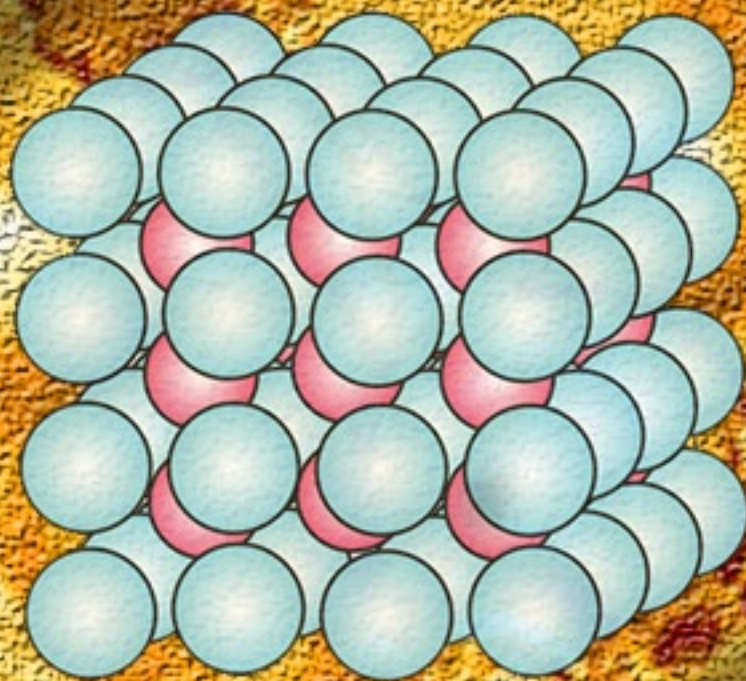


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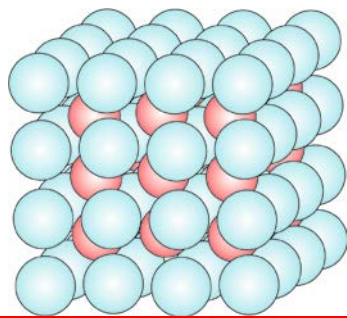
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PHASE CHANGES IN IRON-CARBON ALLOYS IN SOLID STATE AT CONCENTRATED ENERGY FLOW TREATMENT

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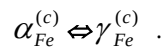
Abstract: The paper studies the mechanism, kinetics and morphology of phase changes primarily at heating by concentrated energy flows (CEF). The objects of study have been a medium carbon low-alloy steel 37Cr4 (DIN), a high-carbon tool steel X210Cr12 (DIN) and grey cast irons with flake and spheroidal graphite (GG 15, GG 30, GGG 50 - DIN) treated by plasma and electron beam heating.

It has been established that the mechanisms of phase changes at heating with CEF differ considerably from the familiar ones and can be classified as mechanisms of the following type: of migration by plastic deformation; of migration with a wave effect; of baric migration; of thermokinetic migration and of accelerated migration under the impact of electrodynamic fields and radiation. These mechanisms have been tested and proven by the fixed imbalance conditions of the structures obtained in the experiments.

Key words: CONCENTRATED ENERGY FLUX; SURFACE TREATMENT; PHASE CHANGES; SOLID STATE TRANSFORMATION

1. Introduction

According to the theory of phase changes, the transformations in the iron-carbon system take place in balance or imbalance conditions. The phase changes under thermokinetic conditions may be caused by either classical diffusion or other mechanisms called diffusionless. These assumptions refer to phase changes at different velocities. In this case both theories, the diffusion theory and the energy theory, determining the mechanism of transformation fix the single possible case of phase changes based on diffusion: the formation of crystallization centers and their expansion. The basic force of phase changes at heating, apart from the concentration differences, is the heat treatment under balanced (gradual) temperature elevation. The diffusion mobility of carbon is considered to be greater, i.e. the main reason for phase changes is the re-distribution of its atoms and at a final phase a polymorphic re-distribution of iron atoms takes place by the diagram



CEF treatment considerably differs from classical heat treatment in the following parameters [1-4]:

- it is not thermal in its pure form; it is accompanied by a number of phenomena taking place along with heat treatment – electron, photon, plasma, electromagnetic, acoustic and baric. On no account should it be considered that these components of energy treatment remain unchanged or can be ignored, theoretically at least;

- it is highly inhomogeneous in time, i.e. it is of pulse-dynamic or quasipulse character which by itself causes a wave effect of treatment. The latter, in turn, encompasses both heat treatment and the other types of energy treatment;

- CEF is highly inhomogeneous not only in time but in space. This causes a field effect in the distribution of energy parameters. Each point in the field, to be more precise – in the material – appears to be under the impact of energetics impacts of different magnitude and direction.

Taking into account all the above mentioned, the processes of phase changes, especially those at heating, should also be based on other mechanisms of atom migration, not only on purely diffusion ones [5-7]. The study of these changes and the mechanism of their accomplishment is the purpose of the paper.

2. Analysis

Kinetics and morphology of the changes in graphite and carbides

In the classical theory of heat treatment, when heating is accomplished at relatively low velocity (about up to 10² K/s at speed methods of heating such as bath, flame and induction heating) a mechanism and kinetics of phase changes in iron-carbon alloys have been accepted and proven and it is typical of them that they

are accomplished in compliance with the theory of balanced transformations. In this case it is considered that the transformations are complete, i.e. they take place until the total disappearance of phases, which are unstable at the elevated temperatures irrespective of that some inhomogeneity of their chemical composition is allowed. The mechanism of changes is diffusional caused by the differences in the concentration and the elevated temperature, being the same in all parts of the macro- and microvolumes. In this case the quantitative proportion between different phases is taken on the basis of the existing balance lines in the Fe-C (Fe₃C) diagram. As a consequence of the gradual heating and the time sufficient for re-crystallization, it is considered that, for example, ferrite turns into austenite from an initial balance condition from energetics point of view without the presence of deformation defects such as duplicates, increased dislocation accumulation (low angle boundaries), slippage planes of crystallographic plates.

Graphite is considered to be an absolutely stable phase, i.e. no likely changes in its phase condition or quantitative proportion with other phases are considered.

Carbides are also relatively stable. They do not change like the stoichiometric proportion between chemical elements. Only dissolution in austenite is allowed. The iron carbide is only in the form of Fe₃C.

As was already mentioned, the kinetics of the physical and chemical processes in time and space at CEF treatment make it possible to analyze phase change morphology in its basic aspects: high and ultra high velocities of heating, existence of mechanisms of atom migration different from the classical diffusion mechanisms, high heterogeneity of the conditions of transformation of each point of macro- and microvolumes in time and space.

The moment the cycle of heating terminates, high-velocity cooling commences. In this case the term “homogenization” is provoked by the temperature of overheating and the turbulent mixing of the liquid phase of melting. At this point, processes unfamiliar to the theory of phase transformations of iron-carbon alloys into solids may be observed: partial or complete dissolution of the graphite phase in the molten metal; washing away of the graphite in the molten metal and change in the locations of graphite inclusions; partial or complete evaporation of graphite; intensive migration of the carbon from the graphite inclusions in solid state; partial or complete dissolution of carbides in the solid phase and the molten metal.

As a consequence of these processes, at a follow-up crystallization both considerable change in the number and quantitative proportion between phases and increased homogenization in the macro- and microvolumes may be observed. In addition, the higher the velocity or the heating temperature, the higher the degree of the homogenization of the molten metal and the alloy after crystallization.

A tendency towards leveling the concentration in solid state is observed particularly with regard to the carbon content at the

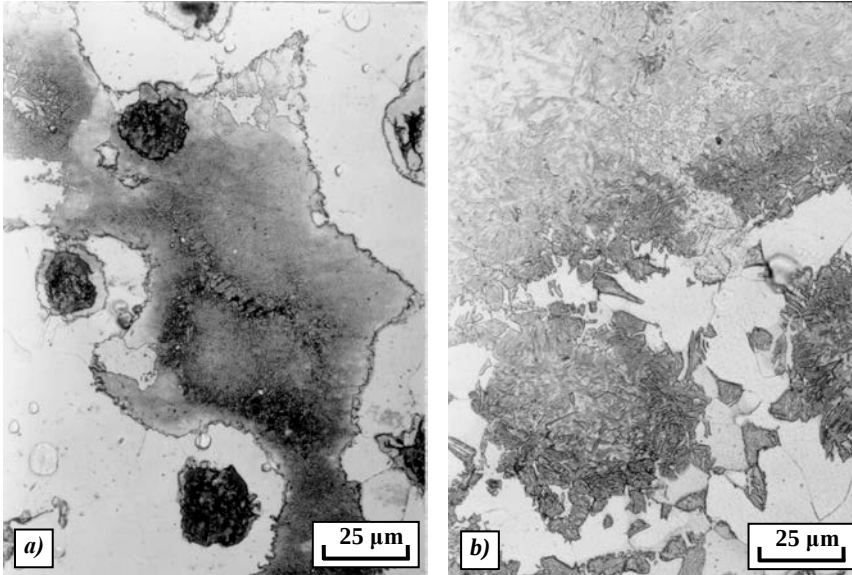


Fig.1 Particularly and fully dissolution of graphite in phase changing from solid state zone of GGG 50 after electron beam treatment by parameters: $N_s=3.6 \cdot 10^3$ w/cm², $v=1.2$ cm, $E_v=3.10^2$ J/cm³ – a) beginning and - b) end of zone.

“perlite-graphite” and “ferrite-graphite” boundaries at CEF heating. Of course, the migration of carbon towards ferrite is more obvious than towards perlite due to considerable concentration differences. Fig.1 shows the tendency of carbon to migrate from the graphite in the ferrite with the increase of temperature on the surface of treatment.

The migration path considerably increases around the graphite inclusions which are close to the surface and are undissolved in the molten metal (see fig.2). It is theoretically possible for the graphite inclusions, i.e. the carbon in the solid phase, to be completely dissolved. Undoubtedly, this process is also connected with the migration of iron atoms from the austenite in direction opposite to the movement of carbon atoms.

Partial and complete “assimilation” of carbides after CEF treatment in the zones of phase changes in solid and liquid state is typical of chrome and tungsten tool steels. As a result of the solid phase overheating and the follow-up melting, chrome, tungsten and combined carbides dissolve in the austenite or in the molten



Fig.2 Incompleteness due to partial evaporation of graphite inclusion at the bottom of the molten bath in GG 15 upon laser treatment with the following parameters: $N_s=1.9 \cdot 10^4$ w/cm², $E_v=1.58 \cdot 10^4$ J/cm³.

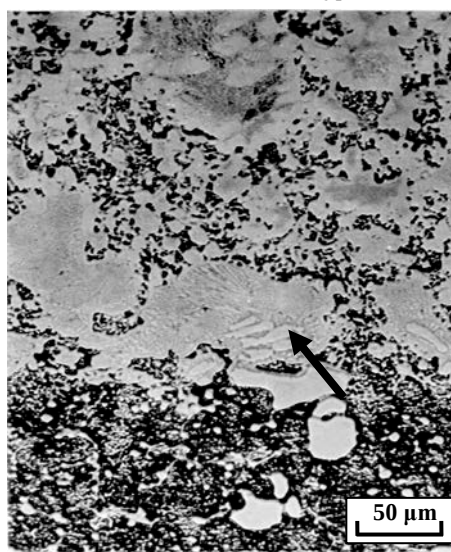


Fig.3 Partial and complete dissolution of carbides in X210Cr12 upon laser treatment with the following parameters: $N_s=2.6 \cdot 10^4$ w/cm², $V=1.6$ cm/s, $E_v=1.62 \cdot 10^4$ J/cm³.

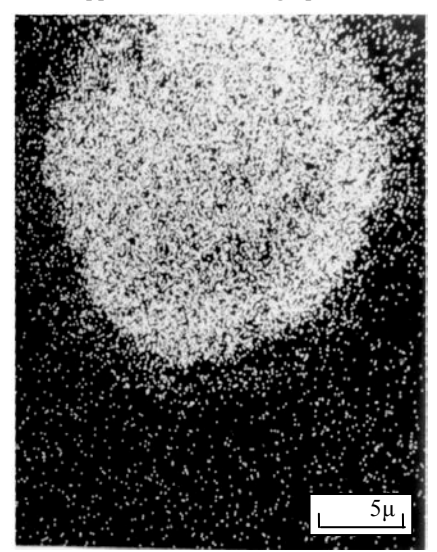


Fig.4 Carbon migration from graphite and “halo” formation with increased carbon content B4500-2 upon electron beam treatment with $E_s=2 \cdot 10^3$ J/cm².

metal which in itself is a typical process of homogenization (see fig.3)

A common feature of the migration of carbon from graphite and carbides is the direction of the prevailing migration flow opposite to the heat flow. This fact verifies our hypothesis about the field effect and the existence of thermokinetic migration. The considerable velocity of carbon movement from the graphite inclusions justifies the thesis about baric migration. In practice, the unlimited possibilities for migration in the molten metal facilitated by its mixing lead to the complete dissolution of carbides and carbon despite the limited time of treatment.

The migration flow at the graphite-ferrite, graphite-austenite and graphite-perlite boundaries is characterized by the formation of a “halo” around the graphite inclusion and by carbon content exceeding considerably or to a lower degree the content of the adjacent phases (see fig.4). This migration flow is intensified under the influence of the baric factor: the increased pressure in graphite, its lower thermal capacity and increased temperature in comparison with the adjacent phases and structural components. The pressure which graphite exerts on its surface leads to deformation in the zones subject to tensile stresses, i.e. in the adjacent phases and reactive congestion in the mass of the graphite inclusion. These stresses of second order are especially high at the graphite-metal base boundary. Depending on the intensity of treatment they may reach colossal values and may lead to changes in both the metal base and the graphite. Theoretically, a phase transition of the carbon from the graphite polymorphic modification into the metastable phase of diamond is possible. Such theoretical possibility is absolutely grounded in the cases of shock hardening (with power density of 10^{10} W/cm²).

