The synthesis of nanocomposite structures on the surface of geometrically complex products

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Abstract. The paper presents the technology of nanocomposite structure synthesis in the surface layer of geometrically complex products under the impact of low-temperature plasma and the results of experimental study of their properties. An example is given of practical application of the nanocomposite structure product to improve the efficiency of ultrasonic dimensional processing.

1. Introduction
The current stage of production development in various fields is characterized by tougher working conditions for products made of metals and alloys. This requires continuous improvement of existing and development of new manufacture technologies in order to find the conditions allowing to take full advantage of opportunities for working at high temperatures, external power loads and corrosive environments.

One promising technology is the technology of forming composite structures on the working surfaces of products that ensure high and uniform hardness, wear resistance and dynamic strength [1-3].

Due to the low energy efficiency, traditional methods of gas thermal hardening and ion-plasma sputtering are time-consuming, which results in substantial thermal deformation of the whole product [4-6]. Creation of durable coatings based on conventional additive technologies with time dividing powder (or other material) application and subsequent intensive energy impacts do not ensure high dynamic strength of composite structures, including the bond with the matrix. In this respect, it is expedient to use the technology of composite structure formation directly within the surface layers of the products, i.e. in the original matrix. One such technology is the nanostructuring technology geometrically complex surfaces, which is carried out by high-performance multiplier effect on the interaction of electrostatic and electromagnetic fields [6]. Optimal interaction of the fields and environment properties is ensured by the special design of the plasma torch, the original waveguide system for the transmission of electromagnetic microwave energy from the magnetron to the product, the pumping system (vacuum of 300 Pa) and the supply of the process gas mixture. As a result, in the plasma torch low-temperature plasma is formed that provides intensive heating only of the workpiece surface layer, which leads to the formation of a more complex than the original structure. It is comprised of the amorphous phase based on particles < 10 nm and nanoclusters of 30-70 nm. This provides high dissipative properties, strength and surface hardness. The transition layer between the amorphous layer and the matrix ensures the strength of the entire structure.

2. The results of experimental studies of the synthesis process
The study of the formed nanocomposite structure included examination of its morphology, chemical composition as well as its physical and mechanical properties. The research was carried out on P6M5 steel and RX10 carbide samples treated at the minimum and maximum parameter value combinations of electromagnetic and electrostatic fields with the use of analytical complex on the basis of a scanning electron microscope TESCAN MIRA LMU, double microscope MIS-11, analytical balance and mechanical property precision tester NANOVEA Ergonomic Workstation.

Examination of the morphology of the steel workpiece allowed to identify a ~2 µm thick layer on its surface which clearly shows the areas around the carbide grains containing numerous flat irregularly shaped particles ~100 nm thick and arranged in the form of a sphere or cloud (Figure 1, a). Outside the layer the number of particles is reduced considerably. There were also detected 350-550 nm inclusions of modified shape (from round to elliptical), the occurrence of which is possible only in the event of dissolution of the carbide grains and / or splitting them into smaller ones (Figure 1, b). The maximum number of inclusions (65% of total) are detected at the depth approximately equal to the average radius of undissolved grains, which corresponds to 0.7-0.8 µm, and the minimum (35% of total) may be located at their border, i.e. at the depth of 1.4-1.6 µm. The presence of the meniscus (a layer in the molten state) around the carbide grains in the region of their interface with the base material is the most characteristic feature of underlayer formation.

![Figure 1](image1.png)

**Figure 1.** A cloud of nanoscale particles (a) formed around partially dissolved carbide grain in the surface layer of the sample workpiece after treatment in a low-temperature plasma of combined discharge (b).

Examination of the surface morphology of the steel workpieces revealed the formation of nanoclusters on them. Clusters and larger structural elements of the surface (matrix grains) are joined into a whole by amorphous binder (Figure 2, a). Surface morphology analysis has also found that the plasma impact on them is carried out by groups of Ø40-50 nm nanoscale beams. In defect-free surfaces the traces of these groups are homogeneous and seen as solid virtually indistinguishable homogeneous zones. On the surfaces with different relief defects, such as irregularities of droplet phase type (Figure 2, b), microprotrusions, etc, the formation of beam focusing lenses takes place. The consequence is the electrostatic field distortion which leads to plasma uniformity breach and manifests itself in layering and regrouping beams towards their increased concentration to the extent of filamentation.
**Figure 2.** Electron microscopic image of the carbide sample surface:
a – nanoparticle inclusions; b – droplet phase.

**Figure 3.** Electron microscopic image of the carbide sample surface in the zones of blind holes, reflow (a) and sagging (b).

