Creation of wear-resistant frictional surfaces by implanting materials based on tungsten carbide

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Abstract. The influence of the implanted tungsten carbide on the formation of wear-resistant structures, formed in the process of implementation of the combined electro-processing technology in the friction surfaces, is studied. It has been shown that during the thermal force influence in the deformation zone, there is intensive austenization of the steel with the dissolution of the tungsten carbide powder and the subsequent formation of the composite nanostructures as a result of decomposition of the supercooled austenite, supersaturated with tungsten. The results of tribological testings of cylindrical samples by the normalized method are presented.

1. Introduction

The tungsten compounds with carbon, which are W₂C and WC tungsten carbides, are essential from a practical point of view. These carbides have a high level of hardness, wear resistance and refractoriness, which is an exceptional combination of properties to create wear-resistant and heat-resisting alloys.

In the steel, tungsten forms carbide W₆C, which under austenitization is partially transformed into a solid solution, thus providing obtaining of martensite alloyed by tungsten, which prevents martensite disintegration during heating, thus providing the required red hardness of the steel. The undissolved part of the W₆C carbide leads to an increase of wear resistance of steel.

On the basis of tungsten carbide (WC, W₂C), the most effective tool hard alloys, containing 85-95 % of WC and 5-14 % of Co, are created. Heat resistant and wear-resistant alloys-stellites (3-5 % W, 25-35 % Cr, 45-65 % Co) are applied to the surfaces of machine parts, subjected to significant wear, with the help of welding.

The main objective of this research is the development of technology of saturation of the surface layer of carbon steel with tungsten carbide in order to achieve high wear resistance of the surface layers of machine parts, working under different conditions of friction.

2. Materials and methods

Currently, synergy-technologies are being intensively developed [1]. These technologies include not only the Additive Technology classification ASTM standard [2], but also traditional hardening techniques such as induction heating, plasma deposition, surface modification, ion implantation, and others [1]. A special feature of these technologies is the use of highly concentrated energy sources.
The main objective is to provide the surface phenomena of synergy-technologies in sequential formation of structures of functional surface layers of different materials or gradient structures and management of the properties of these structures with different physical and high-force action. At the same time, a key element of surface phenomena of self-organization is a sustainable and stable formation of a layer of a certain thickness with a given structure and phase composition, providing the required set of service properties. One of the key issues is the question of structure formation processes in the emerging layer.

Taking into account the experience gained during implantation of detonation synthesis [3] of nanodiamonds in order to create wear-resistant surface layers on friction surfaces of machine parts, the combined electric and mechanical treatment technology (hereinafter - CEMTT) [4], presupposing the formation of the layers implanted with tungsten carbides, with further electric and mechanical hardening of the treated surface, has been considered.

The hardening effect during EMT is achieved due to the fact that high heating and cooling rates are provided, and a high degree of the austenite grain fragmentation produces the fine-grained structure of the surface layer hardening, having high physical and mechanical and performance properties [3-5].

The technology is implemented with a specific installation, which is a technological complex, consisting of the multi-purpose machine (used for mechanical treatment of workpieces) with the appropriate tools and devices to fix the workpiece to be treated; the supply of electric current of high strength and low voltage; the power unit for converting the industrial electric power; the control unit treatment mode; switching tools and supply of lubricating and cooling technological environment; the block for connection with the PC.

Implantation of tungsten carbides into the surface layer during electric and mechanical treatment is performed on the basis of certain modes. They are applied to the surface prior to such treatment as coating, previously stirred with the consistent graphite lubricant in a certain ratio (for better current conductivity). Tungsten carbide particles are embedded in the surface layer reinforcing it. Then electric and mechanical treatment (EMT) is performed on the same surface in reinforcing modes [3,4].

Austenization of the steel surface layer in the contact zone takes place during a high-temperature plastic deformation at high temperatures and pressures. Carbon included into the coating, consisting of graphite and tungsten carbides, diffuses into the surface layers, increasing the carbon content in the austenite during solid phase saturation. When conducting investigations, the friction surfaces of cylindrical samples were treated with the tungsten carbide powder (Table 1), obtained at the plant of refractory metals, CJSC ‘Wolfram ‘Company’ (Unecha, Bryansk Region), according to the specification of the German company ‘Element Six GmbH’.

