delamination of the coating (Fig. 2b). It was ascertained that delamination was the dominant mechanism responsible for the wear of thermally sprayed specimens. In addition, the surfacing method was characterised by laboriousness and low efficiency.

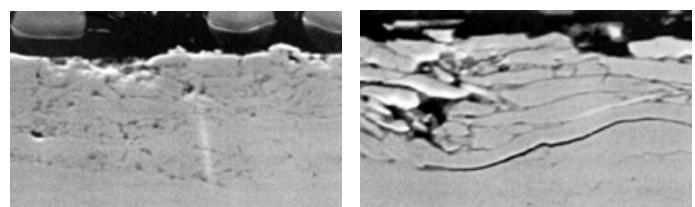


Fig. 2. Microstructure of the subsurface layer of the thermally sprayed coating after spraying and hardening heat treatment: a – microcracks in the sprayed layer; b – formation of separate lamellas and their delamination [15]

In cases of crystallisers used in continuous steel casting lines, the deposition of a wear resistant layer is performed using the ultrasonic spraying HVOF of a XuperCoat™ ceramic composite with tungsten carbides [16] (Fig. 3). Depending on operating conditions, the use of the above-presented solution increases the service life of crystallisers by between and 8 times in comparison with that of galvanised crystallisers.



Fig. 3. Copper crystalliser sprayed with XuperCoat™ composite using the HVOF method [16]

Work [17] informs that the use of plasma spraying when surfacing copper with protective layers having various chemical compositions increases wear resistance by between 1.5 and 3.0 times in comparison with that of pure copper. However, it should be noted that the use of thin coatings (between 0.5 mm and 0.7 mm) under conditions of intense gas-abrasive wear does not significantly increase the service life of elements.

The production of new and the repair of worn elements involves the use of various surfacing methods. Surfacing not only makes it possible to increase the service life of a given element but also provides the high strength of joints of the base material and filler metal [18, 19]. The surfacing of steel with copper and copper alloys is not accompanied by any specific problems. Many researchers state that, in the above-named case, the simplest and, at the same time, the most effective solution should involve gas-shielded metal arc surfacing or submerged arc surfacing [9, 20]. The primary disadvantage of arc surfacing is significant penetration depth, potentially leading to the excessive mixing of the non-ferrous metal with steel, resulting in the reduction of operational properties of the surfaced metal as well as the formation of cracks and gas pores in the deposited layer [20]. However, in spite of the fact that arc welding is characterised by significant penetration depth, the submerged arc welding method is sometimes used for the welding of copper with copper or copper with steel having a thickness restricted within the range of 5 mm to 40 mm [9, 13, 21]. Greater versatility is characteristic of gas-shielded surfacing methods, the primary advantage of which is the possibility of observing the process and readjusting the parameters during surfacing [20, 22]. During metal arc surfacing processes, penetration depth can be reduced by optimising electric parameters and using small diameter wires ($\varnothing < 2.0$ mm) [23, 24].

However, there are very few publications

concerning the surfacing of elements made of copper and its alloys. More detailed information can be found on the plasma powder surfacing of copper and its alloys with cobalt and nickel alloys [25]. It should be noted that the above-named method enables the relatively low melting of the base material [4, 17, 25, 26].

Reference publications also contain information concerning the electron beam surfacing of copper with layers having a thickness restricted within the range of 1.5 mm to 2.0 mm [17, 27]. The aforesaid technology enables the favourable penetration of copper surface with a layer based on refractory metal carbides. As a result, the service life of surfaced elements has been extended by twice. The disadvantages of the method include the high cost of complicated equipment and the fact that a certain amount of deposited powder does not enter the weld pool during the surfacing process. The solution to the problem includes, first, the powder flame spraying of a chromium-nickel coating with titanium and niobium carbides and, next, the partial melting of the layer using the electron beam [27]. The additional operations have complicated the surfacing of the blast furnace top and increased the probability of the formation of imperfections in a surfaced element.