In the situations we studied, the quantity of carbon in the adjacent phases increases and can reach the concentration of the stoichiometric proportion of cementite 6.67% carbon at boundary surface. In this case a carbide encasing is observed around the graphite. It is possible that carbide is obtained under the specific heating conditions, with the temperature not having reached the critical melting temperature. We call this cementite synthesized. What is typical of it is that it appears around the graphite in the

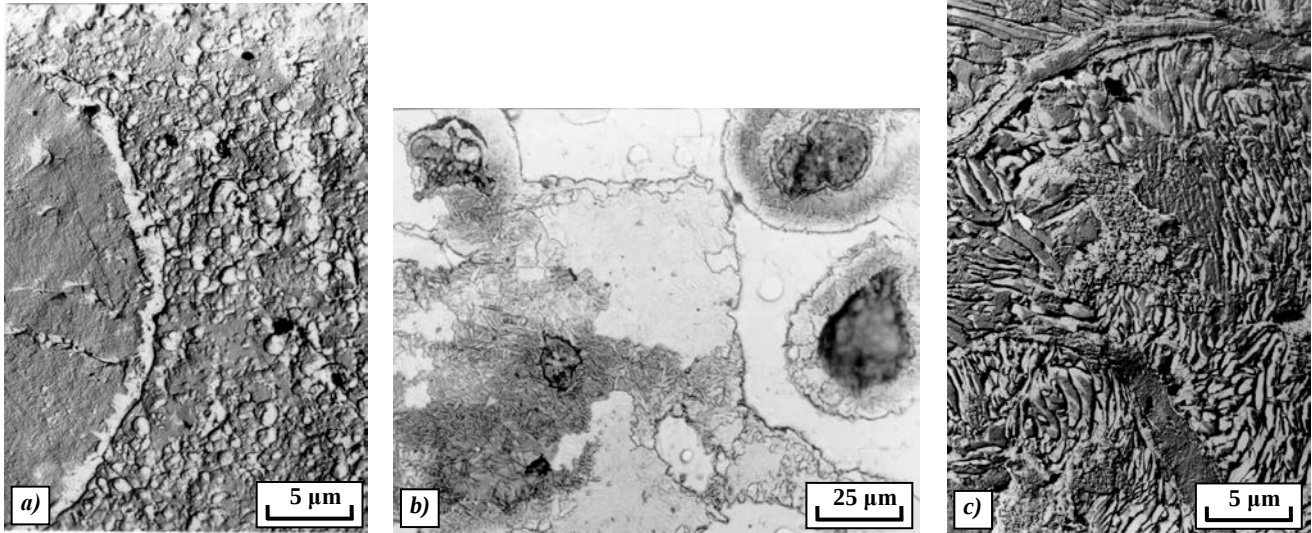


Fig.5 Synthesized carbide at grain boundaries to the graphite in iron by spheroidal – a), b) and wrought graphite – c) after arc-plasma ($N_s=9.2 \cdot 10^3 \text{ w/cm}^2$ - a) and b)) and electron beam ($N_s=7.2 \cdot 10^3 \text{ w/cm}^2$ - c)) treatment.

phase change zones in solid state, fig.5. The observation of the synthesized cementite in the zones around the graphite inclusions verifies the possibility of obtaining metastable conditions also in the process of heating. Due to the imbalance and dynamic character of the synthesis, it is likely for the carbide obtained to be provisionally called cementite as its stoichiometric formula may be different from M_3C . For example, it may be of carbide M_2C type, without excluding $M_{23}C_6$, M_7C_3 , M_6C or MC . In the situation of real alloys, carbides may also be of a mixed type between iron and other alloying elements. Obtaining metastable carbides under the conditions of very high velocities of heating is equally possible as the synthesis of Fe_3C carbide is.

It should be emphasized that the obtaining of synthesized carbide is connected with relatively minimum time of treatment (approximately 10^{-1} sec.). This means that the energy of treatment is also insignificant, i.e. heating and cooling are accomplished at high velocities, the resulting melting on the surface being at a very small depth. In this case the isolation of the graphite inclusions by means of the synthesized carbide may be favorable for enhancing the mechanical and corrosion-resistant properties of the cast iron in the surface layer.

The mechanism, kinetics and morphology of the changes in ferrite

Unlike the theory of classical phase transformations of ferrite-austenite, in our case we have grounds to consider that at the initial stage of transformation ferrite is in imbalance energy state. As a result of the dynamics of the thermal processes connected with

high velocities of heating and considerable temperature gradients within the microvolumes it is absolutely possible to observe microplastic deformations of the ferrite by the well-known patterns of movement of dislocations, slippage of crystallographic plates and duplication. Low angle boundaries are likely to form, without the real chance of reversion and re-crystallization due to the insignificant time of treatment. This microplastic deformation will be most clearly expressed at close order of phase location with a coefficient of expansion, heat capacity, density and heat conduction capacity different from those of the ferrite. Carbides and graphite are typical examples of such phases. With this regard, the perlite ferrite will tend to be most burdened with microdefects of microplastic deformation character. The perlite ferrite will have a relatively high level of Gibbs' free energy, and a high gradient of distribution in its volume respectively, and ultimately a great difference in the chemical potentials in the elementary microvolumes [8-10].

This means that the transformation of ferrite into austenite is absolutely likely to start not on the surface along the boundary of the grains where the concentration gradients are most significant and the concentration of submicrodefects as per classical theory – greatest. In other words, the classical theory of ferrite transformation into austenite envisaging the obtaining of crystallization nodes and their development under some time-energy circumstances tends to be inapplicable.

All considerations mentioned above provide for the opportunity to formulate the hypothesis of diffusionless

polymorphic transformation of ferrite into austenite under CEF treatment conditions. What is more, this austenite apart from having the hereditary properties of the deformed ferrite, it has an additional phase peening resulting from the ferrite-austenite transformation. When, at the follow-up cooling taking place in a millisecond period of time, the highly unstable austenite appears to be in the conditions of martensite transformation it undoubtedly will turn into low-carbon martensite.

When heating the ferrite at high velocities under the conditions of superheating, the metastable transformation is only possible

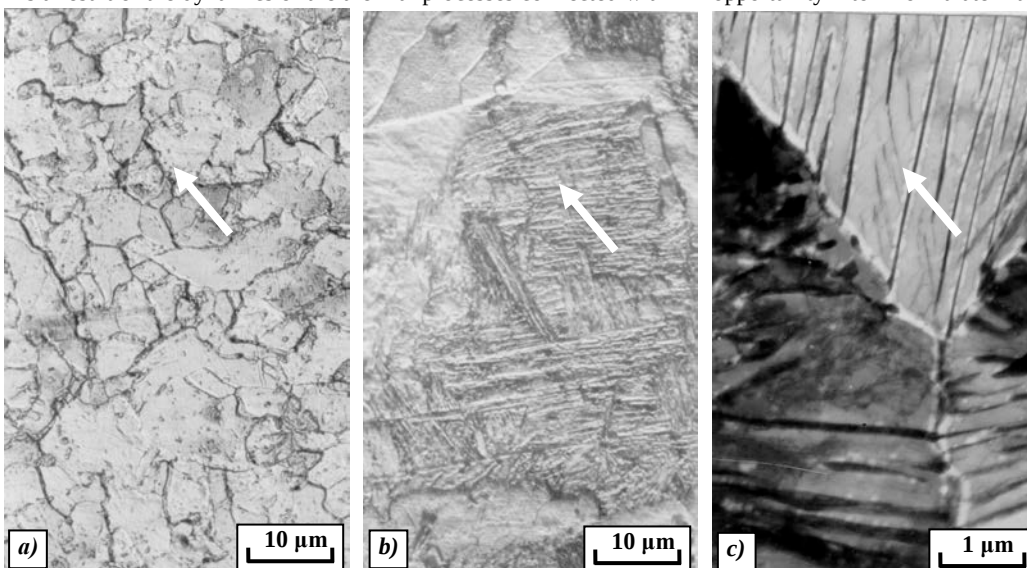


Fig. 6 Microstructure of Armco iron upon hardening: a) - Armco iron surface layer; b) - perlite of 37Cr4 steel; c) - upon laser treatment ($N_s=1.6 \cdot 10^4 \text{ w/cm}^2$).

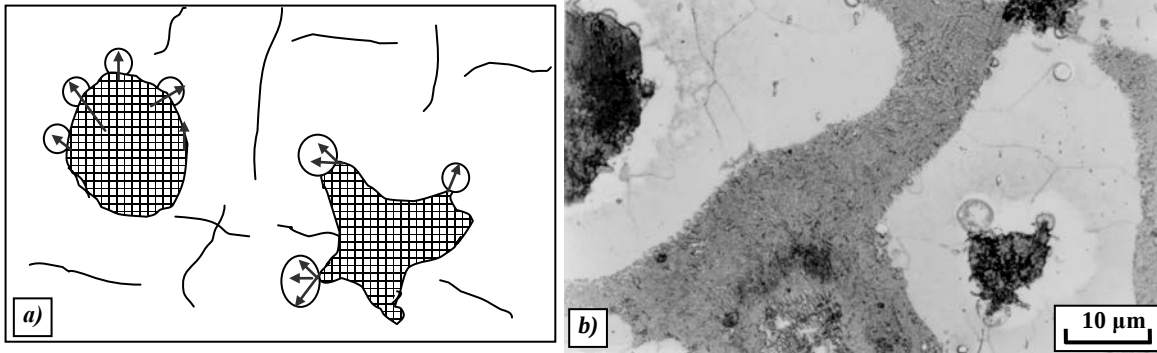


Fig.7 Diagram (a) and photography (b) of the initial stage of carbon migration in the ferrite of GGG 50 upon electron beam treatment with the following parameters: $N_s=3.6 \cdot 10^3 \text{ w/cm}^2$, $v=1.2 \text{ cm/s}$, $E_v=3 \cdot 10^3 \text{ J/cm}^3$.

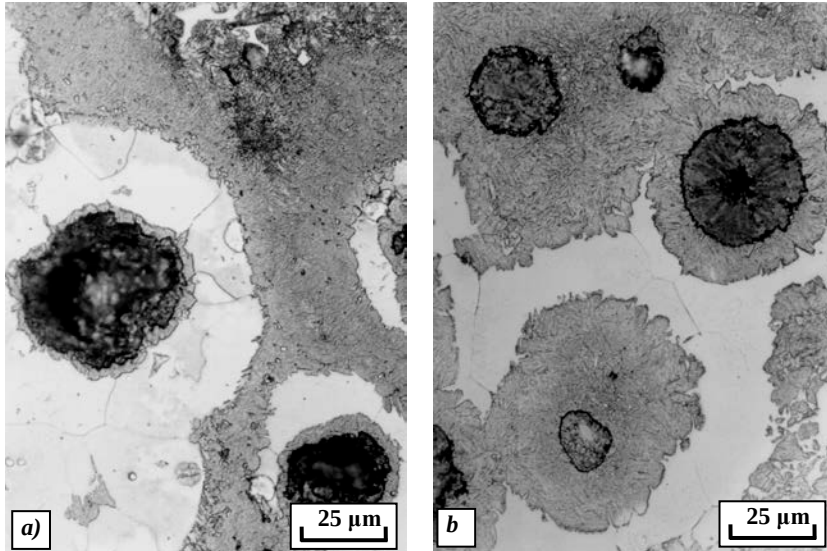


Fig.8 Interim stage (a) and final stage (b) of carbon migration in the ferrite of GGG 50 upon electron beam treatment with the following parameters: $N_s=3.6 \cdot 10^3 \text{ w/cm}^2$, $v=1.2 \text{ cm/s}$, $E_v=3 \cdot 10^3 \text{ J/cm}^3$.

thermodynamically. The austenite differing in composition from the balanced one is unstable and its existence may be explained from thermokinetic point of view. Of course, in imbalance heating conditions, there are circumstances determined by concentration fluctuations which define the existence of stable austenite as well. If fluctuation genesis of austenite with carbon concentration different from the balanced one is assumed, then this austenite will tend to obtain a stable condition very rapidly. Such a tendency may be eliminated by constant introduction of new quantities of energy in the system and by maintaining a great difference in the free energies of the final ferrite phase and the emerging austenite phase even in the conditions of rapidly growing migration activity of the atoms caused by the fast heating. At heating, at each moment of new austenite crystal emerging they may appear to be unstable due to the lack of carbon. With the further increase in temperature, more favorable conditions for carbon re-distribution are created which may not take place and part of the ferrite may not turn into austenite despite the high degree of overheating.

In this respect, the time factor is of vital importance and ferrite transformation into austenite is considered to be diffusionless with a mechanism of migration corresponding to slippage of crystallographic plates with a certain peculiarity such as incomplete transformation (see fig. 6a and b). The resulting austenite features a number of slippage planes situated in the most favorably oriented crystallographic plates partially inherited from the ferrite.

When the mode of cooling commences the austenite turns into ferrite by a similar diffusionless scheme. In this case we could call the newly formed metastable phase cubic martensite, i.e. a phase formed under the conditions of low-carbon imbalance austenite with close-packed martensite morphology. To be more

precise, this is a kind of mosaic modified ferrite with block orientation of the mosaic formations (fig.6b). Unlike cubic martensite obtained at voluminous heating (fig.6a), the dimensions of the ferrite grains and of the mosaic blocks are with less dispersity and with less clearly outlined grain boundaries.

The possible increase of carbon content in austenite, martensite respectively, may be facilitated by the avalanche (wave) migration caused by the thermal shock of CEF treatment in the interval from the beginning of ferrite-austenite transformation to the beginning of martensite transformation.

The hypothesis of diffusionless moment of the transformation of ferrite into austenite was absolutely verified by our experiments (fig.6). The ferrite in the space among the cementite plates turns into austenite and after that into close-packed low-carbon martensite. The untransformed ferrite in the form of separate continuous or broken areas of thickness less than 0.2

boundaries with the cementite. The martensite inherits the defective structure with the clearly visible slippage planes from the microplastic deformation (fig.6c).

A feature typical of this transformation is the characteristic heredity of the structures with certain subdefects, phase peening and preservation of the cementite armature, i.e. the ferrite phase takes part in the reinforcement effect, the cementite retaining its specific morphology and properties. At the same time, the close-packed low-carbon martensite features the defectiveness inherited from the ferrite, the phase peening obtained and finally, the high-strength properties preserving relatively plastic ferrite transition zone at the boundary with the cementite.

The issues considered above allowed for an objective explanation of the enhanced strength properties and heat resistance of the structures obtained in low-carbon steels after CEF treatment in comparison with those after traditional hardening.

Of course, the ferrite phase transformation mechanism described does not exclude the possibility for changes in the variations well-known by the classical theory of heat treatment, as well as in the combined mechanism which includes the diffusionless period as an initial or attending phase of ferrite transformation. There are actual thermodynamic and concentration conditions for these.

The mechanism of the transformation of ferrite into austenite in the grains at a distance from the phase boundaries with cementite and graphite is similar to the classical one with some conventions. They concern mainly the migration paths of carbon atoms movement from adjacent phases abundant in such atoms or structure compounds (graphite, cementite and perlite).

The mechanism, kinetics and morphology in the area of ferrite-graphite phase boundary

The migration of carbon atoms from the compact graphite inclusions to ferrite forms the character of the phase changes at CEF treatment. The picture of interaction can be divided into three stages: initial, interim and final. The initial stage coincides practically with the temperature at the beginning and with the transformation of perlite into austenite. It is mainly characterized by

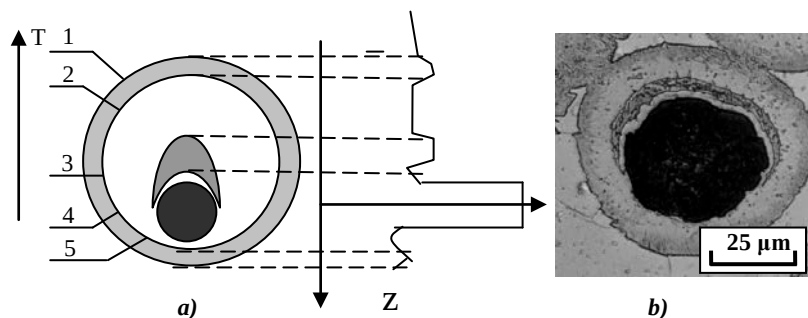


Fig. 9 Field and wave character of the migration flow of the carbon in ferrite: (a) diagram, (b) photograph of GG 30 structure upon electron beam treatment with $E_s=1.6 \cdot 10^3$ w/cm² with structure upon cooling: 1 – high carbon martensite; 2 and 4 – low carbon martensite; 3 – quazi-ledeburite; 5 – graphite.

the appearance of migration nodes at the graphite-ferrite boundary. These nodes are located at the side of higher temperature, i.e. closer to the surface of treatment (fig.7) or around the peaks at the non-spherical form of graphite.