The impact of such beams leads to the formation of micron reflow zones and blind holes of 0.7-1.0 µm diameter (Figure 3a). The intense local heating in reflow zones in combination with plasma layering causes uneven volumetric heat release and thus, uneven heating of the surrounding areas, which leads to surface subsidence and the formation of nano-sized steps or closed terraces which outwardly appear as a nested set of closed curves (Figure 3, b) as well as to the formation of small clusters, reducing the amount of the amorphous phase and, consequently, a marked embrittlement of the surface.
Chemical composition study was carried out on the hard alloy samples using X-ray sensor INCAPentaFETx3, OXFORD Instruments, which is part of an analytical complex TESCAN MIRA\LMU. The depth of the analyzed layer was about 1 µm. The initial structure of the sample surface layer consisted of aluminum (13.83 wt.%), titanium (38.01 wt.%), carbon (16.87 wt.%), nitrogen (27.96 wt.%), and oxygen (3.35 wt.%).

The comparison of the chemical composition of the sample surface fragments treated in the minimum plasma exposure modes shows that its local changes are caused by the processes occurring at the surface, and are associated with the changes in the structure of the plasma flow emitted by the inner edge. Thus, the flow impact on the tops of large droplets (Figure 4, a) is different from the peripheral sections (point 5), where reduction of the nitrogen concentration and its alignment with carbon and aluminum concentrations are registered. Furthermore, slight fluorine concentration was found, which means sublimation of fluoroplastic insulation of the sample support.

Similar changes were observed in the vicinity of the melt zone (Figure 4, b). In the area of maximum impact of the beam (point 4) there is maximum (54% from baseline) reduction in the nitrogen concentration and an increase in the concentration of carbon and titanium, which indicates substitution processes and/or carbon-nitrogen displacement. This eventually leads to nitrogen, carbon, and aluminum concentration leveling off.

Exposure to plasma, leading to subsidence surface processes, is accompanied by changes in terms of convergence of titanium and nitrogen concentrations, as well as aluminum and carbon (Figure 4, c).

Thus, the change in the chemical composition of the surface layer in the minimum modes of plasma exposure is mainly due to the polymerization processes of island films of Al\textsubscript{15}C\textsubscript{7}N\textsubscript{2}O\textsubscript{5}-type formation, and layering structure processes can only be observed in the area of surface subsidence.

Changing modes to maximum plasma exposure has caused changes in the chemical composition (Figure 4, d, e) both similar to the effect on the minimum modes and new, which are characterized by the complete replacement of the nitrogen with nanostructures of Ti\textsubscript{57}C\textsubscript{34}Al\textsubscript{5}O\textsubscript{2}-type formation (Figure 4, f).

The study of physical and mechanical properties of the structure included a quantitative and semi-quantitative measurement and evaluation of its roughness as well as hardness investigation.

When measuring the roughness of steel specimens, initially the values of each trough and ridge of microroughnesses located in the linear field of the microscope were measured, and then the mean and standard deviation (Ra) from it was calculated. The obtained values show (Table 1) that, firstly, the roughness is reduced (2.93 times on average), and secondly, the degree of reduction depends on the initial state of the surface, i.e. on its technological heredity.

Measuring roughness of hard alloy samples was carried out on a lapped hardened plate surface (12 roughness class). After the installation of the specimen on the plate, a loose strap of thin silk thread with a light cup of thin plastic (0.3 g) at the end was put on the specimen. The starting force was determined with the help of some drops of water in the cup. When the load reached the value that balanced friction force, the specimen was displaced and began its movement. The amount of this load was determined by weighing to the nearest 0.01 g.

For each sample the average starting force was determined by 10 passages, both before and after plasma exposure. The results showed (Figure 5) that after low temperature plasma exposure the breakaway force decreases on average 1.4 times, due to microroughness blunting and reducing the height and number of contact points of engagement between vertices.

The study of electron microscopic images allowed to specify the mechanism and to identify the causes that lead to the reduction of the height of the microscopic irregularities. They are associated with the protruding microdefects deformation and their transformation into planar defects. The processes of film formation and changes in the chemical composition of the surface layer which change the conditions of contact interactions at the atomic level play an important role here.

The study of hardness was performed with loading the indenter (Berkovitch pyramid) with weights of 50 and 100 mN. Processing of the obtained data (Figure 6) included the construction of the distribution of hardness and elastic module values as a result of the decomposition of print depths.
range into intervals, followed by counting the number of parameter values have fallen in each interval, their averaging and dividing each array members by its maximum value.
Figure 4. The chemical composition of the surface of the cemented carbide samples when exposed to plasma at the minimum (a-c) and the maximum (d-f) modes.

Table 1. The roughness of the surface of steel sample workpieces before and after combined discharge low-temperature plasma exposure

| No | Roughness by Ra, µm | Reduction Ra, times |
|----|---------------------|---------------------|
|    | initial | after treatment | Ra, times       |
|-----|---------|-----------------|----------------|
| 1   | 0.68    | 0.20            | 3.4            |
| 2   | 0.41    | 0.14            | 2.9            |
| 3   | 0.50    | 0.22            | 2.3            |
| 4   | 0.33    | 0.19            | 1.7            |
| 5   | 0.21    | 0.18            | 1.1            |
| 6   | 0.40    | 0.06            | 6.6            |
| 7   | 0.47    | 0.09            | 5.1            |
| 8   | 0.24    | 0.12            | 1.9            |
| 9   | 0.20    | 0.19            | 0.9            |
| 10  | 0.48    | 0.16            | 3.0            |
| 11  | 0.40    | 0.12            | 3.3            |
| 12  | 1.10    | 0.46            | 2.3            |
| 13  | 0.55    | 0.15            | 3.7            |
| 14  | 0.34    | 0.11            | 3.4            |
| 15  | 0.36    | 0.15            | 2.4            |

Figure 5. Comparative charts of breakaway effort of hard alloy samples before (black) and after (gray) low-temperature plasma exposure.

