Phase transformations in functional coatings of tungsten carbon steels

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Annotation. Structural and phase transformations in tungsten-containing functional coatings of carbon steels, obtained in high-energy processes of implanting tungsten carbide micropowders by the method of complex pulse electromechanical processing, were studied. It is shown that during thermoforce action in the deformation zone, an intensive austenization of steel occurs with the dissolution of a powder of tungsten carbide with the subsequent formation of composite gradient structures as a result of the decomposition of supercooled austenite supersaturated with tungsten both by the diffusion mechanism and by the spinodal decomposition mechanism. It is shown that individual zones of the tungsten-containing phases of the alloy are in the liquid-phase state and undergo spinodal decomposition with the formation of highly disperse carbide phases of globular morphology.

1. Introduction
Synergetic technologies [1] are currently developing intensively, which include not only additive technologies according to the ASTM standard classification, but also traditional strengthening technologies, for example, induction heating, plasma spraying, surface modification, ion implantation, etc. [2]. The main task of synergistic technologies is to ensure the self-organization of surface phenomena in the sequential formation of structures of functional surface layers of different materials or gradient structures and to control the properties of these structures under various physical high-temperature and force influence. At the same time, a key element of self-organization of surface phenomena is the conservative and stable formation of a layer of a certain thickness with a given structure or phase composition that provides the required complex of service properties. One of the key issues is the question of the processes of structure formation in the resulting layer. In this paper, we investigated the phase composition and processes of formation of gradient structures of functional coatings obtained in high-energy implantation processes: by combined pulse electromechanical processing [3, 4].

2. Materials, methods, research results
The functional friction surface of carbon steel 45 is treated with a powder of tungsten carbide (particle size up to 9 µm) using the combined electromechanical processing technology [3, 4]. The powder of tungsten carbide is manufactured at the refractory metals plant of ZAO "Company “WOLFRAM” (Unecha, Bryansk region), according to the specification of German company Element Six GmbH. Combined electromechanical treatment includes two stages. At the first stage (the mode of “high-
temperature plastic deformation”), a tungsten carbide powder is implanted from a special graphite coating applied to the surface of the workpiece during the roll-over of the 95X18 steel roller on the workpiece surface under a certain load. Particles of tungsten carbide, mixing with plastically deformed metal, are introduced during deformation into the formed functional surface layer.

At the second stage (the mode of “high-temperature thermal hardening”), a roller made of pseudo alloy “tungsten carbide-copper” is used to ensure a combination of high temperatures and pressures in the contact zone, under the influence of which, at the time of the electric pulse, the austenitization of surface layer of steel occurs in the contact zone of the roller and the treated surface. At the same time, carbon from the coating in the solid-phase process of high-temperature saturation diffuses into surface layers of the part, increasing the carbon content in the austenite. Tungsten carbides partially dissolve in austenite to the limit of its saturation with tungsten.

As a result of processing, a two-layer gradient structure is formed on the functional surface consisting of the first upper hardened layer of (180 ... 220) \(\mu m\) thick (Fig. 1, a) saturated with initial particles of tungsten carbide, the second lower layer of (200 ... 250) \(\mu m\) thick, consisting of the cellular structure of austenite grains, the boundaries of which are reinforced with a carbide-tungsten mesh (Fig. 1, b).

![Microstructure of layers 1 and 2](image)

**Figure 1.** a – microstructure of layer 1 (particles of tungsten carbide) and layer 2 (mesh of tungsten carbide along boundaries of austenite grains), x250; b – cellular structure of supercooled austenite in layer 2 (mesh of tungsten carbide along boundaries of austenite grains), x5080

Microstructural studies were carried out on a Zeiss Ultraplus Field Emission Scanning Electron Microscope of ultrahigh-resolution based on Ultra 55, Germany. In Fig. 1 the microstructure of layers 1 and 2 is shown, in Table 1 the result of energy-dispersive analysis of layers is presented. Layer 1 is a mixture of implanted tungsten carbide WC particles and a matrix base of steel 45.

**Table 1.** The energy-dispersion analysis to Fig. 1, wt%

| Points | C  | Al | Fe  | Cr  | Cu  | W   | 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 |
Consequently, during the implantation in the “high-temperature plastic deformation” mode, intensive plastic mixing of tungsten carbide particles occurs in the volume of the steel in the solid state and their partial dissolution in austenite. In Table 1, there are elements of Cr and Cu. Their appearance is associated with the use of various rollers. In the “high-temperature plastic deformation” mode, a 95X18 steel roller is used, and the chromium from the roller partially diffuses into tungsten carbide (point 2, Fig. 1, a). In the “high-temperature thermal hardening” mode, a roller made of pseudoalloy “tungsten carbide – copper” is used, and copper, which is in a pseudo-alloy in unbound state, passes into a solid solution of austenite from the roll (points 3 – 6, Fig. 1, a). The energy-dispersion analysis and the character of structure formation show that in the “high-temperature thermal hardening” mode, at the time of passage of the power electric pulse in combination with the maximum deformation load on the roller the maximum amount of energy is allocated in layer 2, which transfers the system to a metastable state with subsequent formation of a cellular structure (Fig. 1, b).

