Characteristics and Abrasive Wear Resistance of Plasma Alloyed Layers Based on Tin Bronze and Chromium Carbide

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Abstract
This paper presents a study of the characteristics and resistance to abrasive wear of surface alloyed layers during plasma heating of powder pre-coating of a mixture containing tin bronze and chromium carbide. It has been established that, depending on the composition of the mixture, the thickness of the coating, the processing mode, the resulting layers differ in structure, chemical and phase composition. The addition of chromium carbide with a mass fraction of 20% makes it possible to increase the microhardness of the alloyed layer based on tin bronze up to 700 HV with the formation of a martensitic structure. Tests for abrasive wear were carried out at a load of 5, 20, 50 N and with codirectional rotation of the holder to the abrasive wheel. The obtained results showed that the wear resistance of the Fe-Cu-Sn and Fe-Cr-C-Cu-Sn alloyed layers is higher compared to the Cu-Sn layer. In particular, the Fe-Cr-C-Cu-Sn layer is the best.

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1. INTRODUCTION

Surface hardening of steel with an alloying layer is widely used in engineering technology. The approach to alloying steel surfaces with copper has long been one solution for improving antifriction properties, corrosion resistance, biocorrosion resistance, and other properties [1-4]. It is known that Cu-X copper-based alloys, where X is Fe, Cr, V, Nb, Mo, Ta and W, belong to an immiscible binary system with high mechanical strength, electrical conductivity and magnetism (for Fe - Cu) and also high thermal characteristics [2-4]. An alloy of the Fe-Cu system is a promising basis for creating materials that combine good mechanical strength, wear resistance, and corrosion resistance with high thermal and electrical conductivity [5-7]. However, the Fe-Cu system practically does not mix in equilibrium at room temperature and up to 600°C and has a positive heat of mixing [1,8]. However, Fe-Cu immiscible alloys obtained by traditional solidification methods are subject to
microstructure segregation, which is caused by two liquid melts with different densities, which has become a major obstacle to limiting the application of Fe-Cu immiscible alloys in industry [9]. Fe-Cu based materials are used in a wide range of applications, from friction materials and high voltage sliding contacts to magnetoelectronic and spintronic devices [8,10–12]. The combination of copper and iron is often carried out in order to save money while reducing the cost of copper and increasing the hardness of the alloy due to the presence of iron [1,2,13,14]. Currently, in order to improve the properties of materials, not pure copper is introduced into the iron base, but alloys based on it, such as bronze powder. The combination of Fe, Cu and Sn has been shown in the creation of composite alloys of the Fe–Cu–Sn system [14–17]. Iron, copper, and tin composites are used in various tribological applications due to their high hardness, high strength, and moderate wear resistance [16,17]. It was noted in [17] that the ultimate strength and resistivity of Cu–Sn–Fe alloys increase with increasing Sn and Fe content. In determining the cohesive energy between atoms in a metal-to-metal transition layer using traditional (Fe–Sn) and proposed (Fe–Cu–Sn) technologies, it was proved that copper should be used to increase the bonding strength of the babbitt layer to the steel substrate. In the case of combining elements according to the Fe–Cu–Sn scheme, the cohesive energy for Sn increases, and in the sequence according to the Fe–Sn scheme, it decreases. In [18], the authors noted that Cu–Sn synergism is more positive than that of Cu or Sn in their separate addition. Thus, in comparison with alloys of the Fe–Cu, Fe–Sn, Cu–Sn system, the alloy of the Fe–Cu–Sn system is the most proposed for creating functional coatings that provide wear resistance and corrosion resistance.