Specialist methods enabling the making of bimetallic steel-copper joints include explosion welding, pressure welding, friction stir welding etc. [11, 12, 17, 28]. Although the above-named processes enable the obtainment of reliable joints, their application in the deposition of wear resistant layers is often limited by the shape and dimensions of elements (products).

Selection of wear resistant materials for copper surfacing

Reference publications inform about several classes of materials meeting requirements related to the above-presented operating conditions of copper elements:

- heat-resisting alloy steels with chromium, molybdenum, nickel etc.;

- high-alloy high-chromium iron-based alloys (sormait);
- nickel or cobalt-based alloys.

Heat-resisting steels of the Fe-C-Cr-Mo-V alloy system are commonly used for the hardening of elements of metallurgical equipment exposed to cyclic thermal changes and high dynamic loads combined with abrasive wear. Steels having a high tungsten content are characterised by the highest hardness and heat resistance at high temperature, yet their resistance to temperature changes and toughness are relatively low [29]. The replacement (partial or complete) of tungsten with molybdenum decreases the heat resistance of the steels, yet significantly increases their resistance to abrupt temperature changes. During surfacing, heat-resisting steels are susceptible to cracking. Because of this, surfacing is either preceded by preheating or accompanied by heating during the process.

High-carbon high-chromium steels having a carbon and chromium content of up to 5% and 30% respectively are commonly used for the surfacing of elements exposed to intense abrasive wear and gas-abrasive wear at

high temperature [29]. Although various methods can be used to deposit protective layers, it should be noted that one of the major problems related to surfacing technologies is the prevention of cracking. Usually, the prevention of crack formation involves the preheating and simultaneous heating of an element up to a temperature of 600°C. After surfacing, the element is placed inside a furnace previously heated to a temperature restricted within the range of 650°C to 700°C and left to cool slowly along with the furnace. However, even the above-presented measures do not guarantee the elimination of cracks.

Nickel-based alloys are characterised by high-temperature creep resistance, favourable resistance to thermal fatigue, high resistance to various types of corrosion and low susceptibility to crack formation during surfacing. Typical nickel-based alloys are Hastelloy and Inconel of the Ni-Cr-Mo-Nb alloy systems [29]. According to numerous publications, the use of nickel-based alloys enables the obtainment of materials characterised by the most favourable weldability, corrosion resistance and wear