As a result of the carbon migration in the ferrite the temperature of ferrite-austenite transformation and austenization in the zone around the graphite inclusions is lowered. In the follow-up cooling the austenite turns into martensite which forms a dense hard shell around the graphite. Due to the increase in the temperature of the graphite and the pressure exerted on it and as a result of the increase in the volume at the austenite-martensite transformation, the graphite becomes denser and the volume of its node decreases until it disappears (see fig.7).

The volume occupied by the martensite expands continuously. As a result of the increased carbon content it changes from close-packed into fine-grained (fig.8).

When increasing the treatment power density accompanied by an increase in velocity, i.e. by a decrease in energy density, a considerable concentration of the isotherms around the CEF axis is observed (see fig.9). This inevitably causes an increase in the temperature gradient, a formation and a clear expression of the wave and field character of the migration processes.

The wave and field character of the migration flows of carbon and other components cause the formation of a specific structure with variable contents and properties in line with the field and the wave formed. They are clearly expressed in laser, arc-plasma and electron beam sources having highly heterogeneous temperature fields obtained in the cases of pulse or pulse-intermittent treatment, as well as at the high power density of CEF [11-14].

3. Conclusions

Taking into account the issues discussed above, one should bear in mind that phase change processes at heating should be based not only on pure diffusion mechanisms of atom migration but also on a variety of other mechanisms which are as follows:

- the mechanisms of migration by plastic deformation. This mechanism depends on both the baric treatment of an energy pulse and on the temperature fields highly inhomogeneous in terms of time and space. At certain parameters of the treatment it may turn out that there are considerable differences in the temperature of phase boundaries or in a particular phase. This inevitably causes atom migration by the mechanism of slippage or an avalanche movement of dislocations and results in a phase transformation, e.g. "ferrite-austenite" without a preliminary diffusion process of re-distribution of carbon to have taken place. In any case, this process will be accompanied by phase peening and by an increase in the degree of the energetics imbalance of the new phase.

- the mechanism of migration of wave character of component distribution in macro and micro aspect. In this respect, the tendency towards balancing the concentration in the pure diffusion process may be deformed to a great extent. This means that at certain parameters of treatment there may not be a tendency towards balancing the concentration; just the other way round, there may be a reverse effect, i.e. there may be areas with highly

increased or decreased content of a particular component, e.g. carbon or another alloying element.

- the mechanism of baric migration, i.e. atom movement from microvolumes with a higher pressure to ones with a lower pressure and density. This mechanism would be particularly appropriate for surface layers where CEF treatment causes pulse pressure increase. It could also be accomplished in separate microvolumes, for example at the phase boundary graphite-metal base. Graphite dramatically increases its volume at elevated temperature. Moreover, it heats to a higher temperature due to its greater heat conduction and lower heat absorption differing in order from those, say of ferrite or austenite. With regard to this, the elevated temperature in the area of graphite inclusions may lead to the emission of graphite vapors at a certain moment of time which in turn would lead to an upsurge in pressure.

- the mechanism of thermokinetic migration or in other words, atom migration from volumes with lower temperature towards volumes with higher temperature. This mechanism is similar to that of a heat pump, well-known from the theory of fluid movement. At CEF treatment the epicenter of the heat field, i.e. the area with the highest temperature, is in the point of intersection of the source axis and the material surface in the spot of treatment. It is expected that with this mechanism, the more mobile carbon atoms would flow towards this center and a concentric field similar to the thermal one would be formed.

- the mechanism of accelerated migration under the influence of electrodynamic fields and radiation – electron, ion or neutron and photon. This mechanism has prevailing significance in the so called zones of energy transformation straight under the treatment surface. Hence, imbalance phases and compounds could be expected to form in this case.

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EFFECT OF THERMOMECHANICAL TREATMENT WITH MULTIPLE PLASTIC DEFORMATION ON THE NANOPHASE HARDENING OF DIE STEEL WITH REGULATED AUSTENITIC TRANSFORMATION

ВЛИЯНИЕ ТЕРМОМЕХАНИЧЕСКОЙ ОБРАБОТКИ С МНОГОКРАТНОЙ ПЛАСТИЧЕСКОЙ ДЕФОРМАЦИЕЙ НА НАНОФАЗНОЕ УПРОЧНЕНИЕ ШТАМПОВОЙ СТАЛИ С РЕГУЛИРУЕМЫМ АУСТЕНИТНЫМ ПРЕВРАЩЕНИЕМ

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Abstract: A new class of die steels for hot deformation, namely, steels with regulated austenitic transformation realized during exploitation (RATE) have been developed in Russia. These steels are characterized by the technological advantages typical of traditional α -solid solution-based steels and, when working in the austenite state, assure the enhanced tool life. The structure, phase composition and hardening of RATE steel have been analyzed by an example of steel containing 0.41 % C, 1.04 % Si, 3.59 % Mn, 2.41 % Cr, 5.07 % Ni, 2.40 % Mo, 0.69 % V, 0.51 % Ti, 0.25 % Co subjected to thermomechanical treatment, which includes the austenization and multiple plastic deformation. The nanophase hardening occurs in RATE steels being in the austenitic state, during multiple plastic deformation at temperatures of 450-750 °C. The precipitation of nano-sized heat-resistant excess phases ensures the inhibition of recrystallization processes at operating temperatures, inhibits the grain growth, and increases the stability of the austenite.

KEY WORDS: HOT-WORK TOOL STEEL, DISPERSION HARDENING, NANOPHASE HARDENING, RECRYSTALLIZATION, AUSTENITE, $\alpha \rightarrow \gamma$ TRANSFORMATION

1. Introduction

The durability of die tools largely determines the profitability of hot-forming processes of precision workpieces. When work surfaces are heated to temperatures of to 600-650 °C, traditional die ferrite steels hardened with carbide or carbide and intermetallics assure the adequate stability [1]. However, at the higher temperatures, even the most heat-resistant of the steels undergo intense softening, which is the main reason for the rapid failure of tools. The application of heat-resistant austenitic alloys is also limited owing to their tendency to cracking, poor machinability and high costs of their components.

A new class of die steels for hot deformation, namely, steels with regulated austenitic transformation realized during exploitation (RATE) have been developed in Russia in 1970-1980. These steels are characterized by the technological advantages typical of traditional α -solid solution-based steels and, when working in the austenite state, assure the enhanced tool life.

RATE steels undergo the $\alpha \rightarrow \gamma$ transformation at operating temperatures and demonstrate the high stability of the supercooled austenite in the pearlite region. This allows one to eliminate the austenite decomposition during possible cooling of the tool to 500-350 °C and to use the low-temperature thermomechanical treatment for hardening the surface layers of the tool. The feature of the steels consists in the fact that they use the stresses and high temperatures to increase the strength of the tool (Ozerskiy-Krugljakow effect) [2]. This is a fundamentally new concept in choosing alloying systems and hardening treatment conditions for die steels for their operation at temperatures of 600-800 °C.

It is known that, when being in the austenitic state, steels of this class, tend to either deformation, or dispersion, or complex hardening under conditions of temperature and force loads applied to the tool directly during its operation [2, 3]. The use of multiple plastic deformation at 450 °C assures the significant improvement of strength properties of the steel at test temperatures up to 800 °C without a substantial decrease in its ductility [4]. In this case, the optimization of the thermomechanical treatment diagrams of RATE steels, which assures the additional nanophase

strengthening of work-hardened austenite is of interest because the nature of the hardening of the steels has not been studied exhaustively. This fact may also be of particular interest in the study of the nature of hot work hardening.

There are only few foreign publications related to tool steels with the close chemical composition in the literature, which are focused mainly on the features of the microstructure of these steels [5].

In present study, we analyze the structure, phase composition and hardening of RATE steel (by an example of steel containing 0.41 % C, 1.04 % Si, 3.59 % Mn, 2.41 % Cr, 5.07 % Ni, 2.40 % Mo, 0.69 % V, 0.51 % Ti, 0.25 % Co) subjected to thermomechanical treatment comprising the austenization and multiple plastic deformation.

2. Experimental procedure

We studied RATE steel (containing 0.41 % C, 1.04 % Si, 3.59 % Mn, 2.41 % Cr, 5.07 % Ni, 2.40 % Mo, 0.69 % V, 0.51 % Ti, 0.25 % Co, less than 0.03 % S, less than 0.03 % P).

Steel was subjected to oil hardening from a temperature of 1020 °C followed by double tempering at 610-620 °C and 560-580 °C for 2 h (the hardness is 42 HRC) that is typical heat treatment of the steel. This treatment simulates the process of operation and prevents the tool from the pre-out of the tolerance before the $\alpha \rightarrow \gamma$ transformation.

Cylindrical specimens of the steel 10.00 ± 0.03 mm in height and 7.00 ± 0.03 mm in diameter were cut from an initial billet 13.32 ± 0.02 mm in diameter were used to carry out the thermomechanical treatment (TMT). The axis of the cylindrical specimen was coincides with the axis of the initial billret. TMT was performed using an installation Gleeble System 3800. After testing, transverse specimens for subsequent investigations were cut from both the edge and middle parts of the cylindrical specimen (Figure 1).



Fig. 1. Scheme of cutting samples for investigation

Figure 2 shows the TMT diagram of TMT. The TMT includes the austenization at 1150 °C, cooling to a temperature of 450 °C, holding for 15 min and subsequent compressive deformation (5 cycles with 2 % deformation in each cycle; the rate of deformation is 0.1 c⁻¹). Further heating was performed at a temperature of 750 °C, which corresponds to the operating temperature of die; the subsequent compressive deformation was realized in accordance with the same mode. After the TMT, the specimens were cooled

for 5 min. The structure of the steel in the initial and treated states was studied by optical and transmission electron microscopy.

Metallographic analysis of the structure of samples was performed at magnifications x100 and x500 using the Buehler optical microscope and sections etched in a 5 % nitric acid solution.

Electron microscopic studies of the structure were performed using thin foils, a JEM-2100 (JEOL) transmission electron microscope and an accelerating voltage of 200 kV. The foils were prepared from plates cut from the specimens, which were thinned to a thickness of ~100 μm by mechanical grinding. After that, the foils were thinned by jet electrolytic polishing at room temperature and a voltage of 20 V using an electrolyte containing 100 ml HClO₄ and 900 ml CH₃COOH.

The phase composition of the specimens was determined using a DRON 3M diffractometer and monochromatized CoKα radiation.

The Vickers microhardness measurements was measured at a load of 1 N (the holding time is 10 s) using a Micromet 5101 (Buehler) tester equipped with Mitron MTV-62W1P digital camera and «ImageExpert MicroHardness 2» software.

3. Results and discussion

Figure 3 shows micrographs the structure of the steel subjected to TMT, which were taken with an optical microscope. The average grain size in samples cut from the edge and the middle areas of the cylindrical specimen was 14 and 23 μm, respectively. The light areas are probably areas of residual austenite (Figure 3 d).

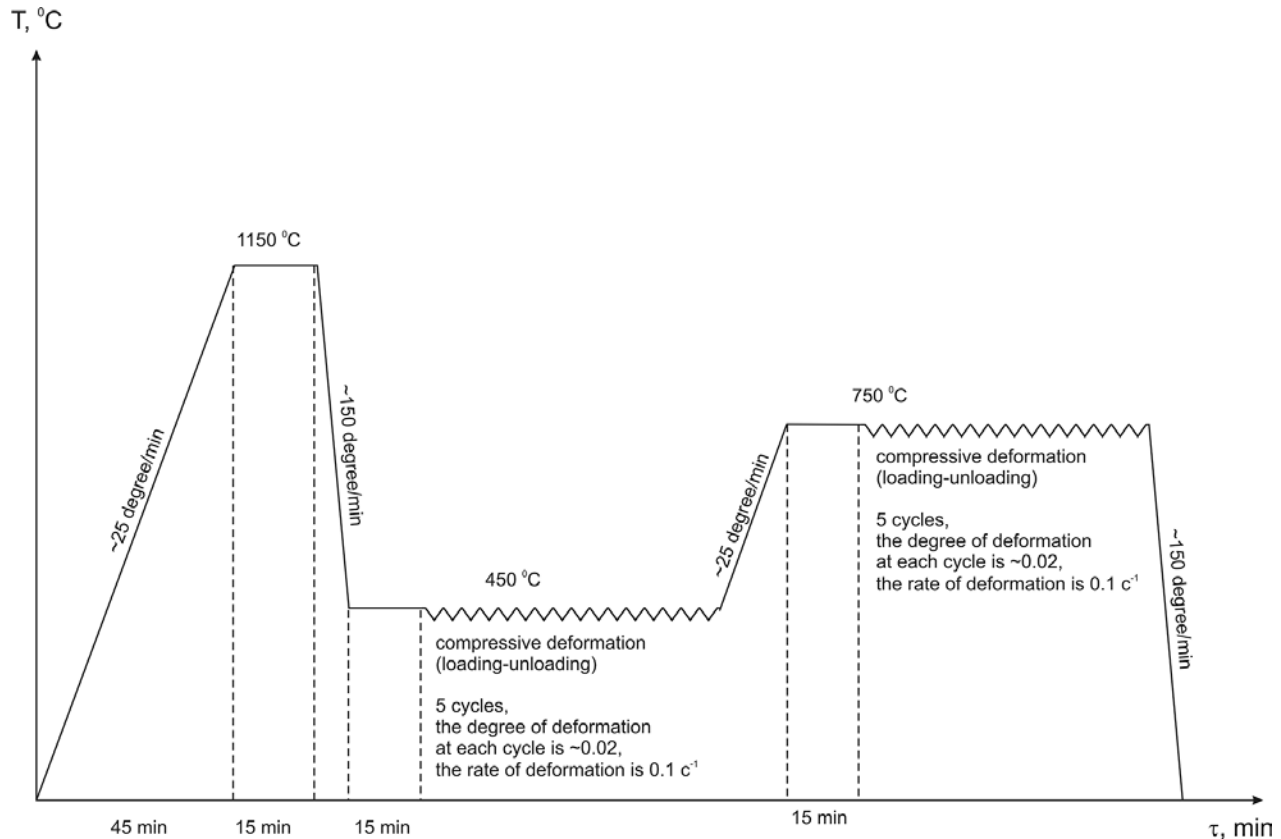


Fig. 2. Diagram of TMT of die steel

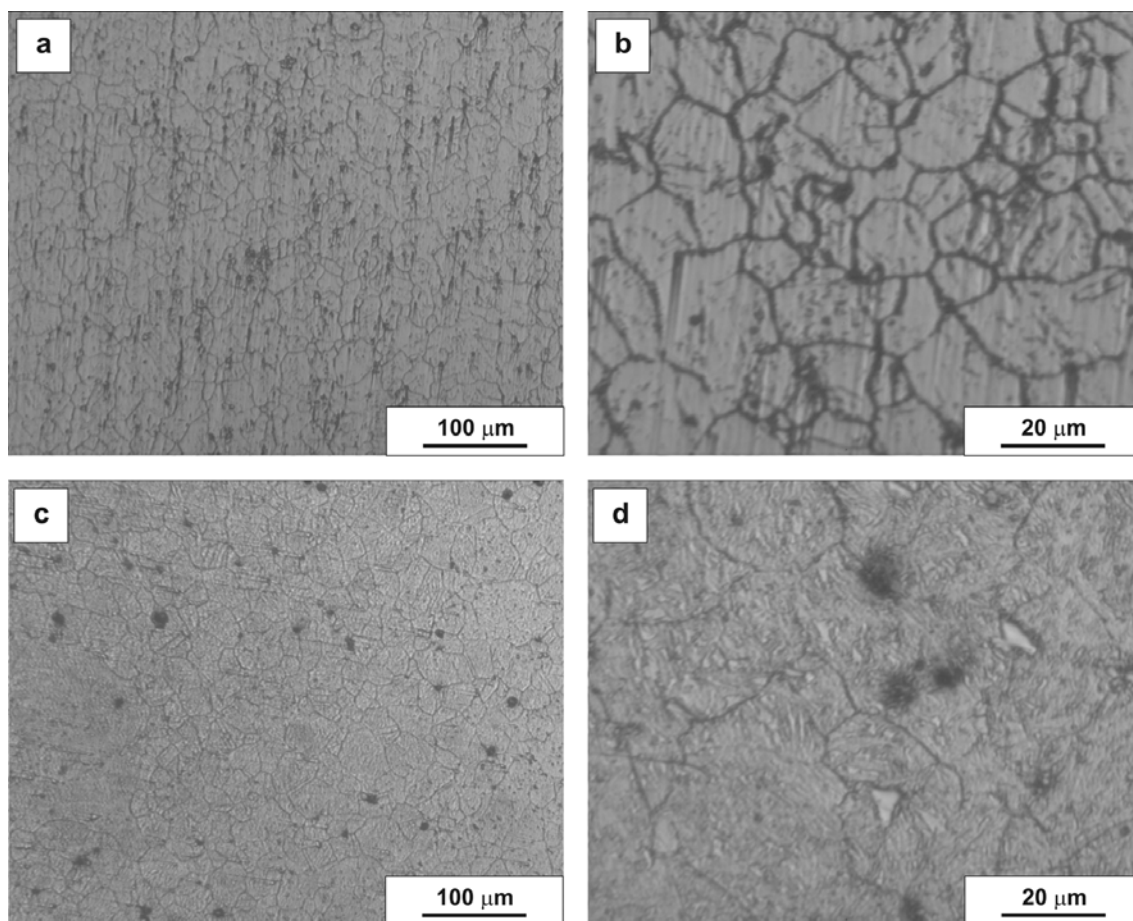


Fig. 3. The microstructure of the samples of the steel subjected to TMT (optical microscopy):
a, b – edge of the cylindrical specimen; c, d – middle of the cylindrical specimen.