Thus, when pulsed implantation of tungsten carbide powder into steel 45 by the combined electromechanical treatment, the temperature in the active zone is higher than the temperature of the peritectoid reaction of 1060 °C in the Fe –W system. The maximum boundary for steel heating during thermo-impact treatment during implantation can be considered a boundary up to 1300 °C. Consequently, a cellular supercooled austenite with a tungsten carbide mesh along grain boundaries is formed in the steel structure, which is identical to the structure of a cast high-speed steel with a complex carbide eutectics resembling ledeburite and located along the boundaries of austenite grains.

In some regions of the structure, when passing from layer 1 to layer 2 (Fig. 1, a), unusual structural formations were found near the clusters of large particles of tungsten carbide powder (Fig. 2, a). These structures have a pronounced eutectic structure; however, they consist of filamentary tungsten carbide crystals alternating with isolated globular particles of tungsten carbide with a high degree of dispersion (Fig. 2, b). Moreover, the filaments themselves consist of coagulated tungsten carbide tiny globules.

![Figure 2.](image_url)

**Figure 2.** a – eutectic type structure and globular crystals of tungsten carbide in the transition zones of the hardened layer in the functional layer of steel 45, x50800; b – crystals of globular shape along boundaries of tungsten carbide particles, x40340

Table 2 shows the energy-dispersion analysis of globular structures to Fig. 2, b. A peculiarity of this structure is a kind of carbide “fringe” made of globular, close to the spherical form tungsten carbide particles, along the phase surface of tungsten carbide particles (Fig. 2, b, zone 1), at that smaller tungsten carbide particles are covered with carbide “fringe” in several layers (Figure 2, b, zones 2 and 3).
The extraction of significantly larger carbide globules in supercooled austenite is also unusual (Fig. 2, b, zones 4 and 5).

Table 2. The energy-dispersion analysis to Fig. 2. b; wt%

| Points | C     | Fe | W     | Total |
|--------|-------|----|-------|-------|
| 1      | 36.17 | -  | 63.83 | 100.00|
| 2      | 38.50 | 7.11| 53.39 | 100.00|
| 3      | 38.90 | 4.08| 57.02 | 100.00|
| 4      | 40.07 | 21.71| 35.22 | 100.00|
| 5      | 38.26 | 22.90| 35.69 | 100.00|

The formation of highly disperse filamentary carbide structures (Figure 2, a) and globular carbide structures in the form of a “fringe” (Figure 2, b) cannot be explained from the standpoint of the release of excess tungsten from a supersaturated austenite by the diffusion mechanism of decomposition, as in the case of the formation of a cellular type structure (Figure 1, b).

The Vickers micro hardness in functional surfaces was measured on a micro hardness tester mod. PMT-3M with a load of 200 g. The measurement of prints diagonals was carried out using a metallographic inverted microscope of mod. Metam LV-34 with the use of the automated analysis system “Micro-Analysis View”.

Table 3 shows the Vickers micro hardness values for a multilayered hardened gradient structure of a wear-resistant functional surface (Fig. 1).

Table 3. Micro hardness of the surface layer of steel 45 hardened with tungsten carbide

| Micro hardness of layers, HV, MPa |
|---------------------------------|
| Layer 1                        | Layer 2         | Layer 3         | Matrix          |
| 741…846                       | 546…633        | 431…525        | 304…332        |

3. Discussion of the results

An evaluation of the character of the processes of structure formation shows that, in accordance with the Fe – W diagram, the temperature in the functional layers with the austenite cellular structure exceeds the temperature of 1060 °C that corresponds to the peritectoid reaction. Under these temperature conditions, a polymorphic transformation of iron takes place with the formation of austenite and the dissolution of tungsten carbide in austenite.

For example, in the austenite of steel P6M5, with an optimal heating temperature for quenching (1200 ... 1230), °C about 8% of W may be dissolved. In steel P18, about 8% W also may be dissolved in austenite, but at temperatures (1270 ... 1290) °C. Consequently, the maximum boundary for steel heating during thermo-impact treatment during pulse implantation can be considered a boundary up to 1300 °C.

When cooled, the austenite solution is supersaturated with the tungsten and is stabilized. With further cooling, the structure of stabilized supercooled austenite is formed, and the excess of tungsten is released as a mesh of tungsten carbide along the boundaries of austenitic grains, slightly doped with tungsten. In this case, the resulting structure is identical to the structure of a cast high-speed steel, corresponding to complex carbide eutectics, resembling a ledeburite and located along grain boundaries.