Table 1. The brand of the tungsten carbide powder, the particle size, the oxygen and carbon content

| Brand of tungsten carbide powder | Average size of particles according to Fisher Scale, µm | Oxygen content, wt % (max) | General Carbon (typical content), wt % | General Carbon (minimal content), wt % | Free Carbon, wt % |
|---------------------------------|----------------------------------|--------------------------|----------------------------------|-----------------------------------|-----------------|
| WC1,0                           | 0.8…1.3                          | 0.20                     | 6.13…6.18                       | 6.08                             | 0.06            |
| WC1,5                           | 1.3…1.8                          | 0.20                     | 6.13…6.18                       | 6.08                             | 0.06            |
| WC2                             | 1.8…2.5                          | 0.10                     | 6.13…6.18                       | 6.08                             | 0.05            |

The tungsten carbide powder is applied to the surface of cylindrical samples made of steel 45 (Figure 1). As a result of treatment, a multilayer structure, consisting of a hardened layer with the thickness of (180 ... 220) µm (Figure 1, layer 1), the first lower sublayer with the thickness of (200 ... 250) µm (Figure 1, layer 2), the second lower sublayer with the thickness of (20 ... 40) µm (Figure 1,
layer 3) and a matrix, consisting of normalized steel 45, are formed on the surface. The microstructure research was conducted using the auto-emission scanning electron microscope of ultrahigh resolution ‘Zeiss Ultra plus’ on the basis of ‘Ultra 55’, Germany (‘Zeiss Ultra plus’ Field Emission Scanning Electron Microscope).

Figure 1. The surface structure of the steel sample hardened with tungsten carbide.

Vickers microhardness was measured with the microhardness meter ‘PMT-3M’, with a load of 200 g. Measuring the diagonals of prints was conducted with the metallographic inverted microscope ‘Metam LV-34’ with the use of the automated analysis system ‘Micro-Analysis View’. The Vickers microhardness values (Figure 1) for the reinforced multilayer structure (MPa) are the following: layer 1 — 741…846; layer 2 — 546…633; layer3 — 431…525; matrix — 304…332. The Vickers hardness of the R18 steel, heat-treated at elevated temperatures, is the following: 200°C – 815MPa; 400°C – 755MPa [6]. Comparison of the hardness data shows that, in fact, the surface layer of carbon steel 45 is a gradient structure of the P18 tool steel, and it is close to the steel by its properties.

3. Results and discussion

Figure 2 shows the microstructure of layers 1 and 2 in Table 2, which represents the chemical composition of the phase. Layer 1 is a mixture of tungsten carbide WC particles on a steel basis. Therefore, in the process of implanting, the plastic mixture of tungsten carbide in a volume of steel transformed into the solid state.

Table 2. Energy-dispersive analysis of Figure 2, wt %

| Points | C   | Al | Fe  | Co | Cu | W   | In total |
|--------|-----|----|-----|----|----|-----|---------|
| 1      | 16.8| -  | 4.0 | -  | -  | 79.2| 100.0   |
| 2      | 7.6 | -  | 6.4 | 14.7| -  | 71.3| 100.0   |
| 3      | 3.3 | -  | 84.2| -  | 2.9| 9.6 | 100.0   |
| 4      | 3.6 | -  | 83.6| -  | 2.7| 10.1| 100.0   |
| 5      | 15.1| 0.6| 71.5| -  | 4.0| 8.8 | 100.0   |
| 6      | 11.8| 0.7| 76.9| -  | 2.1| 8.5 | 100.0   |
| 7      | 11.3| 0.6| 88.1| -  | -  | -   | 100.0   |
Layer 2 (Figures 2, 3) is ferrite undersaturated with tungsten. Along the boundaries of its grains, the grid of tungsten carbide is located. Therefore, in the process of implantation, the maximum amount of energy is emitted in layer 2, which pushes the system into a metastable state, followed by formation of the cellular structure (Figure 3).