According to transmission electron microscopy (TEM) and electron microprobe analysis (EMA) data, numerous nano-sized (50-200 nm long) Laves phase- (Fe_2Mo), σ -phase-like (FeCr) particles and particles of complex compounds are observed in the structure of the steel in the initial state (Figure 4). The structure also contains isolated large titanium carbide inclusions (more than 1 μm in diameter).

TEM images of the microstructure of the steel subjected to TMT are shown in Figures 5 and 6.

Previously, high-temperature method of X-ray phase analysis showed that 100 % of the austenite is present in the steel structure when heated to a temperature of 1100-1150 $^{\circ}\text{C}$ [3]. The structure formed in the steel during TMT is similar to the lath (needle) austenite. The structure also is characterized by the nano-sized precipitates 10 - 400 nm in size. The average size of the particles and their volume fraction are lower substantially than those for the initial state of the steel. It is likely that, among the found particles, particles, which were present in the initial steel and were not completely dissolved in solid solution during austenization, and particles precipitated during multiple plastic deformations in the course of TMT are observed.

The structure of the steel subjected to TMT (sample cut from the edge of the cylindrical specimen) is characterized by nano- and submicron-sized particles (50-400 nm in length) of complex compounds; particles of (Ti, V)C carbides are also observed (Figure 5). The structure also contains numerous small spherical particles 10-20 nm in diameter, whose chemical composition could not be determined.

The structure of the steel subjected to TMT (sample cut from the middle of the cylindrical specimen) is characterized by nano- and submicron-sized particles (50-300 nm in length) of complex compounds and particles of FeCr intermetallic compounds as well (Figure 6). The amount of particles of the secondary phases in the specimen is less than that in the specimen cut from the edge of the cylindrical specimen; this fact can explain the slightly higher grain size for the specimen cut from the middle of the cylindrical specimen.

Optimum temperatures of austenization of RATE steels usually are within a range of 950-1050 $^{\circ}\text{C}$ [3]. In present study, the austenization temperature was increased to 1150 $^{\circ}\text{C}$ in order to realize the complete dissolution of particles present in the initial structure of the steel; this is likely to ensure the precipitation of smaller particles during subsequent multiple plastic deformation in the course TMT.

According to X-ray phase analysis data, the structure of the steel in the initial state consists mainly of α -Fe and a small amount of γ -residual. The structure of the steel subjected to TMT also consists of α -Fe and γ -residual; however, the volume fraction of the austenite in the specimen cut from the edge of the cylindrical specimen reaches ~40 %.

The phase composition of particles present in the steel structure and observed by TEM, is not defined by X-ray diffraction analysis owing to their extremely small sizes.

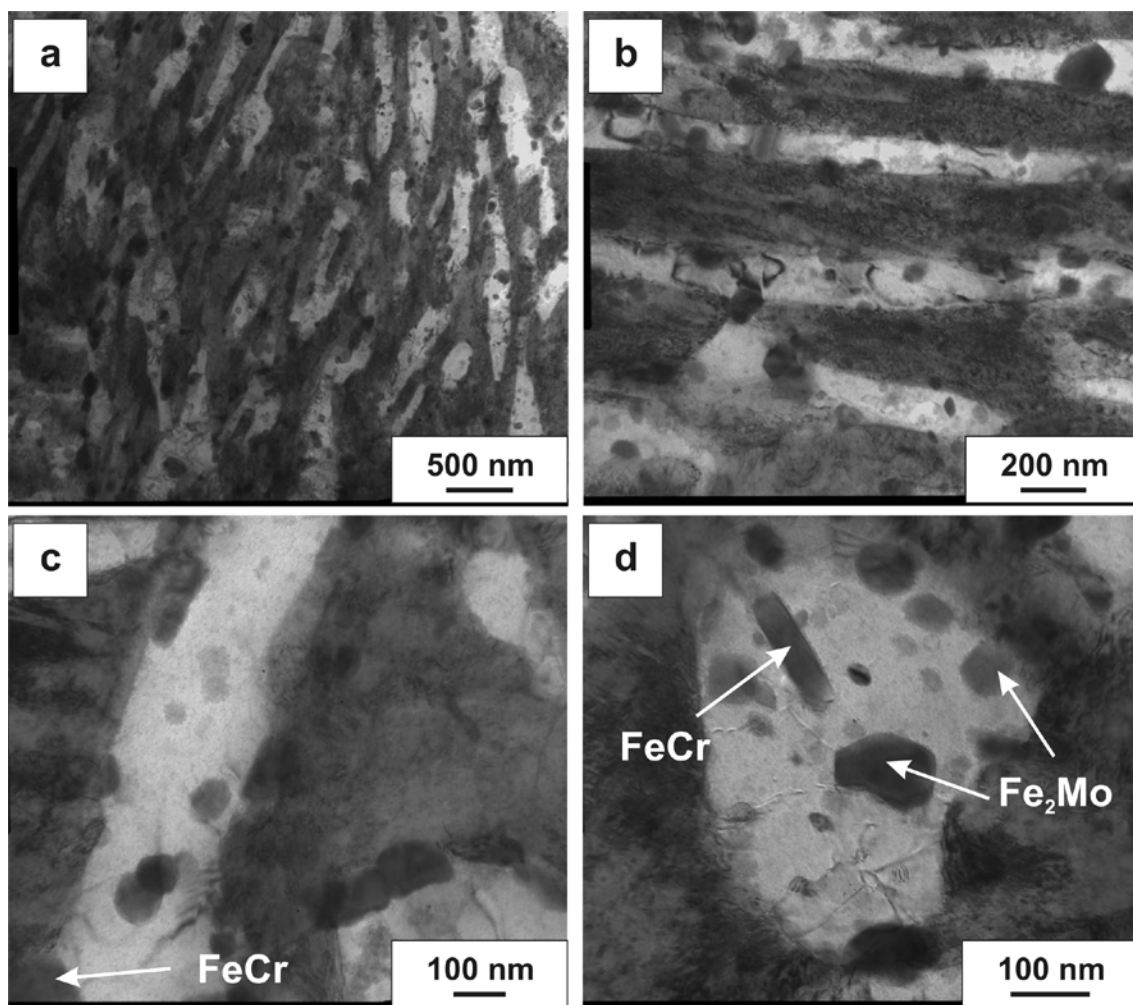


Fig. 4. The microstructure of the samples of the steel in the initial state

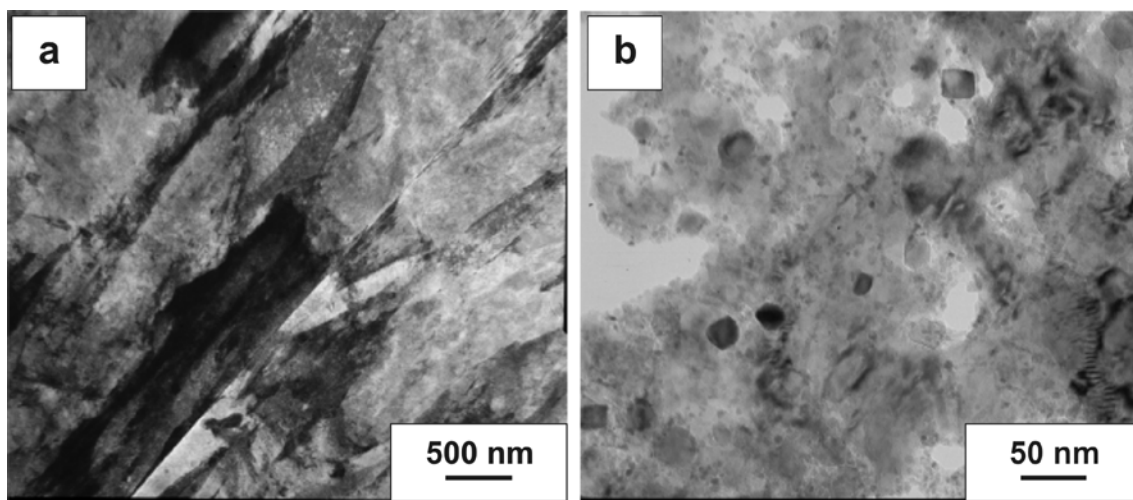


Fig. 5. The microstructure of the samples of the steel subjected to TMT (the edge the cylindrical specimen)

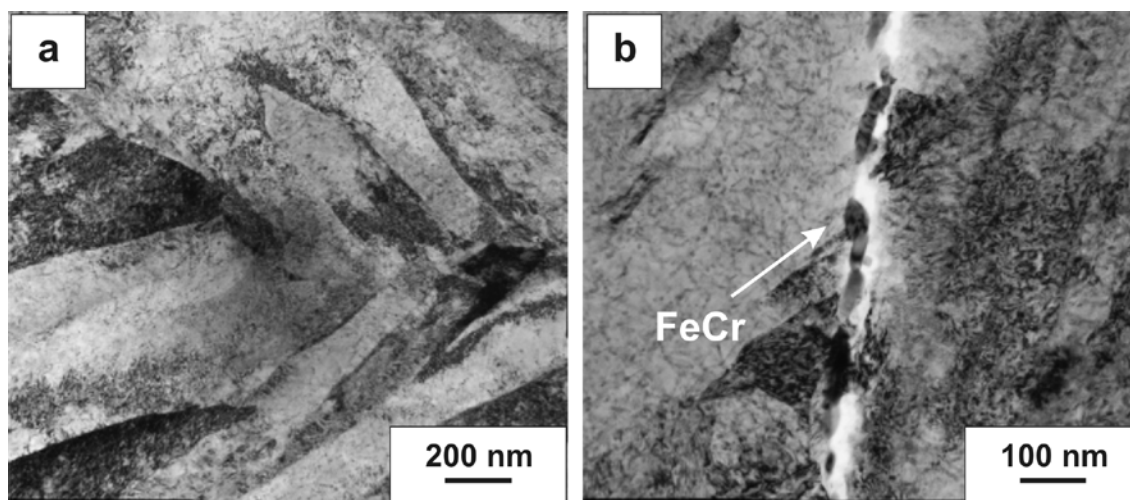


Fig. 6. The microstructure of the samples of the steel subjected to TMT (the middle of the cylindrical specimen)

Figure 7 shows the "loading-unloading" curves measured for the steel specimen in the course of TMT. It is seen that the multiple plastic deformation under cyclic loading ensures the significant hardening of austenite at a temperature of 450 °C. At a temperature of 750 °C, the tendency to deformation hardening appears much weaker, while the high level of the hardened state, ~ 540 MPa, takes place.

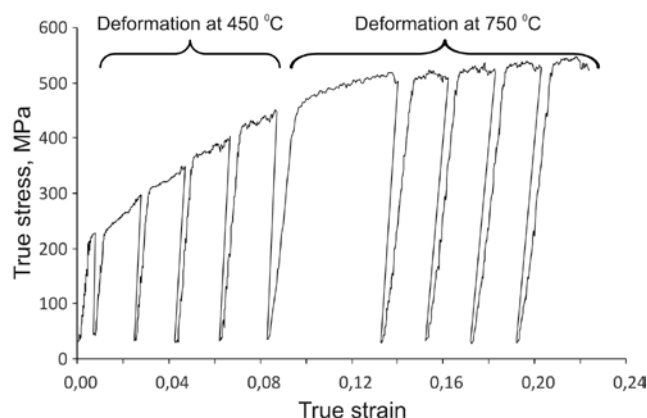


Fig. 7. The "loading-unloading" curves measured for the steel specimen during TMT

It should be noted that two competitive processes usually occur simultaneously in RATE steels during operation at 750 °C; these are the hardening (as a result of work hardening of austenite) and softening (due to the polygonization and recrystallization). However, the onset of recrystallization process of supersaturated solutions are not always accompanied by a significant loss of strength, when the growth of nuclei inhibited by the second phase particles, which cause the considerable phase work hardening [6]. In the present study nano- and submicron-size particles of complex compounds and particles of intermetallic compounds as well are responsible for the holding of the hardened state of the steel at a temperature of 750 °C.

Figure 8 demonstrates the microhardness distribution along the diameter of cylindrical specimen of the steel before and after TMT. After TMT, the maximum microhardness reaches ~640 HV (as compared to that for the initial state ~475 HV). For the specimen cut from the edge of the cylindrical specimen, the microhardness of the edge is higher than that in the center (640 and 540 HV, respectively). For specimen cut from the middle of

the cylindrical specimen, the microhardness of the edge is lower than that observed for the center (580 and 640 HV, respectively).

Higher microhardness indicates an additional strain hardening of a thin surface layer of the edge of the cylindrical specimen of the steel, which was in contact with the punch of Gleeble System 3800.