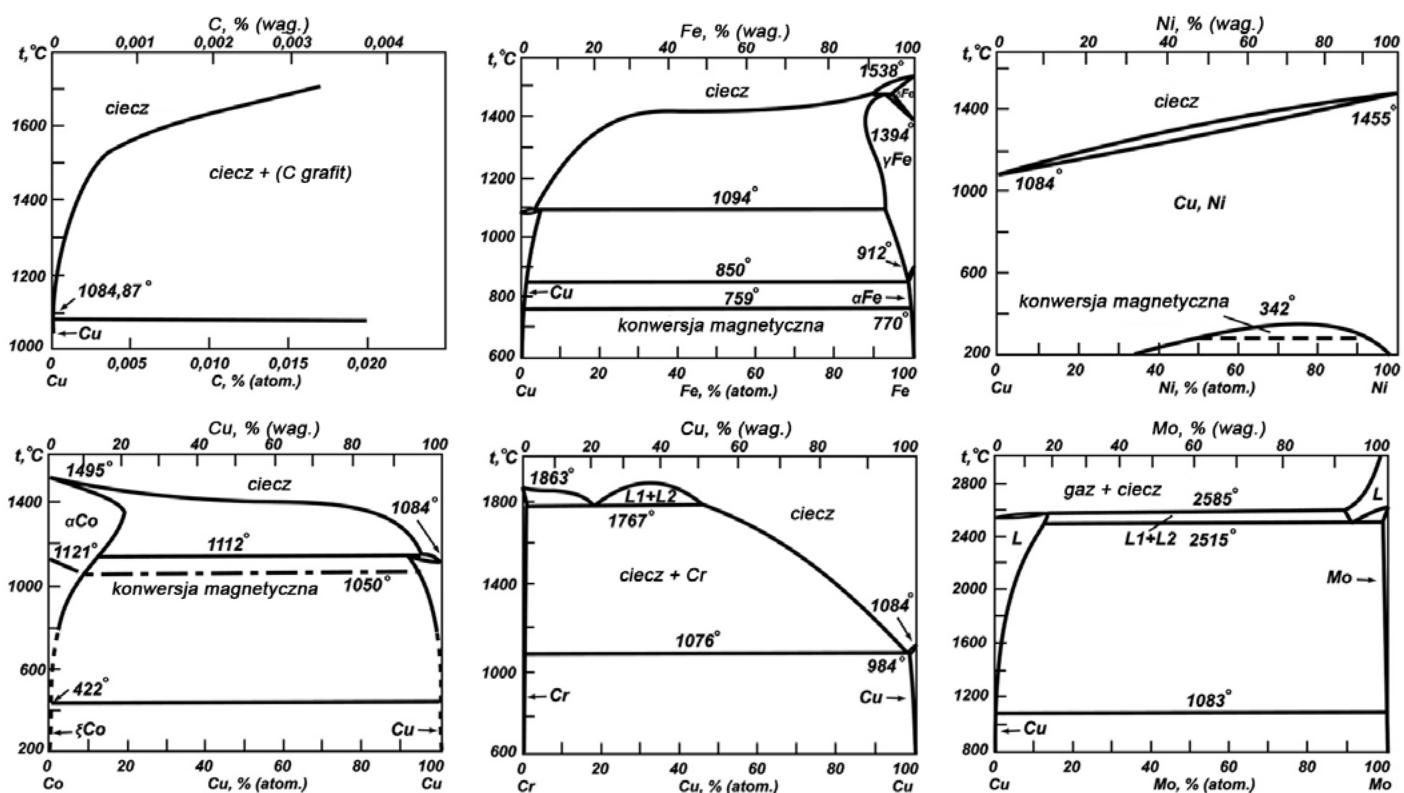


Fig. 4. Diagrams of phase equilibrium of dual systems: Cu-C (a), Cu-Fe (b), Cu-Ni (c), Cu-Co (d), Cu-Cr (e) and Cu-Mo (f) [30]

resistance [6, 7, 21, 27 etc.].

Cobalt-based alloys belonging to the Co-Cr-W system are characterised by high wear resistance, high-temperature creep resistance, high corrosion resistance etc. in many aggressive environments [29]. The hardness of such alloys at temperature above 650°C is higher than that of nickel-based alloys. The primary disadvantages of cobalt-based alloys include high cost and susceptibility to cracking.

An important aspect, in terms of weldability, is the intersolubility of alloying elements of steels as well as of the above-named alloys and copper. Phase equilibrium diagrams related to dual alloys are presented in Figure 4.

Carbon

The diagram of the phase equilibrium of the Cu-C system (Fig. 4a) indicates that copper in both the solid and liquid state is in equilibrium with carbon. The solubility of carbon in liquid copper (in % by weight) amounts to 0.0001 at 1100°C, 0.00015 at 1300°C and 0.003 at 1700°C. It has been proven that near the boiling point carbon dissolves in copper up to 1% by weight. During intense solutioning, carbon precipitates from the solution in the form of graphite [30].

Iron

Copper and iron form a solution containing up to 3.0% of iron dissolved in copper melted at a temperature of 1025°C (Fig. 4b). The solubility of copper in α-Fe at a temperature 1470°C, 1370 °C and 1100°C amounts to 10.0%, 12.0% and 8.0% respectively. The intense supercooling (by 100°C and more) leads to the formation of the area of immiscibility of iron and copper in the liquid state. The critical solution temperature is by 20°C lower than the liquidus temperature in the equiatomic alloy [30].

Nickel

Among structural metals, only in the Cu-Ni system the component metals are characterised by unlimited intersolubility and the formation

of the continuous series of solid solutions (Cu, Ni) with the cubic space lattice during crystallisation (Fig. 4c). There are computational data concerning the boundary of delamination of the solid solution and the critical immiscibility point, corresponding to a concentration of 69.7% Ni and a temperature of 342°C and related to the magnetic conversion of Ni [30].