The spinodal decomposition process [5, 6] of solid solutions based on tungsten can explain formation of local structures shown in Fig. 2. Fig. 3 shows the microstructure of the spinodal decomposition of a liquid tungsten-containing phase. Calculation of the level of specific energy release per mass unit of the particle at the front of the motion of implanted tungsten carbide particle is 0.9 · 10^9 J / kg. This level of energy release not only melts the metal in the vicinity of the moving particle, but also possibly partially evaporates it, and a particle of tungsten carbide actually moves in
the channel of the melt. These phenomena contribute to the activation of mutual diffusion of W, C and Fe. As a result, carbidisation occurs (point 1, figure 2, b) during the movement process and the formation of WC carbide in accordance with the W – C diagram. In addition, tungsten carbide particles dissolve in micro volumes of high-carbon steel melt. In Fig. 2, particles of tungsten carbide have a smoothed, oval surface, which indicates the dissolution of surface layers.

Thus, in the process of implantation, the surface of large particles of tungsten carbide is actually enveloped by a shell of a melt saturated with tungsten. When the particle stops, in fact, an instantaneous quenching of the melt with significant super cooling occurs and its crystallization by the mechanism of spinodal decomposition into a phase with a low content of tungsten (austenite, points 4 and 5, Fig. 2b) and a phase with a high tungsten content (spherical tungsten carbide crystals, points 2 and 3 of Figure 2, b).

During the spinodal decomposition, in the general case, the diffusion flux is determined not by the concentration gradient, but by the gradient of chemical potential. In this case, diffusion processes lead to a state characterized by the condition of chemical potential continuance in the given volume $\mu = \text{const}$ and the system bundles into concentration zones in which the crystallization of condensed phases occurs. Consequently, the system crystallizes in the form of spherulitic crystals. Moreover, the crystallization process starts on the phase separation surface of the “WC carbide – melt” as on a substrate, forming a carbide “fringe” along the separation surface (Fig. 2). In particular, Fig. 3 shows spherical crystals of TiO$_2$, the crystallization of which occurred under conditions of considerable supersaturation of the system and subsequent spinodal decomposition.

![Figure 3. Spherical crystals of TiO$_2$ (taken from [7], Fig. 6.12, a)](image)

In Fig. 1, a the structure is formed as a result of spinodal decomposition of a solid solution of tungsten, with the formation of filamentary crystals of tungsten carbide, alternating with isolated globular particles of tungsten carbide of high degree of dispersion. Moreover, the filaments themselves consist of coagulated tungsten carbide tiny globules.

It was shown in [7] that the intermediate decomposition structures arising at the stage of kinetic stabilization of the spinodal transformation are quasi-stationary and are far from complete thermodynamic equilibrium. As a rule, in early stages of the spinodal stratification, a granular relaxation structure without phase boundaries is formed. At later stages, one of phases is dispersed within the other phase in the presence of a stable interphase boundary, which fully corresponds to the nature of the microstructure shown in Fig. 2. Such structures are formed by periodically repeating fragments and are metastable in general case. Thus, the formation of structures shown in Fig. 2 occurs by a single mechanism of spinodal decomposition of the solid solution and the melt, respectively.

Table 3 shows the values of micro hardness of functional layers of steel 45. The high micro hardness level of the functional gradient layer on steel 45 is explained by the high degree of
reinforcement by tungsten carbide particles (Figure 1) and the composite hardening of the austenite cellular structure (Figure 2), and by a significant decrease in the size (approximately 5-fold) of the austenite grain of the cellular structure (Figure 2) and an increase in hardness in accordance with the Hall-Petch law [8 – 10].

The increase in hardness is associated with the process of nanostructuring of materials as a result of spinodal stratification. The Hall-Petch law investigates the dependence of the mechanical properties of materials on the grain size. Thus, in polycrystalline materials in a large range of grain sizes, an increase in hardness is observed with a decrease in the size of crystallites.

As the size of the grain decreases, the strength and hardness of the material increase. The Hall-Petch relation describes well the mechanical properties of materials with a grain size of more than 50 nm, in which deformations occur mainly along a dislocation mechanism. Consequently, controlling the processes of spinodal stratification in the crystallization of alloys determines the practical application of the use of nanostructuring to obtain the required properties of the material.

4. Conclusions

1. Structurization in high-energy implantation processes is determined by the conditions of supercooling and proceeds according to two mechanisms – the classical diffusion mechanism of the decomposition of supersaturated solid solutions and the spinodal decomposition of both solid solutions and local liquid-phase zones.

2. A consequence of the implementation of these mechanisms of structure formation is the formation of a gradient structure of the functional surface, characterized by the crystallization of globular and filamentary tungsten carbides, which compositely strengthen the cellular structure of stabilized austenite.

3. With combined pulse electromechanical processing when implanting tungsten carbide, the temperature in the contact zone of the roller and the part reaches 1300 °C, which leads to intensive dissolution of tungsten carbide particles, supersaturation of the austenite with tungsten and its subsequent disintegration into highly disperse structures.

4. Near the tungsten carbide particles, where local molten zones are formed ($t_{\text{max}} = 1450$ °C), at the same time surface dissolution processes occur with subsequent carbidization and spinodal decomposition of the melt enriched with tungsten, followed by the formation of a highly disperse carbide-austenite structure reinforced with globular inclusions of tungsten carbide.

5. The processes of spinodal stratification are the technological basis of nanostructuring of alloys in the course of their crystallization.

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