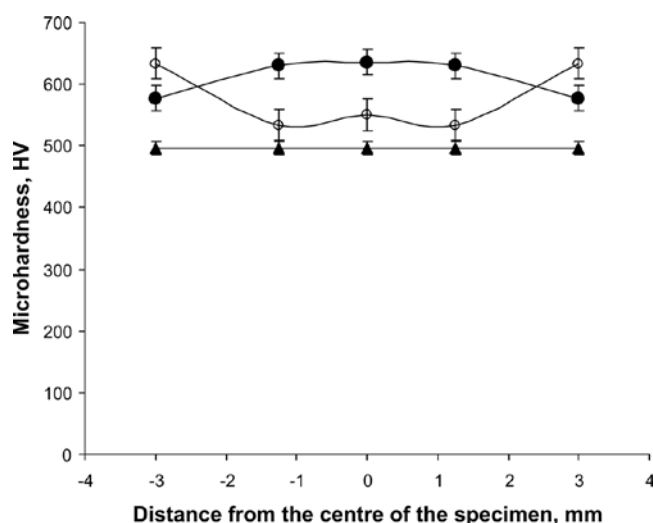


Fig. 8. Distribution of the microhardness along the diameter of the specimen of the steel before and after the TMT
 ▲ - specimen in the initial state, ○ - the edge the cylindrical specimen after TMT; ● - the middle of the cylindrical specimen after TMT

The similar hardening occurs within the thin surface layer of tool, which is directly sensing the cyclic thermal and mechanical loads under the contact with a deformable metal during the operation, and enhances its stability [7]. Herewith the life of the tool itself is known to depend substantially on the properties of the thin surface layer.

4. Conclusion

1. It is shown that, along with the deformation, dispersion and complex hardening processes, the nanophase hardening characterized by the high thermal stability of "hardening state" occurs in RATE steels being in the austenitic state, during multiple plastic deformation at temperatures of 450-750 °C.

2 The precipitation of nano-sized heat-resistant excess phases ensures the inhibition of recrystallization processes at operating temperatures, inhibits the grain growth, and increases the stability of the austenite, which is one of the main factors of the steel hardening during TMT.

3 The higher stability of the austenite creates a reserve for the accumulation of hardening during the operation, provides its stabilization and, thereby, improves the stability of die tools.

4 The additional hardening of the thin surface layer by nano-sized particles, which, when contacting with the deformable metal during operation, receives directly the cyclic thermal and mechanical stresses, also increases the tool life.

5 The use of steels with RATE and methods of hardening treatment in the austenitic state can improve the tool life when pressing hard-copper alloys such as Л63, БрАЖН10-4-4 (Russia); CuZn37, CuAl10Ni5Fe4 (EU); C27200, C63000 (USA) by 6-10 times compared to conventional die 3X2B8Φ (Russia); X30WCrV9-3 (EU); H21 (USA) steel.

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PULSED-DISCHARGE TECHNOLOGY OF METAL-MATRIX COMPOSITE MATERIALS OBTAINMENT

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Abstract: A brief analysis of studies in field of metal-matrix composite (MMC) materials production with use of pulsed-discharge technology (PDT) is performed in present paper. It is shown that high voltage electric discharge (HVED) in liquid allows obtaining homogeneous highly disperse blend of complex chemical composition. Consolidation of blend by method of spark-plasma sintering (SPS) ensures preservation of grain size, which allows achieving high strength characteristics of MMC.

Keywords: PULSED-DISCHARGE TECHNOLOGY, HIGH VOLTAGE ELECTRIC DISCHARGE, SPARK PLASMA SINTERING, POWDERS, COMPOSITE MATERIAL

1. Introduction

Dispersion-hardened metal-matrix composites are widely used in automotive, aviation and defense industry thanks to a combination of properties of metal (a significant ductility and fracture toughness) and ceramics (high strength and elastic modulus) in them. Widespread of MMC is largely due to the presence of ceramic inclusions in composite that significantly increase wear-resistance of material in tribological applications.

Increase of functional and physical-mechanical properties is possible both by changing composite composition and by changing the technological process of its production.

The idea of PDT of MMC materials obtainment is based on the possibility of effective use of newest methods of highly concentrated energy flows impact on disperse systems – high voltage electric discharge dispersion, activation and synthesis of polydisperse micro- (from 10^{-5} to 10^{-7} m) and nanosized (from 10^{-7} to 10^{-9} m) composite powders and the relatively low-temperature method of their compaction – spark-plasma sintering [1]. Multiple cyclic dynamic loads during HVED impact on materials particles contribute to the development of radial cracks caused by tangential stress from compression waves. Molecules of fluid adsorb on formed surface and do not allow to link up the edges of the crack, performing a wedging action. Therefore, the cyclical impact of HVED forms conditions conducive to fatigue failure of the material. Two destruction mechanisms are possible simultaneously: development of radial cracks caused by tangential stress from compression waves and destruction, caused by compression wave reflection from a free surface of a solid material and its conversion into a stretching wave. Moreover, volume microcavitation, destruction of particles during their collision with chamber walls and particles mutual abrasion during their mixing in all volume of chamber also take part in process of dispersion to varying degrees. In case of conductive metal powders treatment, discharge current that is passing through the particles is also an important factor of impact; it causes particles dispersion and change of their phase composition due to ablation process.

The use of hydrocarbon liquid as working medium during powder mixtures treatment allows synthesizing nanocarbon of different allotropic modifications as a result of hydrocarbon chains pyrolysis by discharge channel plasma. Active nanocarbon is capable of entering chemical reactions with metal powder particles with formation of hardening phases of carbides.

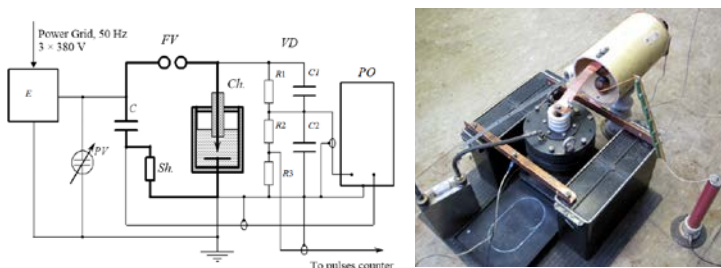
It is known that consolidation is final and primary stage of MMC production. During sintering of powder blend under prolonged impact of high temperature the processes, which lead to growth of materials grain, are initiated; this significantly decreases materials strength characteristics. Use of spark-plasma (electric discharge) sintering[2], which can be classified as PDT, allows preserving ultrafine high modulus inclusions and inhibits growth of matrix material grains.

The aim of present work – a brief analysis of studies in field of metal-matrix composites production with use of PDT.

2. Materials and methodology of research

Studies of HVED impact on physical-chemical properties of powders were performed on mixtures of 75 % Fe – 25 % Ti, 75 % Fe – 20 % Ti – 5 % B₄C mass composition.

HVED treatment of powders in fluid was performed on experimental stand, schematic diagram and photography of which is presented on fig. 1. Kerosene of TC-1 mark was used as a working medium during high voltage treatment of metallic powders and their mixtures.



E – energetic part, *PV* – kilovoltmeter, *C* – capacitor, *Sh* – coaxial shunt; *Ch* – working chamber; *PO* – oscillographer; *F* – air discharger; *VD* – voltage divider and its elements: *R*₁, *R*₂, *R*₃, *C*₁, *C*₂

Figure 1 – Schematic diagram of stand for HVED treatment

Optical microscope BIOLAM-I (БИОЛІАМ-І) with maximal magnification $\times 1350$, raster scanning electron microscope REMMA-102 (PEMMA-102) with magnification range from $\times 10$ up to $\times 250000$ and raster high definition electron microscope EVO-50 of Carl Zeiss manufacture were used for evaluation of size and form of particles. Samples of powder for optical and electron microscopy were prepared according to GOST 23402-78.

Studies of phase composition and crystal structure were performed by X-ray structural analysis with general-purpose diffractometer DRON-3 (“ДРОН-3”) (Cu_{K α} radiation).

Consolidation of powder materials in vacuum with passage of superposition of direct and alternating current (10 kHz) with 1,2 kA amplitude was performed on “GEFEST-10” (“ГЕФЕСТ – 10”) experimental SPS device (which was designed in IPPT of NAS of Ukraine [3]).

Consolidated specimens resistance to abrasive wear was determined by gravimetric method on SMC-2 (СМІІ-2) friction machine by “Roller – Block” scheme. As a friction pair were used: immobile cylindrical specimen ($d=10$ mm, $h=6$ mm) from studied material (Block), and mobile diamond circle 1A1 with AC4 80/63

graininess was used as a roller (counter-body). Determination of specimens mechanical properties was performed on P-5 experimental machine by PRS strength determining method, Rockwell hardness was studied on TP-5006 hardness tester, and microhardness was determined on PMT-3 (IIMT-3).

3. Theoretical evaluation of processes accompanying metal powders HVED treatment

Given that in free disperse systems dispersed particles can move freely throughout the volume of the dispersion medium, processes that occur in such systems can be described from a common position from the point of view of the general laws of sedimentation. The calculation of sedimentation rate was performed according to Stokes' law with Oseen amendment as the most valid for studied range of particle sizes [4, 5]. Modeling was performed for such processes of sedimentation: particles of Ti, Fe and diamond powders in water and of Ti, Fe and B₄C in kerosene, particles of compounds, synthesized during HVED treatment (graphite, Fe and Ti carbides), in kerosene.

Obtained results allowed evaluating possibility of particles of given size range being in given layer of working fluid at each moment after single discharge. Changing pulses passage frequency, while taking obtained regularities into account, during HVED treatment allows controlling efficiency of impact on powder particles in terms of their dispersity. For example, during HVED treatment of Fe and Ti powders mixture, times of their sedimentation from height of $h=1$ cm are ~2 times different. Thus, 2 times increase of discharge frequency during HVED treatment of this powder mixture from 0,5 to 1 Hz should lead to more efficient grinding of Ti particles [6].

Given that the main grinding work is performed by pressure waves [7], short cylinder model was chosen for evaluation of pressure wave amplitudes and pressure maximum in discharge channel P_k was defined:

$$P_k = P_a \cdot b_0(\eta_1), \quad (1)$$

where P_a – interim pressure coefficient, Pa, determined by evaluation (2); $b_0(\eta_1)$ – interim dimensionless function, determined by evaluation (3);

$$P_a = \left(\frac{\rho_0 U^2}{L \cdot l_p} \right)^{0.5}, \quad (2)$$

$$b_0(\eta_1) = \frac{\gamma - 1}{2\alpha_1 \gamma} \cdot \frac{\eta_1^{0.3} \cdot (1 - 0,85\eta_1) (1 + \eta_1^3)^{2\alpha_1}}{(0,37 + 0,6\eta_1^2)^{2\alpha_1 - 1,5}}, \quad (3)$$

where ρ_0 – medium density, kg/m³; U – discharge voltage, V; L – discharge circuit inductance, H; l_p – discharge gap, m; η – fraction of energy, released during first semiperiod of discharge current; γ – adiabatic coefficient of discharge plasma; α_1 – interim dimensionless coefficient, determined as:

$$\alpha_1 = 0,73 + 1,22\eta_1^{\frac{3}{2}} \cdot e^{-1,47\eta_1^3}, \quad (4)$$

Value of γ for kerosene was assumed to be equal 1,3.

Amplitude of pressure wave in discharge equatorial plane $P_m(r_e)$:

$$P_m(r_e) = P_a \cdot b_1(\eta) \cdot \begin{cases} \frac{r_e}{a_m}, & r_e \leq 2,5l \\ 1,3 \cdot \left(\frac{r_e}{a_m} \right)^{-0,5} \cdot \left(1 - 0,1 \cdot \frac{r_e}{l} \right), & r_e > 2,5l \end{cases} \quad (5)$$

where $b_1(\eta)$ – interim dimensionless function, determined by evaluation (6); r_e – distance from discharge channel center to considered equatorial plane point, m; a_m – scale coefficient, determined by equation (7).

$$b_1(\eta_1) = \eta_1^{0,3} \cdot \left(\frac{0,37 + 0,6\eta_1^2}{1 + \eta_1^3} \right)^{0,5\alpha_1} \cdot b_0(\eta_1), \quad (6)$$

$$a_m = \left(\frac{U^2 C_n^2 L}{\rho \cdot l} \right)^{\frac{1}{4}}. \quad (7)$$

Amplitude of pressure wave in any point of discharge chamber:

$$P_m(\varphi, r) = P_m(r) \cdot \left[\frac{3,2}{\pi} \left| \phi \right| \cdot \left(\frac{\left| \phi \right|}{\pi} - 1 \right) + 1 \right], \quad (8)$$

where r – distance from chamber axis to projection of considered point on equatorial plane, m; φ – angle between considered point's radius-vector and discharge equatorial plane, rad.

After conversion of equation (8) from cylindrical to Cartesian coordinates, spatial distribution of pressure wave amplitudes in plane, perpendicular to discharge equatorial plane, can be obtained:

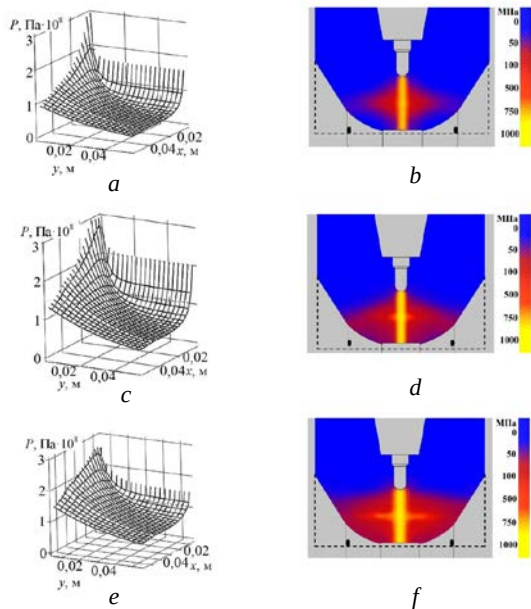
$$P_m(x, y) = P_m(x) \cdot \left[\frac{3,2}{\pi} \left| \arctg\left(\frac{y}{x}\right) \right| \cdot \left(\frac{\left| \arctg\left(\frac{y}{x}\right) \right|}{\pi} - 1 \right) + 1 \right], \quad (9)$$

where x, y – Cartesian coordinates of considered point in plane, perpendicular to discharge equatorial plane, in coordinate system relative to center of discharge channel, m.

Theoretical calculation of spatial distribution of compression wave peak pressures was performed for regimes with single discharge energies of 0,25, 0,5 and 1 kJ [5], with capacitors capacity of 0,2, 0,4 and 0,8 μ F respectively. Current rise rate (di/dt) was 13, 19 and 24 GA/s respectively. Voltage $U = 50$ kV and discharge circuit inductance $L \leq 0,7$ μ H were constant.

Obtained results (see Fig. 2) allowed designing construction of discharge chamber, which provides efficient treatment [8].

Thermodynamic calculation of Gibbs energy change during chemical reactions at HVED allowed to establish, that in chosen range of treatment parameters the initiation of carbide, boride and intermetallic phases formation is possible. It is shown, that HVED treatment provides conditions for solid phases synthesis both in near-channel area and between particles, because dielectric breakdown occurs between them, which leads to self-organization of conductive chains from particle to particle, until one of these chains reaches conductive bottom or wall of discharge chamber. Highly conductive chain is heated by discharge current, transforming into channel, and the powder particles, located in channel or near it, interact with one another in the field of significant temperatures and pressures.