In recent years, the use of highly concentrated sources for surface alloying of structural steels has been increasingly carried out with numerous successful results, including electric arc plasma heating, which provides sufficient heat with high efficiency, short processing time [19,20,21]. To improve the properties of surface hardening, a number of works have already reported on plasma heating of aluminum bronze [22], a mixture of tin bronze and an iron alloy [23], laser cladding of immiscible nanocomposites of the Cu-Fe-Cr-Si-C systems [24], Cu-Fe-Ni-Cr-Si [25], Cu-Ni-Fe-Mo-xCr [26]. However, the number of studies on obtaining an alloyed layer of the Fe-Cu-Sn system is still small, and the quality of the resulting coatings does not meet the expected requirements associated with high hardness, wear resistance, etc. Abrasive wear is one of the most common types of wear. This happens when a harder material rubs against a softer one. In practice, abrasive and other wear mainly cause mechanical damage to metal parts of machines, especially moving parts. Studies on wear resistance have been repeatedly carried out, but mainly only for coatings and alloys of the systems Fe-Cu-Sn [15], Fe-Cu [22], Cu-Sn [27], Cu-Sn-Cr [28]. For alloying the surface of carbon steel, it was proposed to use coatings of the Fe-Cr-Cu-Sn system [20]. Its essence lies in the fact that the composition of the coatings includes soft phases of the Cu-Sn system and hard phases of the Fe-Cr-C system, as a result of which it is possible to increase the surface hardness, wear resistance and corrosion resistance, but at the same time provide resistance to friction as materials from pure bronze.

The purpose of this work is to evaluate the wear resistance of surface alloyed layers obtained by plasma heating of a coating containing tin bronze and chromium carbide. The paper presents the results of studies of the microstructure, measurements of microhardness, determination of the chemical and phase composition in the cross section of the obtained layers and their testing for abrasive wear.

2. EXPERIMENT

2.1 Plasma heating

For surface alloying of steel St3 (GOST 380-2005), tin bronze PRV-Br010 (CuSn10) with the particle size of 1–150 µm was used as the base alloy, chromium carbide with a mass fraction of 20% and the particle size of 1–300 µm was used as an additive, and silicate glue was used as a binder. The preparation of a coating of a mixture of glue and powder is shown in fig. 1. Plasma flashing was carried out on a Kempi PSS5000 welding machine with Oscillator TU50 TIG control (see Fig. 2). The plasma treatment mode for each composition is shown in table 1.
Fig. 1. (a) - polished sample; (b) - sample with a mask; (c) - applying the paste; (d) - formed coating after removing the mask and drying the sample.

Fig. 2. Plasma processing equipment: 1 – source; 2 - camera; 3 - control unit.

Table 1. Plasma processing mode.

<table>
<thead>
<tr>
<th>Sample №</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>PRV-BrO10</td>
<td>PRV-BrO10</td>
<td>PRV-BrO10+20% carbide chromium</td>
</tr>
<tr>
<td>Coating thickness</td>
<td>1,00 mm</td>
<td>1,00 mm</td>
<td>0,25 mm</td>
</tr>
<tr>
<td>Processing speed</td>
<td>2,7 mm/s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current power</td>
<td>100 A</td>
<td>140 A</td>
<td>140 A</td>
</tr>
</tbody>
</table>

2.2. Characterization study of alloyed coating

After cooling in air, the processed samples were cut out on a P100A automatic machine, then pressed with acrylic resin in the form of a round cylinder on a Polylab C50A automatic press. After grinding, polishing, and etching in 5% HNO₃ acid with the addition of ethanol, the microstructure of the studied samples was studied using a MET-2 microscope. The microhardness was measured using an HMV-G21 microhardness tester with a load of 2 N (HV₀.2). Analysis of the chemical composition of the cross section of the obtained layers is performed on a JIB-4500 microscope equipped with an EDS (Energy Dispersive X-ray Spectrometer for Chemical Analysis) analyzer. The phase composition of the resulting layers was studied on a Shimadzu XRD-7000 diffractometer with a polycapillary optics system.