Cobalt

The Cu-Co system (Fig. 4d) is peritectic. The eutectoid transformation takes place in the solid solution. The maximum solubility of copper in α-Co, obtained at a temperature of 1367°C, amounts to 19.7%. In Co-Cu alloys, fast supercooling (by 100°C and more) results in the formation of the area of immiscibility in the liquid state, which is almost symmetric in relation to the axis of the compound. In terms of the equiatomic alloy, the critical solution point is located 90°C below the liquidus curve [30].

Chromium

In accordance with the equilibrium diagram of Cu-Cr (Fig. 4e), the Cu-Cr system is the eutectic mixture containing two solid solutions based on Cu and Cr. The nature of phase equilibria in the high-temperature area in relation to concentration restricted within the range of 0% to 55% of Cu is not clear. It is believed that, within the entire concentration range in alloys containing between 4% and 45% of Cu, the monotectic is presented at a temperature of $1767^{\circ}\text{C} \pm 8^{\circ}\text{C}$ and a concentration of 18.8% of Cu. The area of the separation of the two liquids is restricted within the range of 18.8% to 45% of Cu and within a narrow range of temperature, the upper limit of which does not exceed 1900°C. In addition, there is a dual-phase area (liquid + Cr) within the concentration range of 42% to 97% Cr at a temperature of 1550°C. The maximum solubility of chromium in copper at a temperature of 1076.6°C amounts to 0.89% [30].

Molybdenum

The equilibrium diagram related to Cu-Mo was not based on experimentation as Cu and Mo do not mix in the liquid or solid state. The diagram presented in Figure 4f was obtained solely on the basis of computational methods, in accordance with which the system is characterised by the monotectic and eutectic equilibrium. The computational solubility of Mo in Cu amounts to 1.91% and 2.50% at a temperature of 1900°C and 2100°C respectively. In turn, the solubility of Cu in Mo amounts to 2.3% at a temperature of 950°C [30].

In view of the foregoing, it seems justified to suggest that copper should be surfaced with wear resistant alloys based on iron, nickel or cobalt, subjected to the complex surface alloying with other chemical elements characterised by high intersolubility with copper. The above-presented solution should favour the reduction of chemical heterogeneity and decrease the probability of the precipitation of inclusions both in the base material and in the weld metal.

Problematic weldability of alloys based in iron, nickel and cobalt with copper

When considering the surfacing of copper using wear resistant alloys it should be noted that, according to certain data, during the welding of copper with steel, the increased amount of iron negatively affects the quality of welded joints [31]. The foregoing results from the increased concentration of iron near the fusion line, which, on one hand, increases the hardness of the weld and its strength but, on the other, is responsible for decreased plasticity, leading to imperfections worsening the properties of welded joints [21].

The joint of nickel and copper can be easily obtained through welding performed without or using the filler metal containing copper, nickel and alloys of copper with nickel [1-3]. Although the fusion line of such a joint is sharp and contains intermediate layers, such a

situation is not regarded as an imperfection as the strength of the joint is sufficiently high and the rupture takes place outside the joint area [2].

Significant differences between certain physical properties of copper, iron, nickel and cobalt [32] may worsen their weldability. In addition, the significant oxidisability of copper and the significant absorption of gases by copper also negatively affect its weldability [4]. In accordance with publications [4, 9, 21], primary factors affecting the weldability of alloys based on iron, nickel, and cobalt with copper are the following:

- high thermal conductivity of copper, responsible for high cooling rates and necessitating the use of welding power sources characterised by significant linear energy and the sufficiently high temperature of (usually both) preheating and welding;
- relatively low melting point of copper;
- short time during which the weld pool remains liquid, this limiting its metallurgical workability and necessitating the use of active deoxidisers;
- easy oxidation of copper in the liquid state, leading to the formation of low-melting eutectics and reducing the resistance of the weld metal to the formation of solidifications cracks;
- significant effect of admixtures on the properties and weldability of copper, necessitating the use of metals with strictly controlled contents of oxygen, lead, sulphur, bismuth and antimony;
- high sensitivity of copper to hydrogen, necessitating the application of special measure reducing the content of hydrogen in the welding area (aimed to prevent the formation of gas pores);
- high flowing power of copper;
- significant thermal expansion coefficient of copper, impeding the fixing and maintaining the position of an element during welding and necessitating the use of additional measures preventing the deformation of a structure.