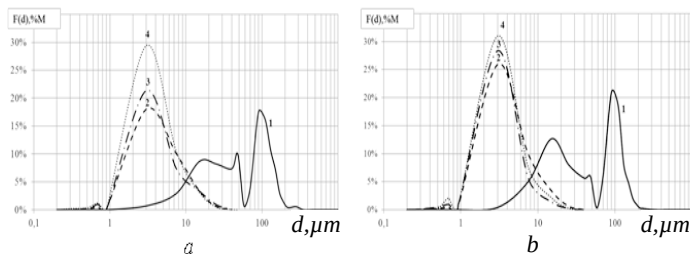


(a, b) – treatment with single discharge energy of 0,25 kJ ($di/dt=13$ GA/s); (c, d) – treatment with single discharge energy of 0,5 kJ ($di/dt=19$ GA/s); (e, f) – treatment with single discharge energy of 1 kJ ($di/dt=24$ GA/s)

Figure 2 –Theoretical spatial distribution of pressure wave peaks

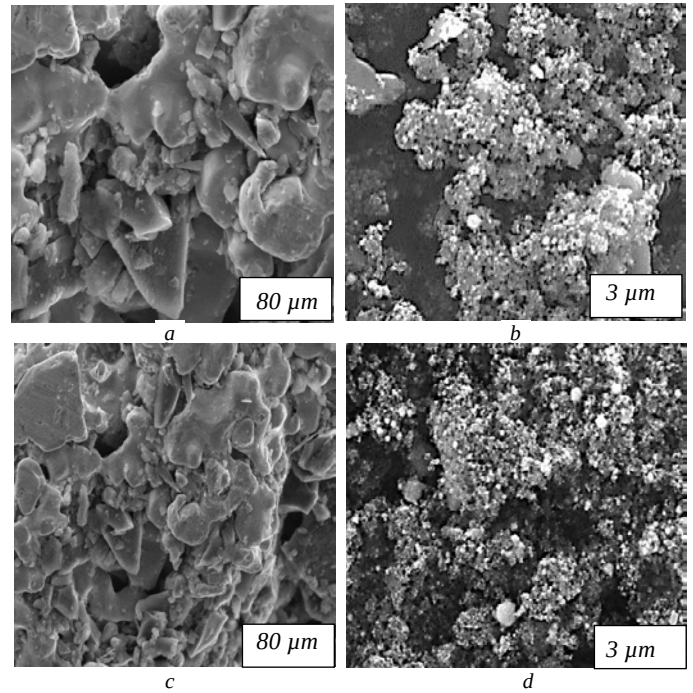
4.Experimental studies of dispersity and phase composition change during powder mixtures HVED treatment

Treatment of 75 % Fe – 25 % Ti and 75 % Fe – 20 % Ti – 5 % B_4C powder mixtures was performed with specific energy of $W_{s\tau}=\text{const}=25$ MJ/kg, which ensures synthesis of necessary amount of carbon for formation of stoichiometric Ti carbide [9]. Current rise rate varied from 13 up to 24 GA/s, which provided different intensity of pressure waves impact (see Fig. 2). Frequency of pulses passing was $f = 0,6$ Hz. Mean diameter of powder particles after treatment in all studied modes decreased from 80 to ~ 3 μm (see Fig. 3) and high modulus (ceramic) TiC (with homogeneity area up to $TiC_{0,92}$) and FeB (with size varying from 10 up to 600 nm) phases are synthesized (see Fig. 4). Worth noting that maximum amount of powder with ~ 3 μm diameter (~ 30 %) was obtained after treatment with maximal considered current rise rate of $di/dt=24$ GA/s (see Fig. 3, curve 4). Most of initial mixture particles had irregular fragmental shape (see Fig. 4, a, c), but after processing they have shape, close to spherical (see Fig. 4, b, d) – this shows, that they were synthesized due to impact of discharge channel current (ablation and electric erosion).



a –75 % Fe – 25 % Ti mixture, b –75% Fe –20 % Ti – 5 % B_4C mixture; 1 – initial mixture; 2 – after HVED treatment with $di/dt = 13$ GA/s; 3 – $di/dt = 19$ GA/s; 4 – $di/dt = 24$ GA/s.

Figure 3 – Distribution of particles percentage $F(d)$ by diameter values



a – initial 75 % Fe – 25 % Ti mixture, b – after HVED treatment with $W_{s\tau} = 25$ MJ/kg and $di/dt = 24$ GA/s; c – initial 75 % Fe – 20 % Ti – 5 % B_4C mixture, d – fter HVED treatment with $W_{s\tau} = 25$ MJ/kg и $di/dt = 24$ GA/s

Figure 4 – Mixtures microphotographs

5. Technological methods of MMC production with use of PDT

Consolidation of prepared blend was performed by SPS method. Heating rate was $\sim 10^\circ\text{C/s}$, holding time was ~ 120 s, sintering temperature was 1100°C , sintering pressure was 60 MPa.

Average hardness of specimens (see Table 1), produced from blend, obtained by HVED processing of 75 % Fe – 20 % Ti – 5 % B_4C and 75 % Fe – 25 % Ti powder mixtures, after sintering was 51 and 40 HRC respectively (see Fig. 5), porosity was not higher, than 4 % (see Table 1, ρ_{theor} – theoretical density, P – porosity).

Table 1 – Properties of MMC, consolidated on “GEFEST-10” (“ГЕФЕСТ-10”) device

№	MMC system composition	Parameters of powder mixtures HVED treatment		Materials properties	
		Specific energy	Current rise rate		
		$W_{s\tau}$, MJ/kg	di/dt , GA/s	ρ_{theor} , g/cm ³	P , %
1	Fe-Ti-B-C	25	19	6,96	4,0%
2	Fe-Ti-B-C	25	24	6,96	1,0%
3	Fe-Ti-C	25	16	7,08	1,8%
4	Fe-Ti-C	25	24	7,08	1,1%

X-ray structural analysis of Fe – Ti – B – C, Fe – Ti – C systems specimens, consolidated by SPS, have shown, that after sintering and thermal treatment, material consists such phases, as TiC and TiB (see Fig. 6).

Size of most hardening phases particles lies in range of 10 – 70 nm (see Fig. 7), most of these particles retain the shape, close to spherical.

Bending strength of obtained MMC is 1350 MPa, hardness is 68 HRC.

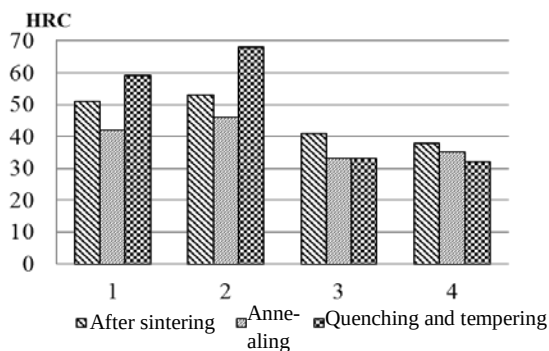
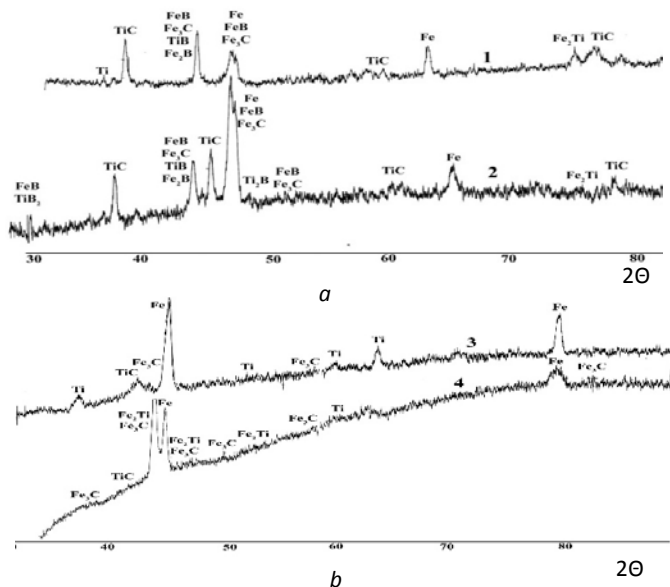
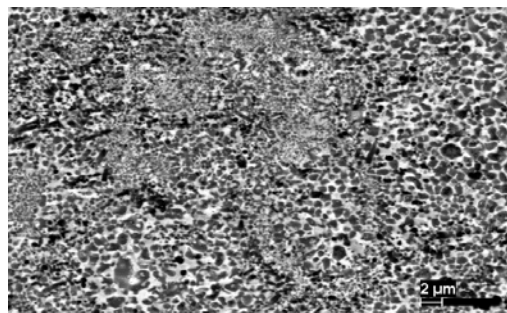


Figure 5 – Specimens Rockwell hardness (C scale)

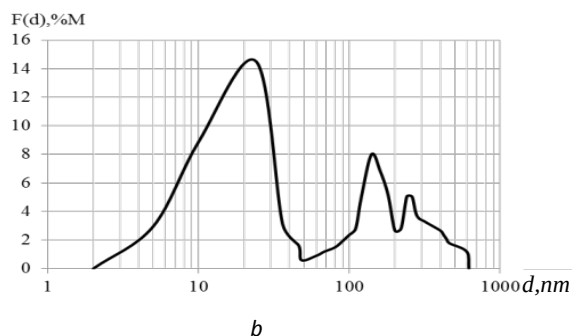


(a) – specimens №1,2, (b) – specimens №3,4

Figure 6 – XRD patterns of consolidated specimens after thermal treatment



a



b

Figure 7 – Structure (a), size distribution (b) of hardening phases in Fe – Ti – B – C system material

Conclusions

1. A holistic approach to technology of multifunctional dispersion-hardened by nanostructured particles MMC obtainment with use of complex of pulsed-discharge technologies (from stage of powders HVED treatment to obtainment of end-product with increased functional properties by SPS method) is developed.

2. Necessary conditions for powders dispersion and high modulus ultrafine phases synthesis during HVED treatment of Fe – Ti – C – (B) system powder mixture in kerosene are theoretically found. It is shown, that the most efficient modes of powders dispersion and carbide (boride) component synthesis are realized with specific energy of 25 MJ/kg and current rise rate of 24 GA/s.

3. Technological methods for obtainment of MMC with density, close to theoretical, hardness up to 68 HRC and ductile strength 1350 MPa, wear resistance that is 35 % higher than wear resistance of high-speed steel R6M5 (P6M5), are developed by SPS of powder mixtures after powders HVED treatment.

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NONEQUILIBRIUM PHASE TRANSFORMATIONS DURING SOLID SOLUTION DECOMPOSITION IN MAGNESIUM ALLOYS CONTAINING THE RARE-EARTH METALS OF DIFFERENT SUBGROUPS

НЕРАВНОВЕСНЫЕ ФАЗОВЫЕ ПРЕВРАЩЕНИЯ ПРИ РАСПАДЕ ТВЕРДОГО РАСТВОРА В МАГНИЕВЫХ СПЛАВАХ, СОДЕРЖАЩИХ РЕДКОЗЕМЕЛЬНЫЕ МЕТАЛЛЫ РАЗЛИЧНЫХ ПОДГРУПП

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Abstract: *The nonequilibrium phase transformation during decomposition of Mg supersaturated solid solutions, containing two rare-earth metals of the different subgroups (cerium and yttrium) are presented and generalized. These processes in the alloys of ternary systems differ from those in the alloys of the adjoining binary systems. They reveal also the similar features in kinetics and the nonequilibrium phase formed during solid solution decomposition*

KEYWORDS: MAGNESIUM ALLOYS, RARE-EARTH METALS, SOLID SOLUTION DECOMPOSITION, PHASE TRANSFORMATION.

1. Introduction

Investigations of magnesium alloys, connected with development of light structural materials with high strength at near room and elevated temperatures indicated, that the best results could be achieved, if the rare-earth metals will be used as alloying elements [1,2]. Action of the individual rare-earth metals on mechanical properties of magnesium is different and this phenomenon is caused by different solubility of every rare-earth metals in solid magnesium and different behavior of them during nonequilibrium transformation consisting of decomposition of the supersaturated magnesium solid solution. In the binary magnesium alloys with the rare-earth metals, belonging to the same subgroup, either yttrium or cerium one, kinetics of the magnesium solid solution decomposition and accompanying this process structural transformations have the close features. But they are different for the rare-earth metals of different subgroups [2]. In the alloys with elements of the cerium subgroup decomposition of the magnesium supersaturated solid solution is accompanied with successive formation zones GP, metastable phases β'' (ordering of the Mg_3Cd type), β' and equilibrium phase β [3]. In the alloys with elements of the yttrium subgroup decomposition of the magnesium supersaturated solid solution is accompanied with β'' phase (Mg_3Cd type ordering), orthorhombic plate-like phase β' and equilibrium phase β [4].

The aim of this publication is to review the results of the investigations of the supersaturated solid solution decomposition in the ternary magnesium alloys containing simultaneously two rare-earth metals belonging to different subgroups accompanied by the nonequilibrium phase transformations. These alloys attract a great attention now as the materials with better combination of advantages, which inherent to magnesium alloys containing the rare-earth metals of one of the subgroups.

2. Materials and methods

By this time decomposition of the supersaturated solid solution in the ternary alloys with two rare-earth metals of different subgroups was studied only in several systems. They are the systems Mg-Ce-Y, Mg-Nd-Y, Mg-Sm-Y, Mg-Sm-Tb, Mg-Sm-Er [5-10]. The supersaturated magnesium solid solutions in them were obtained in them after of annealing at enough high temperatures followed by quenching from them. Annealing temperatures were chosen basing on the known phase diagrams. Decomposition of the supersaturated solid

solutions proceeded during isothermal ageing of the quenched samples at different temperatures in the 200-250°C range. It was checked by the hardness and electrical resistivity measurements and observations of microstructure using optical and transmission electron microscopy (TEM). Preparation of the specimens for the microscopic observations, methods of determination of their properties and the used equipment are described in details in [5-10].

3. The similar features of the magnesium solid solution decomposition

Analysis of the results of the hardness and electrical resistivity measurements during ageing of the magnesium alloys above mentioned different systems revealed a number of the similar features in kinetics of the supersaturated solid solution decompositions. The typical curves of the hardness and electrical resistivity change during ageing for the alloys are presented in Figs.1-4. They show, in general, increase of hardness with increasing ageing time up to maximum with decreasing hardness then. But the hardness increase is not always gradual. In some cases two stages of the hardness increase occur. At the first stage the hardness increase is insignificant and at the second stage after kink the hardness increases steeply up to maximum. In the Figs.1-4 some hardness curves are shown for some binary alloys. One can see, that in the binary alloys of magnesium with the rare-earth metals of the cerium subgroup, Nd and Sm, only one stage in the hardness increase can be seen, unlike binary alloys with the rare-earth metals of the yttrium subgroup, Y and Tb, where two stages of the hardness increase can be seen. Such a change of the hardness during isothermal ageing is inherent to magnesium alloys with other rare-earth metals of each of the both subgroups [2]. Another significant difference in the hardness curves belonging to the binary magnesium alloys with the rare-earth metals of different subgroups is the higher hardness values for the alloys with elements of the last subgroup [2].