2.3. Abrasive wear

The wear test is carried out using a Struers Tegramin-25 Grinding and Polishing Machine with operating screen control, shown in Figure 3. After plasma heating and cooling, the specimen was cut to form a 12x5x10mm parallelepiped (Figure 3-a). To match the holder of a Struers Tegramin-25 grinder and polisher, the test piece was pressed with acrylic resin on a Polylab C50A automatic press. The contact surface of the pressed test specimen consists of the working surface of the coating, which is in 100% contact with the abrasive, and the remaining surface filled with resin. Wear resistance was determined for the studied samples by rotational movements on the surface of abrasive paper based on silicon carbide. Abrasive paper was used with the particle size of 63-80 µm. In the process of testing, the pressing force of the samples is regulated by a force of 5, 20, and 50 N, and the samples subjected to a certain load are pressed against the abrasive wheel and fixed on it with an abrasive skin. When the abrasive wheel rotates, the holder with the sample moves in the direction from the periphery to the center and back. After each period (for example, 20 minutes), the cast samples were broken so that the metal samples did not break, then they were taken for weighing. The sandpaper was not reused, which was used in the test with a different load.

Fig. 3. Grinding-polishing machine Struers Tegramin-25 for wear testing.
3. RESULTS AND DISCUSSION

The cross section with the microhardness distribution of the obtained layers is shown in Fig. 4, 5. At a lower current strength (100 A) and a thick coating (1 mm), the surface alloyed layer consists mainly of molten tin bronze with a low degree of dilution of the substrate. Figure 4-a shows that the main zone has a microhardness below 200 HV_{0.2}, a thin iron-saturated sublayer near the boundary has a thickness of less than 30 µm and a maximum microhardness of no more than 600 HV_{0.2}.

The basic layer structure of the Cu-Sn system is shown in fig. 4 - b, as similar results are given in [27,29] with the main phases, including \( \alpha \)-Cu, \( \delta \)-Cu41Sn11. At a current strength of 140 A and a coating of 0.50 mm, the resulting layer does not have delamination, but there are many local zones rich in tin bronze with a size of several hundredths of a micrometer. It can be seen that the upper zone and the lower zone near the boundary have a higher concentration of microhardness values than the central zone.
Fig. 5. Structure and microhardness distribution of a surface alloyed layer based on a mixture of tin bronze and 20% chromium carbide: (a) – Type of cross section of coating, (b) – central zone, (c) – Border zone, (d) – Edge zone.

The highest quality layer is obtained after plasma heating of a coating of 0.25 mm of a mixture of PRV-BrO10 + 20% chromium carbide. The cross section of the obtained layer is shown in fig. 5 - a, b, c. It is noted that the main structure is equiaxed and columnar crystal grains. The values of microhardness for the central (fig. 5 - b), boundary (fig. 5 - c) and marginal (fig. 5 - d) zones differ slightly, which are in the range of 500-700 HV0,2.

The chemical composition of some points of the alloyed layer of the Fe-Cu-Sn system is shown in Figure 6 - a. It can be seen that the chemical composition is mainly characteristic of three main zones: rich in copper; rich in iron and thermal influence. At point 1, the main elements are tin and copper, i.e. tin bronze plays the role of the matrix, and at point 2 iron plays the role of the matrix. The high oxygen content at point 2 (5.12%) can be attributed to the silicate binder. Copper and tin were not found in the heat-affected zone (point 3). This is proven due to their very limited solubility in iron at low temperatures. To determine the chemical composition of the alloyed layer of the Fe-Cr-Cu-Sn system, a sample was selected based on a mixture of tin bronze and 20% chromium carbide. The chemical composition of some points of the central zone of the layer is shown in Figure 6 - b. Cracks are observed that are filled with tin bronze. The solubility of iron in the copper matrix for doped Fe-Cu-Sn, Fe-Cr-C-Cu-Sn layers is slightly different. The content of chromium in the zone rich in tin bronze (point 3) is significantly lower than in the zone rich in iron (points 1, 2). The tendency to form complex carbides can reduce the solubility of chromium in the bronze matrix.

Fig. 6. The result of determining the chemical composition of the alloyed layers based on the coating: PRV-BrO10 (a); PRV-BrO10 + 20% chromium carbide (b).