The above-presented factors enable the identification of several key issues typically accompanying the welding copper, i.e. the formation of hot cracks, the formation of intermediate layers as well as the significant mutual penetration at the copper-alloy interface [1–3, 19]. The data presented below provide more detailed information concerning the aforementioned issues, yet are primarily concerned with copper-steel types of welded joins or cases where steel is surfaced with copper.

During the welding of copper with steel, a rise in the content of copper in the weld metal above 3% significantly increases susceptibility to hot crack formation [1]. In such a case, during the crystallisation of the weld metal, copper, because of its limited solubility in steel, precipitates along grain boundaries, which combined with tensile stresses and the Rebinder effect triggers the formation of cracks in the metal.

The initial penetration of copper along the boundaries of steel grains is induced by the capillary effect. The foregoing is facilitated by the fact that surface energy on the Fe-Cu boundary is approximately by twice lower than that on the Fe-Fe boundary. As a result, the strength of the boundary of the grain being in contact with liquid copper is reduced, whereas tensile stresses generated in the metal are sufficiently high to tear the weakened boundary open and immediately fill the newly formed crack with copper (Fig. 5). In some cases, the penetration of non-ferrous metals into steel at a depth exceeding 2.5 mm reduces the static and, particularly, fatigue strength of the steel [1]. In addition to typical cracks formed

during the disposition of copper on steel, there are also imperfections which could be referred to as “healed” cracks, i.e. cracks entirely filled with copper or copper alloy.

In accordance with publication [1], the permissible depth of penetration with copper, not detrimentally affecting the mechanical properties of steel is restricted within the range of 0.3 mm to 0.5 mm. However, other data imply that the penetration of copper alloys into high strength steels to a depth of 1.2 mm nearly does not affect the static and fatigue tensile strength, static bend strength and the toughness of bimetallic specimens [2].

The above-named imperfection could be eliminated by providing the weld pool with a specific amount of aluminium [2]. In such a case, welded joints of copper with low-carbon steel were characterised by higher mechanical properties. Providing the weld pool with

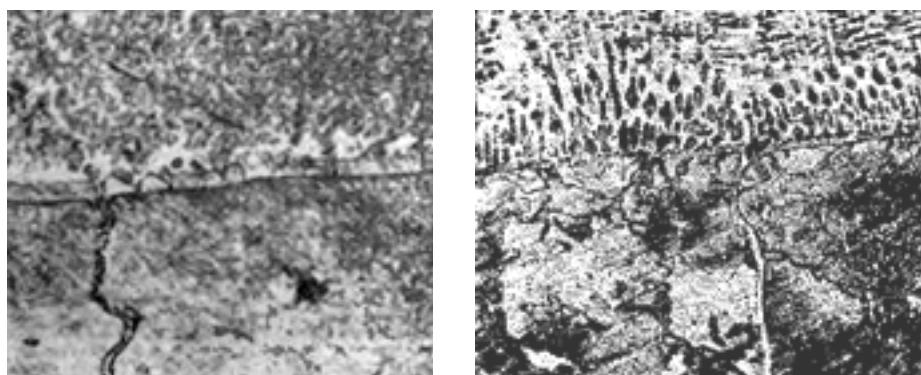


Fig. 5. Fusion zone during the TIG deposition of bronze BrA5 (БрA5, CuAl5) on steel St3 (a) and of bronze BrANZ 6-3-1 (БрАНЖ6-3-1, CuAl6Fe3Ni1) on steel 20 (b), x300 [1]