**Figure 2.** The microstructure of layer 1 (tungsten carbide particles) and layer 2 (the grid of tungsten carbide along the borders of austenite grains)

**Figure 3.** The cellular structure of overcooled austenite in layer 2 (the grid of tungsten carbide along the boundaries of austenite grains).
In accordance with known diagram Fe - W, the temperature of layer 2 is greater than temperature 1060°C, corresponding to the peritectoid reaction. Under this temperature, polymorphic transformation of iron with austenite formation and tungsten carbide dissolution occurs in austenite.

For example, about 8% of W is dissolved in steel austenite R6M5 with optimum heating temperature during tempering (1200 ... 1230) °C. About 8% of W also dissolves in steel R18 in the austenite, but it takes place at temperatures of (1270 ... 1290) °C. Consequently, the maximum limit of steel heating during thermal power exposure through implantation can be considered to be the limit of up to 1300°C.

Upon cooling, the austenite solution becomes oversaturated with tungsten and thus stabilizes. Upon further cooling, the structure of stable overcooled austenite is created and the excess tungsten is released in a tungsten carbide grid along the austenite grain boundaries, slightly coated with tungsten. In this case, the resulting structure is identical to that of cast high-speed steel, corresponding to complex carbide eutectic, resembling ledeburite, and is located along the grain boundaries. A similar structure is observed (Figure 4) in the transition of layer 2 into layer 3, which is much thinner than layer 1, but is also saturated with the particles of tungsten carbide (Table 3).

![Layer 2 and Layer 3](image)

**Figure 4.** The microstructure of layer 2 (tungsten carbide grid) and layer 3 (tungsten carbide particles)

**Table 3.** Energy-dispersive analysis of Figure 4, wt. %

| Points | C  | Fe  | Co | Cu  | W   | In total |
|--------|----|-----|----|-----|-----|----------|
| 1      | 13.5 | 68.3 | -  | 6.2 | 12.0 | 100.0    |
| 2      | 14.5 | 9.1  | 4.2 | 3.2 | 69.0 | 100.0    |

For complex comparative durability tests, the outer cylindrical surface of the samples produced of steels P18 and 45 was investigated using the following techniques:
- bulk hardening, low temperature tempering (P18 steel);
- bulk hardening, low temperature tempering (steel P18), plus coating with solid-solution hardening of connections with different types of atomic bonds of the Ti-Al-N system with a thickness of 3 μm.
applied using PVD technology (in vacuum — using an arc plasma source and separation of the plasma flux);
- bulk hardening, low temperature tempering (steel P18), plus coating with multiphase system structure Mo-Cr-N with a thickness of 3 μm applied using PVD technology (in vacuum — using an arc plasma source and separation of the plasma flux);
- combined electric and mechanical treatment (CEMT) represents formation of the tungsten surface layer implanted with carbides on the surface of steel 45, which was not subjected to thermal treatment and subsequent electric and mechanical hardening of the treated surface.

Samples with coatings based on Ti-Al-N and Mo-Cr-N were manufactured by the LLC ‘NPF ‘Plazmatsentr’ (Saint-Petersburg). Comprehensive comparative tests of the samples were carried out on the automated installation, created on the basis of the friction machine ‘Mi-1M’ with a normalized method.

According to the analysis of the recorded parameters, the following indicators of tribological properties were determined: running-in time $t_0$, h; running wear $h_0$, μm; the average value of the friction factor during normal wear $f$; ratio of the maximum value of the friction factor during running, $f_0$ to $f$; the average value of the wear intensity during normal wear $I_h = (h - h_0) / (L - L_0)$, where $h$ is the total value of sample depreciation during the test, μm; $L$ is the path of friction, completed by the surface of the sample during the test, μm; $L_0$ is the path of friction, completed by the surface of the sample during handling; the value of the wear rate within the total time of testing is $I_{h\Sigma} = h / L$.

Choosing the best method of hardening for friction surfaces according to the parameters of tribological tests can be carried out on the basis of the determination of the above-mentioned criteria and their comparison. Thus, the friction surface is more wear-resistant with smaller values of wear intensity, the duration of handling, the friction factor, as well as with the falling characteristic of the friction factor curve change in time.