The analysis of the distributions confirmed that formed upon low temperature plasma exposure structure is indeed nanocomposite as its surface layer has zones with increased hardness as well as with high elasticity (Figure 7).

3. Practical implementation
As an example of the technology practical use let us consider the process of ultrasonic dimensional treatment of products made of quartz glass, based on the interaction of three main components: a working tool (contactor), powder (working slurry) and the workpiece.

Contactor vibrations are transmitted to the working suspension that performs the functions of the cutting tool. Boron carbide powder, pre-mixed with distilled water in a certain ratio was used as slurry. During the processing, boron carbide grains penetrate the processed material with their sharp edges and facets, while the contactor acts as a ‘hammer’, regularly striking the powder.

It should be noted, however, that along with sufficiently high efficiency of this processing method, there are several problems associated with rapid mechanical wear of the contactor working parts (Figure 8). The main consequence is the deterioration in the geometry (tapering) and the roughness of working surfaces of manufactured products. In this regard, it would be relevant to increase strength and wear resistance of the surface layer of the contactor working part through its nanostructuring, which can further increase the efficiency of ultrasonic treatment process in term of ensuring the specified accuracy and cost reduction.

The quality of nanostructuring process was evaluated through quantitative assessment of changes in physical and mechanical properties of the surface layer of the contactor working part material.
according to microhardness measurement (Vickers) both before and after low-temperature plasma exposure using a technique based on determining of microhardness distribution in the depth of the surface layer [7].

![Graph showing microhardness distribution](image)

**Figure 7.** The distribution of the elastic module (1), and microhardness (2) in the modified layer.

![Contactor Image](image)

**Figure 8.** Contactor.

The measurements of microhardness of three contactors and their comparative analysis confirmed the following:

1. The least solid is the part of the surface layer that is located directly below the adsorbed zone and the zone of the oxides. This is due to the fact that the contactors were subjected to abrasive treatment to form the desired geometry of the working part after manufacturing. As a result, elastoplastic deformation and heating caused extension of the surface layer, irreversible structural and phase changes therein, and subsequent decrease of microhardness.
2. Contactor №1, previously used, was subjected to repeated abrasion with a view to restoring the geometry of the working surfaces. After plasma exposure, their microhardness increased by 1.35 times on average. Operating results made it possible to record the growth of the contactor resistance time by 2.5 times compared to the initial data.

3. Microhardness of the new contactor №2 after plasma exposure increased by 1.25 times on average; resistance time increased by 2 times. It was found that degree of dispersion and boron carbide powder grain shape influence the resistance. The effect is that during processing of the first two workpieces, interaction with the contactor decreases the grain size of the initial fraction from about 35 µm at their distribution center to about 30 µm, and their shape is changed from irregular polygonal to spherical one. It is during this period the contactor wears the most, creating, however, favorable conditions for further processing. This means that there is an additional reserve for increasing time resistance, which can be used in the following way. The transformation of boron carbide original structure occurs in the processing of the first workpiece with a conventional contactor. As a result, a defect layer which exceeds the initial microhardness is formed on its surface. This is a favorable factor from the viewpoint of low-temperature plasma exposure. Thereafter the contactor undergoes plasma exposure, the duration of which does not exceed 15 min., and then it is placed into position for the main processing cycle (note that the installation time is small and achieved through the technologically effective contactor construction).

4. The use of the proposed approach to contactor №3 showed that after plasma exposure its working part surface layer microhardness increases by 1.35 times on average, which is 1.46 times higher than the microhardness of contactor №1. As a result, the resistance time of contactor №3 increased by 3 times.

4. Conclusion
The presented data show that the quality of nanocomposite structure synthesis on the surface of the geometrically complex products is closely associated with the method and the specifics of the prior exposure of the workpiece material changing the properties of their surface layers. All previous machining operations (turning, grinding, polishing with diamond paste) and heat treatment (hardening and annealing) will have different, in terms of magnitude and speed, elastic-power and thermal effects on the surface layer, as each subsequent operation is performed on the already modified surface. In macroaspect, it leads to fluctuations in the surface roughness and the formation of unstable strengthening parameters called wear hardening, which cause significant changes in the structure and properties of the surface layer. Moreover, these changes are random and can be of either positive or negative character. However, the energy of charged low-temperature plasma particles, affecting the surface layer changes its structure from the original high defect structure into a composite one having a higher affinity to the base material, and on this basis provides increased main indicators of operational reliability of products, in particular, indicators of failsafety.

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