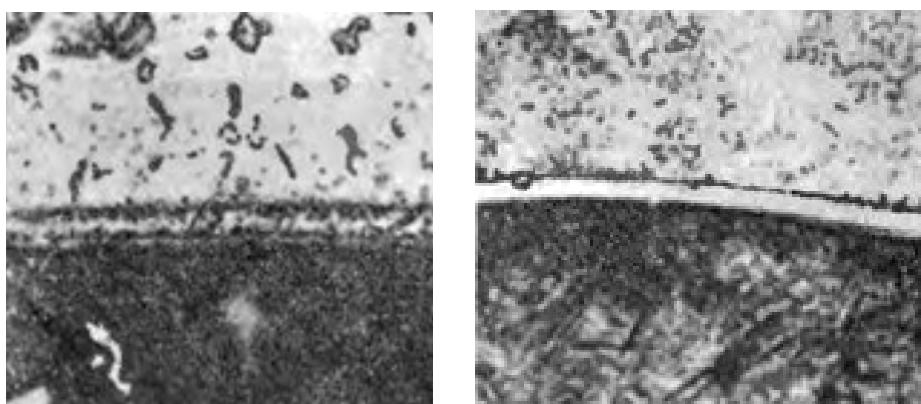


Fig. 6. Brittle interlayers in the fusion zone obtained during the plasma deposition of bronze BrAMc9-2 (БрАМц9-2, CuAl9Mn2) on steel 20 (a) and of bronze BrKMc3-1 (Бр.КМц3-1, CuSi3Mn1) on steel 38HNMA (38XHMA) (b); mag: 300x [1]

aluminium favourably affected the structure of the weld metal and the partially melted (near-weld) zone.

The weldability of copper with steel is worsened by the formation of separating layers in the partially melted zone ("near-weld zone") along the fusion line (Fig. 6). The formation and the development of the aforesaid interlayers is connected with the transfer (diffusion) of certain chemical elements from steel to copper. The prevention of the formation of the interlayers requires the surfacing of intermediate layers using alloys decreasing the possible formation of brittle interlayers and the diffusion of iron in copper and vice versa [1].

Tests concerning the physicochemical properties of welded joints made in the copper-low-carbon steel configuration and operated at variable temperature revealed that an iron content of up to 2% enables the obtainment of the weld metal characterised (within the entire range of test temperature) by similar strength as that of the base material (copper) [13]. The content of iron in copper exceeding 7% results in the significant worsening of the plastic properties of the joint, which could trigger the formation of hot cracks. The complex assessment of the mechanical properties, fatigue strength, service life under thermo-cyclic loads and the nature of cracks revealed that the optimum content of iron in the weld metal of the welded joints made in the copper-low-carbon steel configuration exposed to high and variable temperature should be restricted within the range of 3% to 6% [13].

A problem accompanying the surfacing of copper with wear resistant alloys results from the melting point of wear resistant alloys, significantly higher than that of copper and its alloys. At first glance, the aforesaid situation should increase the penetration of copper. However, because of the high thermal conductivity of copper (more than 4 times higher than that of steel), the low-volume weld pool quickly loses heat and, consequently, flowing power and

wettability, which could result in the unfavourable formation of deposited runs or even the lack of formation and penetration into the base material. One of the methods providing a solution to the problem could be the preheating of an element subjected to surfacing. The fast crystallisation of the weld pool in the surfaced metal resistant to wear may contain single copper inclusions, which could additionally worsen the operational properties of surfaced metal.

The solution to the above-presented problems requires the careful and justified selection of a surfacing technology and filler metals as well as the observance of the relatively narrow range of preheating temperature and the heating of copper element during surfacing. Possible solutions could involve arc surfacing performed using appropriate filler metal wires and plasma powder surfacing performed using alloys based on iron, nickel and cobalt. The quality of the melting of the wear resistant layer and copper matrix may be positively affected by technological procedures decreasing penetration depth and reducing the dilution of the base material in the deposited metal as well as by the adjustment of linear surfacing energy. As regards arc surfacing (more popular in industrial applications) desirable results could be obtained by using filler metal wires having a small diameter, i.e. restricted within the range of 1.2 mm to 1.8 mm, and moderate current regimes providing the stable transfer of the electrode metal and minimum penetration into the base material. On one hand, the complex approach should contribute to the obtainment of the proper penetration of copper with the layer resistant to wear and, on the other, prevent the overheating of the copper base.