The first similar feature of the different ternary systems by hardness change during ageing consist of acceleration of the solid solution decomposition, when the element of the cerium subgroup (Ce, Nd) is added to the alloy containing element of the yttrium subgroup (Y) (Figs 1, 2) and deceleration of it, when the element of yttrium subgroup (Er) is added to the alloy containing element of cerium subgroup (Fig.3). This effect becomes evident, if dispositions of the hardness maxima on the curves relative to the ageing time axis are compared. With change of the ratio between contents

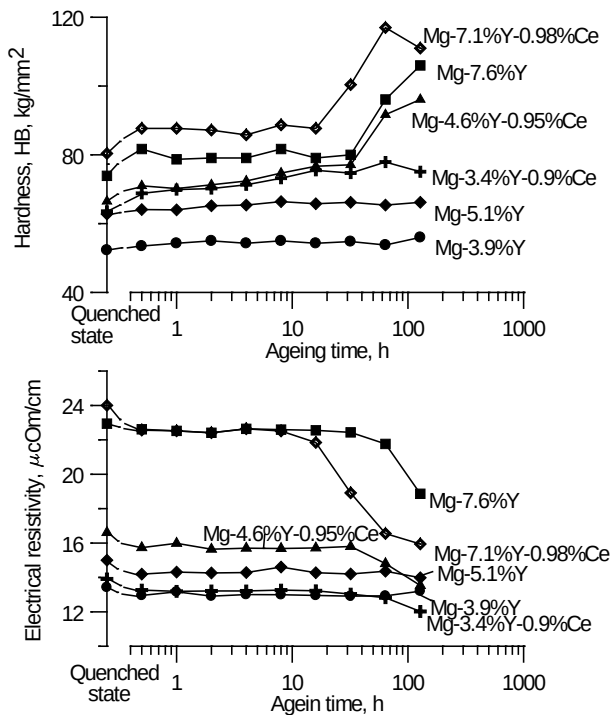


Fig.1. Variation of the hardness and electrical resistivity upon isothermal aging of the Mg-Ce-Y alloys at 200 °C [5].

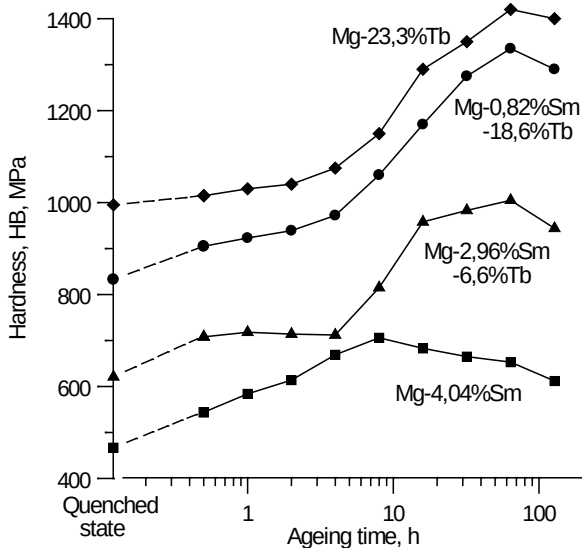


Fig.4. Variation of the hardness upon isothermal aging of the Mg-Sm-Tb alloys at 200 °C [10].

of the rare-earth metals in the alloys in direction of increase of that belonging to the yttrium subgroup instead of that belonging to the cerium subgroup the hardness values become more and character of the hardness curves changes gradually from that being typical for the alloys with elements of cerium subgroup to that for the alloys with elements of yttrium subgroup. This can be seen clearly for the Mg-Sm-Tb alloys (Fig.4).

Another similar feature of the different ternary systems of magnesium alloys with the rare-earth metals of different subgroups is increase of the hardness maximum values, when the element belonging to the cerium subgroup is added to the alloys containing element of yttrium subgroup. This feature is evident in the alloys of the Mg-Ce-Y and Mg-Nd-Y (Figs.1, 2).

Investigations of the ternary magnesium alloys of above mentioned systems indicated, that the phases formed in them during magnesium solid solution decomposition at the stages

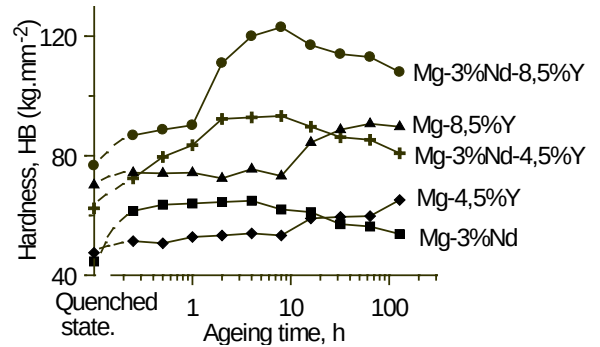


Fig.2. Variation of the hardness upon isothermal aging of the Mg-Nd-Y alloys at 225 °C [7].

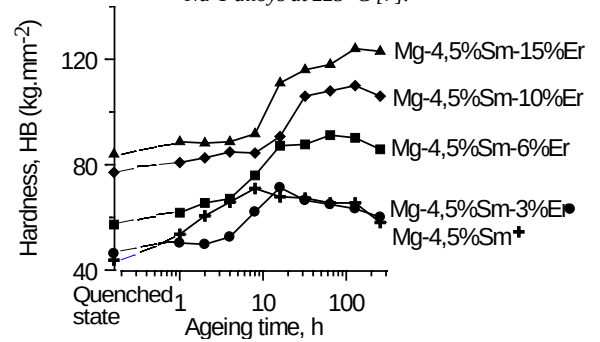
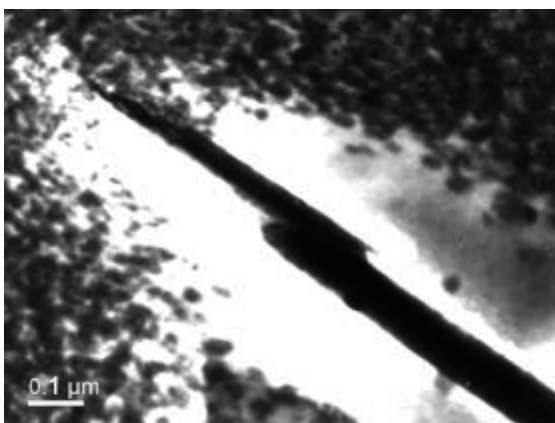
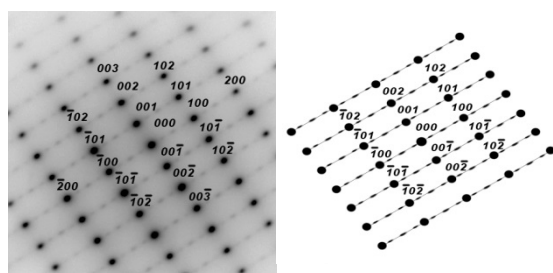
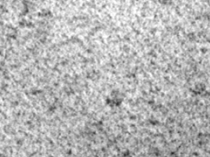


Fig.3. Variation of the hardness upon isothermal aging of the Mg-Sm-Er alloys at 200 °C [9].

of hardening were similar and nonequilibrium (metastable) ones. These phases were also typical for the binary magnesium alloys with the rare-earth metals of cerium and yttrium subgroups. No other types of the precipitated phases were observed in the ternary alloys.

In Fig.5 the microstructure and the related electron pattern of the Mg-Sm-Tb alloy are presented. The alloy was solution treated and aged then at 200°C for 8 h. Such an ageing regime corresponds to the early stage of the solid solution decomposition and, therefore, the precipitates formed are not seen clearly. However, electron pattern corresponding to this structure indicates certain decomposition. They are two sorts. One of these sorts is the system of the point-like superstructure reflexes disposed by every three of them on the lines corresponding length between the large central reflex (000) and that of (100) type belonging to the Mg solid solution. These three superstructure reflexes divide the length between reflexes (000) and (100) into three equal parts. Such a disposition of the point-like superstructure reflexes corresponds to the precipitates of the orthorhombic metastable phase β' observed on the binary magnesium alloys with the rare-earth metals of yttrium subgroup [4]. Along with these point-like superstructure reflexes, the electron pattern contains the parallel continuous lines passing in direction from the central reflex (000) to the reflex (100) of magnesium solid solution. Such parallel lines correspond to the tracks of the reciprocal lattice of the electron diffraction created by Mg solid solution and its existence indicates formation of the zones GP, that is typical for magnesium alloys with the rare-earth metal of cerium subgroup [3].

In Fig.6 microstructures of the Mg-Sm-Y system alloy aged to stage some more the hardness maximum is presented [8]. In its structure shown at two magnifications the plate-like large crystals can be seen. Morphology of these crystals indicates them to be typical ones for precipitates formed during decomposition of the binary magnesium alloys with the rare-earth metals of cerium subgroup. In this event, they are the particles of the metastable phase being that observed in the decomposed Mg-Sm alloys. In the areas between the large plate-like crystals in the structure, presented in Fig.6 there are also the very disperse precipitates. These disperse



4. Conclusions

1. The similar features in kinetics are acceleration of the solid solution decomposition and increase of the hardness maximum, when a rare-earth metal of the cerium subgroup is added to the binary magnesium alloys with rare-earth metals of the yttrium subgroup.
2. solid solution decomposition is that the only formed phases are those occurred in the binary magnesium alloys with the respective rare-earth metals of both subgroups. The phases of both binary systems being disposed within the magnesium solid solution simultaneously.

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SPARK PLASMA SINTERING OF NANOSTRUCTURED BIMODAL COPPER POWDERS

СПАРК-ПЛАЗМЕННОЕ СПЕКАНИЕ НАНОСТРУКТУРНЫХ БИМОДАЛЬНЫХ МЕДНЫХ ПОРОШКОВ

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Abstract: It is known, nanocrystalline metals are characterized by high strength and hardness, but low ductility. One way to increase the ductility is based on the creation materials with bimodal grain structure. General principle of this method is the nano- or ultrafine matrix provides a high strength, and evenly dispersed therein coarse grains contribute acceptable ductility. An important condition for preparing the bimodal material is to control and retention of the bimodal structure during processing. SPS method is promising for the development of materials, where need the collaborative and rapid consolidation of micro and nanosized powders. In this paper as the initial materials used copper powder of different fractional composition - a particle size of 40-90 μm and 50-70 nm. Nanopowder has consisted of micro agglomerates which have been divided during the preparation of the powder mixture. Initial powders were mixed in the mechanical mixer. Experiments were conducted a spark-plasma sintering system model Labox-625. The increasing of sintering temperature results in the density increasing. The pressure and the sintering time can also cause density increasing, but not as much as the temperature. The density of the sintered sample was measured by the Archimedes method. The mechanical property was tested using the hardness testing instrument (FM-800). In order to compare the mechanical properties of mono- and bimodal copper prepared by SPS, samples with a diameter of 10 mm were prepared. As a result, the microhardness of bimodal sample (180 HV) is higher than that of the micro- (63 HV) and nanosamples (159 HV) obtained by SPS. Fabricated by SPS the bimodal copper has a higher microhardness, compared with micro- and nanocrystalline samples. The microstructure of the bulk compact was observed by JEOL 6610LV scanning electron microscopy. The final grain size of the sintered nanomaterial varies depending on the sintering temperature ranging from 200 to 500 nm.

KEYWORDS: NANOSTRUCTURED BIMODAL COPPER POWDERS, SPARK PLASMA SINTERING, MICROHARDNESS

1. Introduction

Optimization properties of nano- and ultrafine materials are important task of Material Science. It is known, nanocrystalline metals are characterized by high strength and hardness, but low ductility [1]. One way to increase the ductility is based on the creation materials with bimodal grain structure [2]. General principle of method is the nano- or ultrafine matrix provides a high strength, and evenly dispersed therein coarse grain contributes acceptable ductility. An important condition for preparing the bimodal material is to control and retention of the bimodal structure during processing. A great advantage over traditional methods, such as methods of severe plastic deformation of producing bimodal materials exhibit electromagnetic methods of consolidation metal powders. SPS method [3] is promising for the development of materials, where need the collaborative and rapid consolidation of micro and nanosized powders. SPS technology can be used to produce materials with improvements in mechanical properties, microstructure, and other properties [4, 5].

2. Experimental

In this paper as the initial materials used copper powder of different fractional composition - a particle size of 40-90 μm and 50-70 nm. The morphology of copper powder is shown in Fig.1. As can be seen, nanopowder consists of microagglomerates which divided during the preparation of the powder mixture.

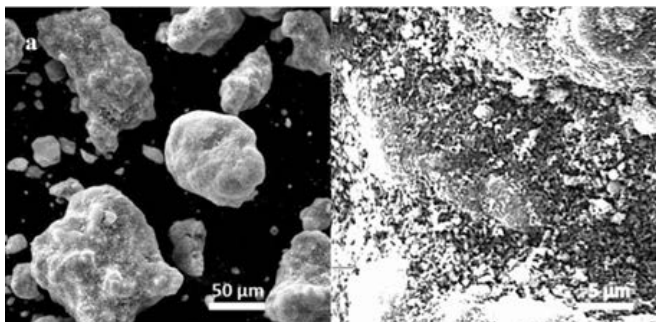


Fig.1(a). The SEM images of raw copper powders 50-70 nm

The copper powder with a particle size of 50-70 nm has been produced by "Advanced Powder Technologies", Russia.

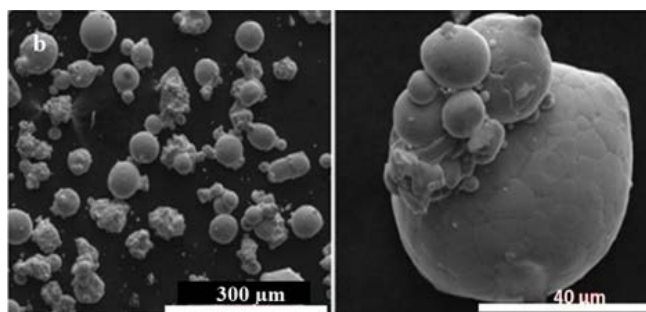


Fig.1(b). The SEM images of raw copper powders 40-90 μm .

The copper powder with a particle size of 40-90 μm has been produced by Alfa Aesar company, USA. The distributions of the powder particle sizes before (a) and after (b) separation are presented in Figures 2a and 2b. The graphs obtained by using data from a laser analyzer of a particle size Fritsch Analysette 22.

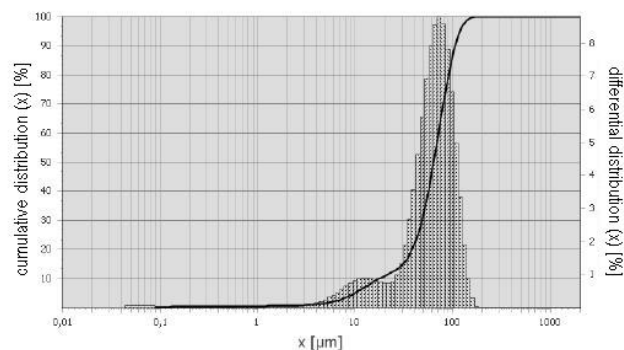


Fig.2a. The particle size distribution of the Cu powder 40-90 microns before separation.

For the SPS-experiments it was used a copper micropowder of a coarse fraction 20-50 microns. Separation of the coarse fraction of copper powder was carried out in laboratory vibration equipment Fritsch Spartan.

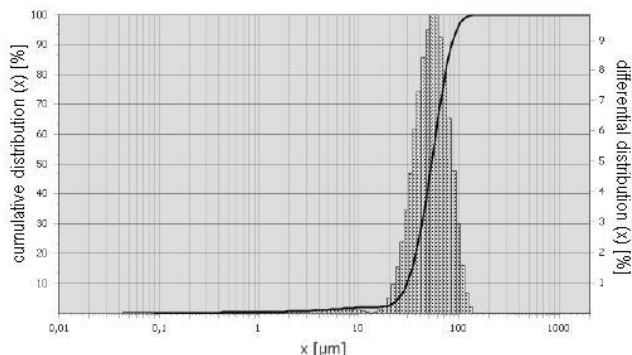


Fig.2b. The particle size distribution of the Cu powder 40-90 microns after separation.

Nanodispersed copper powder contains metallic copper about 98%. In contact with air, metal content decreases to 85-90%. The average particle size of copper nanopowder has from 50 to 70 nm. Nanopowder agglomerates are easily formed, as can be seen in the Figure 1a by a scanning electron microscope JEOL 6610LV.