The result of X-ray phase analysis showed that the main structure of the alloyed layer of the Fe-Cu-Sn system is α, γ-solid solution of Fe, α-Cu, ε-Cu, δ-Cu4Sn11 and β'-Cu3.7Sn (Fig. 7 - a, b). According to the results of X-ray phase analysis, it was found that the main structure of the Fe-Cr-C-Cu-Sn doped layer is α, γ-Fe solid solution, perlite, martensite, eutectic carbide (Fe3C), α-Cu, metal carbide M23C6 (Fig. 7 - c, d).
The resistance of surface layers under wear conditions on the fixed abrasive will be determined from the structure of the alloyed layer, the heat-affected zone (HAZ). An analysis of literature sources on wear tests of surface layers showed that in order to achieve a complete wear process to the base metal zone, several wear areas with different intensity will be observed. The state of the sample surface and, consequently, the resistance to abrasive wear will change with the depth of the hardened layer in the following order: alloyed layer → alloyed layer + heat-affected zone → heat-affected zones + base metal zone → base metal zone.

Table 2. Characteristics of the studied samples

<table>
<thead>
<tr>
<th>Type of surface layer</th>
<th>Thickness of alloyed layer after grinding, µm</th>
<th>Hardness of alloying layer, HV0.2</th>
<th>Hardness of HAZ, HV0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Sn</td>
<td>780</td>
<td>170-200</td>
<td>175-190</td>
</tr>
<tr>
<td>Fe-Cu-Sn</td>
<td>800</td>
<td>385-495</td>
<td>170-220</td>
</tr>
<tr>
<td>Fe-Cr-Cu-Sn</td>
<td>770</td>
<td>500-700</td>
<td>170-210</td>
</tr>
</tbody>
</table>

In the test modes, the speed of the abrasive wheel - 100 rpm and the speed of the holder - 100 rpm were constantly used with changing loads (5, 20, 50 N). The results obtained are shown in fig. 8. First, under a load of 5 N (see Fig. 8-a) the mass loss for the layers of the Fe-Cu-Sn and Fe-Cr-Cu-Sn systems is greater than for the Cu-Sn layer. Although the mass loss of the tin bronze (Cu-Sn) layer is the smallest, the rate of its mass loss increases linearly, and for other layers it decreases with increasing time. With an increase in load by 4 times (20 N), the mass loss of the Cu-Sn layer is already greater than that of the two layers Fe-Cu-Sn, Fe-Cr-Cu-Sn, and the rate of its mass loss also increases linearly. This is due to the high homogeneity of the Cu-Sn layer. It can be seen that all alloyed layers show a greater mass loss than in the case of a load of 5 N, shown in graph 8 (b). In the first series of experiments, the low wear resistance of the alloyed layer of the Fe-Cu-Sn system can be caused by the presence of cracks or unexpected inclusions near the upper zone. On the contrary, the resistance of the layer of the Fe-Cr-Cu-Sn system to wear is associated with the presence of chromium carbide with a higher hardness. At the same time, the alloyed layer of the Fe-Cr-Cu-Sn system not only continues to show outstanding wear resistance, but also maintains this level over time, showing a curve that continues to bend more than other layers. As the test time increases, the curvature of the time-weight loss curve increases.
i.e. it is indicated that the inner sublayers of the surface layer are significantly saturated with a hardening component with high uniformity, and the number of defects is reduced in them. This is also consistent with many studies related to the permeability and solubility of copper in iron, and the diffusion of chromium in steel [30,31].

To test the same samples, the load was increased to 50 N, and the time between two measurements was 10 minutes. The results obtained are shown in graph 8 (c).

It can be seen that the plasma layers of the Fe-Cu-Sn, Fe-Cr-C-Cu-Sn systems continue to demonstrate good wear resistance, and the best of them is the alloyed layer of the Fe-Cr-C-Cu-Sn system. The wear process of a sample with a layer of Cu-Sn quickly reaches the heat-affected zone and in 40 minutes of testing to the main zone of St3 steel. It was found that on the surface of worn zones there are traces of microcutting in the form of clear scratches of different lengths and depths. Microcutting processes are associated with the impact of abrasive particles on the surface, which is confirmed by traces of microcutting in the form of grooves and blades with sharp edges oriented in the direction of movement of the abrasive grains. The interaction of the abrasive particle with the surface consists in removing metal microcircuits and pushing the material to the edge of the formed risk under the action of plastic deformation. In addition to deep scratches on the surface of the doped layer of the Fe-Cu-Sn system, delamination of layer fragments is also observed, which indicates a low cohesive strength associated with the formation of oxide interlayers at interlamellar boundaries. The development of the microcutting mechanism indicates that the hardness of the used abrasive is more than 1.3 times higher than the hardness of the structural components of the melted layer of the Fe-Cu-Sn system.