Test results

The research work involved the performance of experiments related to the arc surfacing and the plasma powder surfacing of specimens made of copper grade M1 (Cu99.9). The arc surfacing process was performed using a self-shielded

flux-cored wire ($\varnothing 1.6$ mm) enabling the obtainment of a surfaced layer based on iron in the C-Si-Cr-Mo system (Fe14 in accordance with EN 14700). The surfacing process was preceded by preheating. Figure 7a-c presents deposited runs, cross-sectional macrostructure and the microstructure of the joint area.

The specimen made of copper grade M1 was also subjected to plasma powder surfacing performed using a wire based on nickel in the C-Ni-Cr-Si-B system (designated Ni₃ in accordance with EN 14700). Figure 8a-c presents deposited runs, cross-sectional macrostructure and the microstructure of the joint area.

Both cases enable the satisfactory formation of deposited runs and the proper melting of both the base material and the deposited material.

Summary

In terms of copper elements exposed to intense abrasive wear and gas-abrasive wear at high temperature, the primary reasons for failures include intense wear and burn-through. The above-presented analysis justified the conclusion that the appropriate selection of a surfacing technology enables the obtainment of layers resistant to abrasive wear. Such layers are made of iron, nickel or cobalt alloys based on copper. The process is feasible, yet connected with significant difficulties.

The test results related to the surfacing of copper grade M1 performed using the self-shielded flux-cored wire providing weld deposit Fe14 (based on iron in the C-Si-Cr-Mo alloy system) and plasma powder surfacing performed using a wire providing weld deposit Ni₃ (based on nickel in the C-Ni-Cr-Si-B alloy system) (in