Testing of the samples was carried out under the following conditions: the sliding speed is $\upsilon = 1$ m / sec; the normal loading force is $N = 100 \pm 0.5\%$, H (which corresponds to the pressures of about 150 MPa, calculated according to Hertz); the kind of initial contact is a saturated plastic one; the type of lubrication is a boundary-type one; the type of lubrication is a plunging one; the leading type of wear is a fatigue one; the lubricant is industrial oil ‘I — 20A’ (GOST 20799 - 88); the indenter material is hard alloy BK8; the total time of each sample testing is 8 hours. Test results of the samples treated with the above-mentioned technology on the modernized installation ‘MI-1M’ are shown in Table 4.

Comparison of the results of tribological tests of samples with a normalized method has shown that the minimum values of the friction factor, the running-in time and wear are characteristic of the tungsten surface layer implanted with carbides, followed by electric and mechanical hardening.

| Tribo-engineering property | Value | Steel P18 | Steel P18 + Ti-Al-N | Steel P18 + Mo-Cr-N | Steel 45 + CEM TT |
|---------------------------|-------|-----------|---------------------|---------------------|------------------|
| Running-in ability       | $t_0$, ч | 1.12  | 0.58  | 0.75  | 0.45  |
|                          | $h_0$, μm | 7.5    | 1.30    | 1.50    | 1.70    |
|                          | $f_0/f$ | 1.61 | 1.42 | 1.46 | 1.19 |
| Antifrictional property  | $f$ | 0.31 | 0.32 | 0.25 | 0.24 |
| Wear-resistance          | $h$, μm | 16.1 | 9.70 | 9.60 | 4.6 |
|                          | $I_h \cdot 10^{-10}$ | 3.44 | 3.12 | 3.09 | 1.44 |
|                          | $I_{h\Sigma} \cdot 10^{-10}$ | 5.55 | 3.35 | 3.32 | 2.03 |
Wear curves for samples coated with Ti-Al-N and Mo-Cr-N systems are characterized by the rapid increase of wear after the wear of the coating. The wear curve for the sample subjected to CEMTT is more stable. The results of tribological tests have shown that the wear rate of the samples with a layer, implanted by tungsten carbides, and the subsequent electric and mechanical hardening during the normal wear period is less compared with:
- heat-treated samples - 2.4 times;
- samples subjected to PVD (coating of the Ti-Al-N system) - 2.2 times;
- samples subjected to PVD (coating of the Mo-Cr-N system) - 2.1 times.

Chichinadze A.V. introduced the system [7] of ten classes of wear resistance, whereby the wear resistance of steel R18 with different coatings according to the test results (Table 4) relates to class 7, and the wear resistance of steel with a gradient of 45 — to the structure of the 8th class.

Thus, high levels of wear resistance of the gradient structure layer to steel 45 implanted with tungsten carbide are a consequence of the composite hardening due to the formation of fine carbide structures, based on tungsten carbide (less than 1 μm) of different morphology (mesh net, thread, grains), and as a consequence of higher hardness values, compared to the layer with a hardness of typical tool steel R18.

4. Conclusions
1. For the first time, it has become possible to apply the coatings on the basis of tungsten carbide by plastic deformation.
2. In fact, the surface layer of carbon steel 45 is a gradient structure of tool steel P18, and as a result, carbide nanocomposite hardening phases with higher hardness of different morphology are distinguished.
3. The gradient structure is a honeycomb supercooled austenite, which is stabilized and reinforced with the tungsten carbide grid consisting of aggregated nanoscale filamentary and rounded tungsten carbide particles.
4. The presence of a gradient structure having an entirely metallic matrix base material provides a monolithic adhesion hardened layers without discontinuity in the process of wear with considerable dynamic loads, which is also confirmed by the tribological tests.
5. Modification of the friction surface of steel 45 by implanting and strengthening nanocomposite powder tungsten carbide by the IKEM method can significantly increase the wear of the friction surfaces, as evidenced by tribological tests.

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