Metallographic studies have shown that traces of microcutting are observed on the surface of worn hardened zones, which is recorded in the form of clear scratches of various lengths and depths (see Fig. 9, 10, 11). Microreliefs and profilograms of the surface roughness of the plasma layers of Cu-Sn, Fe-Cu-Sn and Fe-Cr-C-Cu-Sn systems are shown in Figures 9, 10 after a time of 25 minutes with the test mode: skin 6-N, load 20 N, abrasive wheel speed 100 rpm, holder speed 100 rpm. The study of profilograms showed that the arithmetic mean value and the highest profile height decrease in the following order: doped Cu-Sn layer (0.183 and 1.274 µm) > doped Fe-Cu-Sn layer (0.117 and 0.961 µm) > doped Fe-Cr-C-Cu-Sn (0.099 and 0.742 µm).
Fig. 9. Microrelief of the worn surface of the layers of the Cu-Sn (a), Fe-Cu-Sn (b), Fe-Cr-C-Cu-Sn (c) systems in the experimental mode: 6-N sandpaper, load 20 N, abrasive speed wheel - 100 rpm, holder speed - 100 rpm.

Fig. 10. Profilograms of the worn surface of the layers of the Cu-Sn (a), Fe-Cu-Sn (b), Fe-Cr-C-Cu-Sn (c) systems in the experimental mode: 6-N sandpaper, load 20 N, abrasive speed wheel - 100 rpm, holder speed - 100 rpm.

Fig. 11. Worn surface of samples after testing under a load of 50 N.

After testing under a load of 50 N, the worn surface of the samples is shown in Figure 11. It is noted that on the surface of the Cu-Sn layer there is a greater number of microcuts with a width, most often in the range of 6-10 μm, and on the surface of the Fe-Cu-Sn layer - the number and width of microcuts are reduced. On the surface of the alloyed layer of tin bronze, the micro-cutting is wider and deeper than for the alloyed layer of Fe-Cr-C-Cu-Sn.

4. CONCLUSIONS

It has been established that the surface alloyed layers of the Fe-Cu-Sn and Fe-Cr-C-Cu-Sn systems were obtained by plasma heating of a mixture containing tin bronze and chromium carbide using a current power of 140 A, a processing speed of 2.7 mm/s. The surface alloyed layer of the Cu-Sn system was obtained at a low current power (100 A) and a coating thickness of 1.00 mm. The alloyed layer of the Fe-Cr-C-Cu-Sn system has a higher uniformity and microhardness, which is in the range of 500-700
The low concentration of microhardness values of the layers of the Cu-Sn, Fe-Cu-Sn systems is caused by the unsaturation of precipitation hardening between copper and iron. It was found that the main phase composition of the layer of the Fe-Cu-Sn system is α, γ-solid solution Fe, α-Cu, ε-Cu, δ-Cu₄Sn₁₁, and β’-Cu₃Sn, and for the alloyed Fe-Cr-C layer -Cu-Sn are α, γ-solid solution Fe, pearlite, martensite, eutectic carbide (Fe₃C), α-Cu, metal carbide M₇C₃. The alloyed Fe-Cr-C-Cu-Sn layer obtained from a mixture of tin bronze and 20% chromium carbide is the most effective material providing abrasive wear resistance from 1.2 to 2 times and from 2 to 4.7 times compared to alloyed layers Fe-Cu-Sn and Cu-Sn systems, respectively. Therefore, the wear resistance of coatings increases in a number of alloyed layers of the systems: Cu-Sn < Fe-Cu-Sn < Fe-Cr-C-Cu-Sn.

REFERENCES