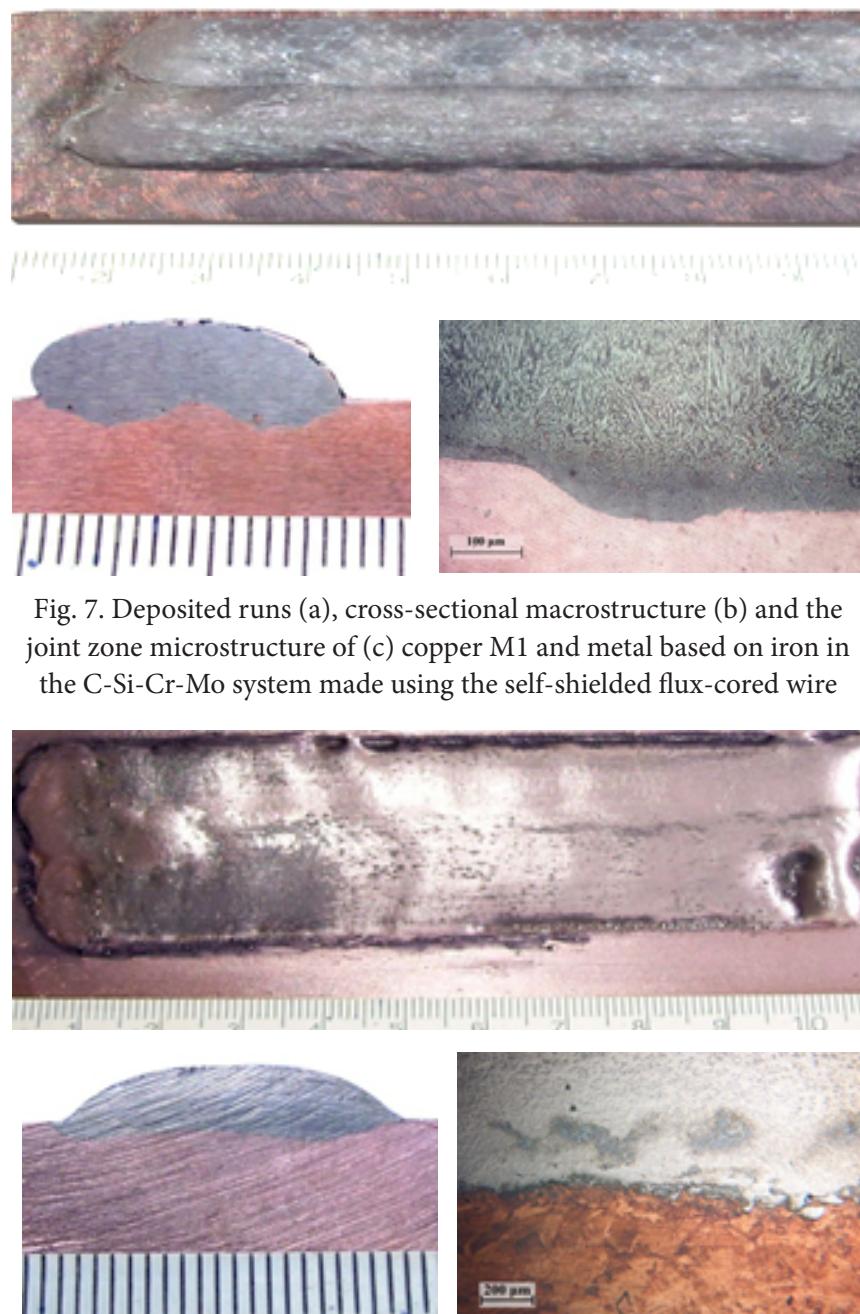


Fig. 7. Deposited runs (a), cross-sectional macrostructure (b) and the joint zone microstructure of (c) copper M1 and metal based on iron in the C-Si-Cr-Mo system made using the self-shielded flux-cored wire

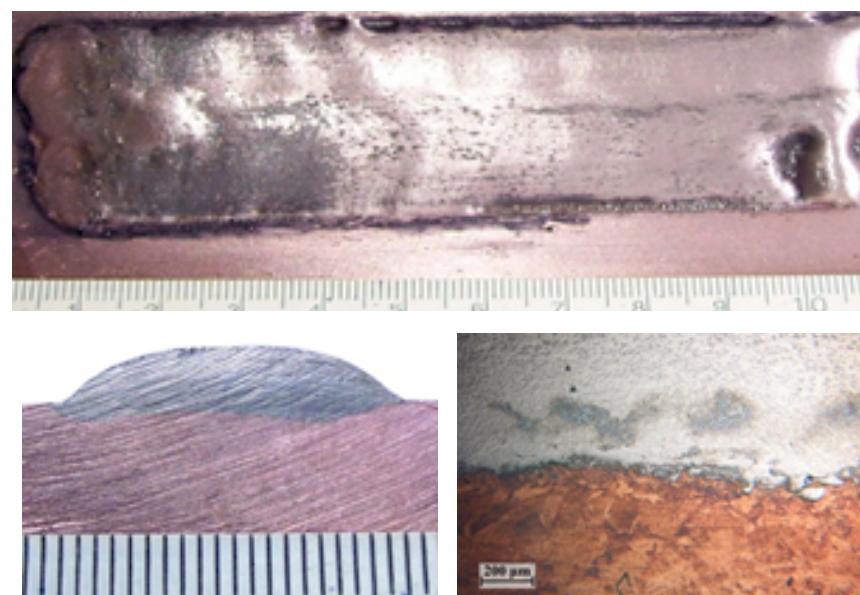


Fig. 8. Deposited runs (a), cross-sectional macrostructure (b) and the joint zone microstructure of (c) copper M1 and metal based on nickel in the Ni-Cr-Si-B system made using the plasma powder surfacing method

accordance with EN 14700) confirmed the correctness of the approach adopted to increase the service life of copper elements exposed to intense abrasive wear and gas-abrasive wear as well as wear resulting from the metal-metal type of friction at high temperature.

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