Initial nanopowders and micropowders were mixed in the mechanical mixer. The bimodal mixture (mass fraction of a micron-sized powder of 30%) was obtained by mixing nano and micro copper powders in a vertical automatic mixer MSK-SFM-2 for 6 hours. The density of the bimodal mixture of copper powder was 7.72 g/cm³. It was measured by an automatic helium pycnometer AccuPyc 1340. The powder sample has a mass of 2 grams. The initial relative density of powder compacts is 38%.

Experiments were conducted a spark-plasma sintering system model Labox-625 with pulse duration of 40 ms. A cylindrical graphite die with inner and outer diameters of 10 and 30 mm was used in the SPS process. The pressure in the vacuum chamber was 6 Pa. The temperature was measured using K-type thermocouple mounted in a hole on a lateral surface of the matrix.

In order to obtain relations of the relative density and microstructure of copper bimodal compacts on the SPS parameters were selected ranges of sintering parameters:

- Sintering temperature was varied from 200 to 600 °C, a pitch of 200°C;
- Pressure – from 20 to 50 MPa, 15MPa;
- Heating rate was fixed parameter - 100°C/min.
- Holding time – from 3 to 9 min, 3 min;

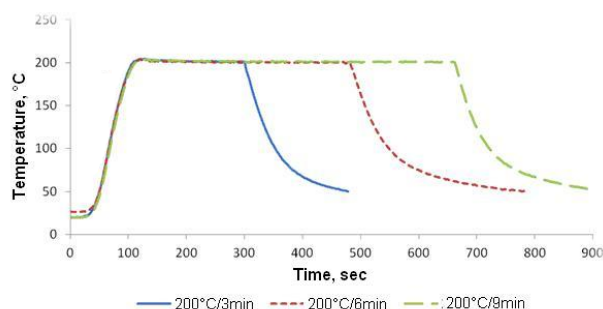


Fig. 3a. Temperature evolution during spark plasma sintering.

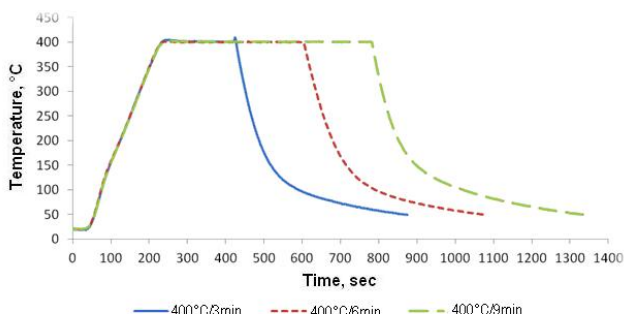


Fig. 3b. Temperature evolution during spark plasma sintering.

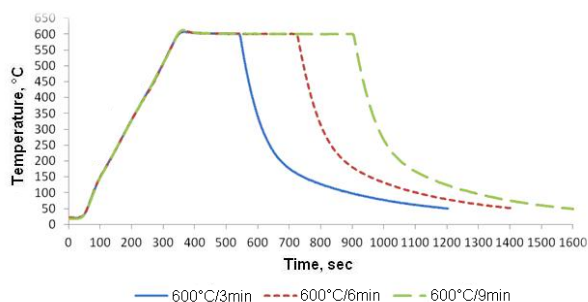


Fig. 3c. Temperature evolution during spark plasma sintering.

Graphs of temperature modes spark plasma sintering are shown in Figures 3a, 3b, 3c.

The relations between different sintering parameters were obtained by the SPS output system. The density of the sample was measured by the Archimedes method. The microstructure of the bulk compact was observed by JEOL 6610LV scanning electron microscopy. The mechanical property was tested using the hardness testing instrument (FM-800).

3. Results and discussion

Fig.4 shows the relation between the relative density of the bimodal copper compact and the sintering parameters. As seen from the graph, at a fixed value of sintering temperature was observed unessential change final density depending on the pressure and holding time. Thus at 200 °C and a selected range of changes pressure and holding time the relative density varies from 64.96 to 69.05% at 400 °C - 75,58-86,59% at 600 °C - 97.90 - 99.45%.

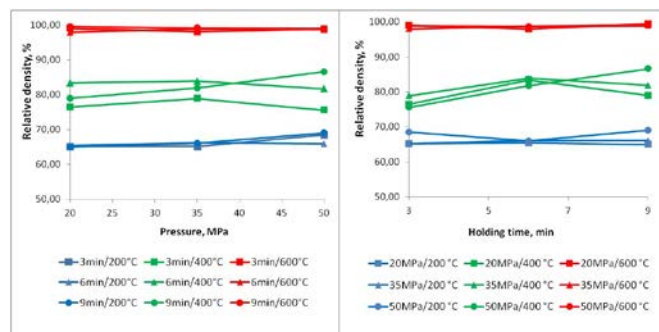


Fig.4. Effect of sintering temperature, pressure and holding time on relative density.

The kinetics of a powder densification during spark plasma sintering for 600°C/6min and different pressures: 20 MPa and 50 MPa are shown in Figures 5a, 5b.

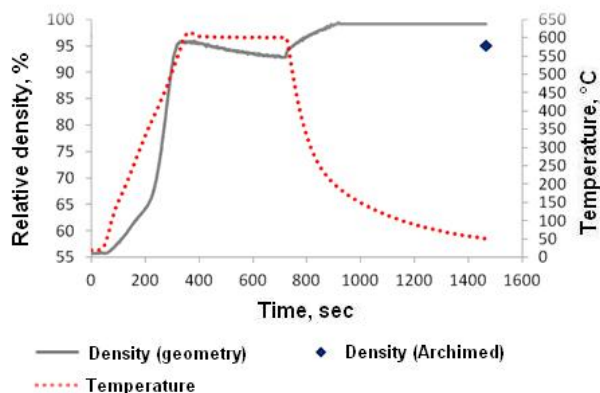


Fig. 5a. The evolution of a powder relative density during SPS for 600°C / 6 min, 20 MPa

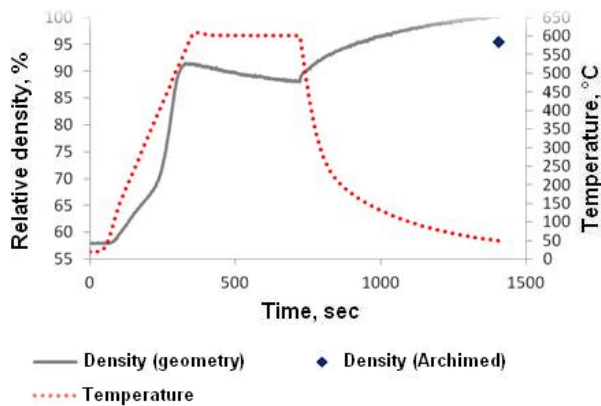


Fig. 5b. The evolution of a powder relative density during SPS for 600°C / 6 min, 50 MPa

Graphs 5a and 5b for the relative density of the compacts were built without correction for thermal expansion of the graphite punches.

Typical microstructure of bimodal copper samples is shown in Fig.6. As can be seen, coarse powder particles are uniformly distributed in the volume of densely sintered nanopowder.

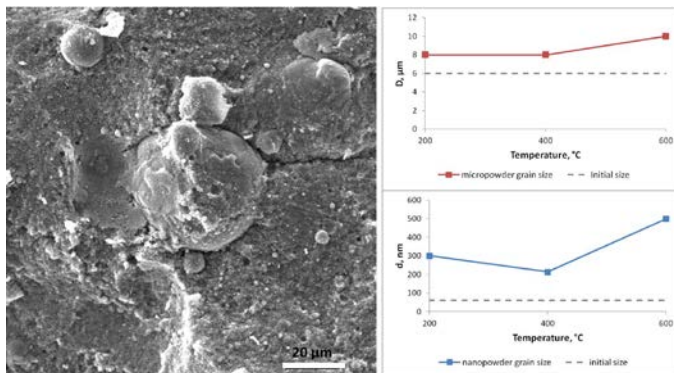


Fig.6. Typical microstructure of bimodal copper ($T=600^{\circ}\text{C}$, $P=35\text{MPa}$, $t=6\text{min}$, $v=100^{\circ}\text{C/min}$) and the relation between grain sizes and sintering temperature.

Since the temperature is a key factor affecting the final density of the samples, the dependence of the grain size was considered on the temperature at fixed values of pressure and holding time. Thus,

the average grain size on the range of temperatures was 8-10µm. The final grain size of the nanopowder varies depending on the sintering temperature ranging from 200 to 500 nm.

In order to compare the mechanical properties of mono- and bimodal copper prepared by SPS, a sample with a diameter of 10 mm was prepared. The following parameters were selected: $T=600^{\circ}\text{C}$, $P=35\text{MPa}$, $t=6\text{min}$, $v=100^{\circ}\text{C/min}$. As a result, the microhardness of bimodal sample (180 HV) is higher than that of the micro- (63 HV) and nanosamples (159 HV) obtained by SPS.

4. Conclusions

In this research, a bimodal Cu was synthesized by SPS successfully. The effects of sintering temperature, holding time, pressure and heating rate on the relative density, microstructure and mechanical properties of the samples were investigated. The results are shown:

- The sintering temperature increasing results in increasing of density significantly. Extending the pressure and holding time can also cause density increase, but not as much as the temperature.
- The sintering temperature has a significant effect on grain size of initial nanopowder, while the coarse grains don't grow.
- The SPS fabricated bimodal Cu has a high microhardness, compared with micro- and nanocrystalline samples.

Acknowledgements

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STRUCTURAL PRINCIPLES OF FORMATION HIGHLY DURABLE TRIBOTECHNICAL MATERIALS BASED ON POLYTETRAFLUOROETHYLENE

СТРУКТУРНЫЕ ПРИНЦИПЫ ФОРМИРОВАНИЯ ВЫСОКОПРОЧНЫХ ТРИБОТЕХНИЧЕСКИХ МАТЕРИАЛОВ НА ОСНОВЕ ПОЛИТЕТРАФТОРЭТИЛЕНА

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Abstract: *The preconditions of forming a structural paradox within the existing technological paradigm, which manifests itself in reducing the parameters of strength and tribological characteristics of composite materials based on polytetrafluoroethylene when administered in their composition of fillers and modifiers of different composition and geometry when the content of 15-20 wt. % Established effects of forming the structural conditions derating improved performance due to the formation of cluster structure of the binder particles (PTFE) and the modifier. The effective technological methods to ensure reducing the likelihood of cluster components in the manufacturing process of highly composites with a filler content of 20-35 wt. %. The technology of producing high-strength wear-resistant fluorine composites, 1.5-20 times superior to common parameters analogues produced under the trademarks "Flubon", "Fluvis", "Superfluvis.". We consider the effective use of highly fluorine composites in mechanical engineering, chemical industry and energy.*

KEYWORDS: FLUORINE COMPOSITES, STRUCTURAL PARADOX, TECHNOLOGICAL PARADIGM, CLUSTER STRUCTURE, TECHNOLOGY FOR STRENGTHENING

1. Introduction

Despite the unique combination of parameters of service characteristics - chemical resistance, heat resistance, low coefficient of friction, products of unmodified polytetrafluoroethylene (PTFE) limited use in the construction of friction units of machines and technological equipment [1-7]. For products of polytetrafluoroethylene characterized by increased wear during operation without an external supply of lubrication and high loading-speed modes, as well as a manifestation of cold flow, which leads to changes in the design parameters of the friction unit.

An effective way to increase the parameters of strength and tribological PTFE is the introduction of the matrix polymer fillers and modifiers of different composition, structure and mechanism of action and dispersion [1-6], as well as workpieces and articles by high flows, including ionizing radiation [6]. The last line, despite the possibility of regulating the parameters of strength and tribological characteristics in a sufficiently wide range of limited use due to technological difficulties of implementation.

In the nomenclature of composite materials of different functionality occupy a special place fluorocomposites, based on polytetrafluoroethylene modified disperse various components of the composition, structure and technology of [1-10]. Despite the existing range of branded fluorocomposites, providing the possibility of manufacturing structural, sealing, tribological and protective elements machines and process equipment with the given parameters of service characteristics, the problem of achieving the maximum values of the parameters of strength, wear resistance is far from the solution and requires the development of new technological approaches that take into account the specific structural features of the macromolecules of polytetrafluoroethylene (PTFE), conditional on the physico-chemical mechanisms and tribochemical processes in static and dynamic contact components and metal-filled materials systems.

Analysis of the literature devoted to the study of physico-chemical and technological aspects of the production and processing of functional fluorocomposites and the use of these products in various fields of technology, evidence of mature traditional methodological approaches based on classical concepts of polymer materials science, physics, chemistry and technology of plastics and composite materials [1-3]. The essence of these approaches is to apply the methods of regulation of the supramolecular structure of PTFE matrix by introducing a dispersed phase modifiers and composite structures - through the use of fiber fragments of organic and inorganic fibers - glass, oksalonovyh, basalt, carbon [1-3].

Filling materials based on PTFE - fluorocomposites - developed effective methods of managing structural parameters at different levels [2, 6, 8], which allowed us to develop and master the industrial brand variety, including a few dozen items with different parameters of strength, tribological and thermal characteristics [3, 7-10]. With all the variety of stamps fluorocomposites (Papers Series "Flubon", "Fluvis" F4K20, F4G10 et al.), In their preparation implemented common technological principle of forming and processing into products, involving a combination of the operations of mixing the components in a predetermined ratio, cold extrusion billets and their hot sintering (monolitizatsii) in air at a given temperature-time mode. This technological principle is similar in essence to those used in powder metallurgy, currently dominates the literature, patent and commercial sources, becoming the basis for technological paradigm functional fluorocomposites [1-3, 8-11].

The current technological paradigm functional fluorocomposites led to the achievement of a certain level parameters of strength and tribological characteristics which excess within it is not possible or is costly material and energy resources, reduces the effectiveness of the practical application of the products obtained [1-3, 8-12]. The inefficiency of traditional approaches in the implementation of technology of functional fluorocomposites particularly pronounced when creating filled materials containing more than 20% by weight. components of different composition and dispersion, which dramatically narrows the range of their practical application in tribological and sealing systems operating at high loading-speed and temperature conditions. The result is a scarce resource exploitation friction units of special equipment, vacuum, cryogenic plants and sealing elements of compressors for compressed and liquefied gases [3, 6-8]. Meanwhile, the analysis of the mechanisms of destruction and wear products from highly filled material indicates the potential of an incomplete as matrix polymer (PTFE) and modifying component (typically of high strength and wear).

The purpose of this study was to develop the principles of improving the technology of machine fluorocomposites based on the concept of multi-level modification proposed in [13].

2. Preconditions and means for resolving the problem

As a basic binder used in the preparation of fluorocomposites commercially available polytetrafluoroethylene (PTFE) marks F-4PN, F-4PN90, F-4TM differing average size of the powder fraction (JSC "HaloPolymer", Russia). For reinforcement PTFE matrix fragments used carbon fiber (HC) received mechanical

dispersion of the carbon tape brand LO-1-12N (JSC "SvetlogorskHimvolokno", Belarus) with the size fractions less than 200 microns. Structural modification of PTFE was carried out in the introduction of carbon black (TS) grades P234 and P803 with a mean size of individual particles 20 and 80 nm, respectively, as well as polytetrafluoroethylene Ultrafine (UPTFE), an oligomeric polymer products termogazodinamicheskikh synthesis polytetrafluoroethylene, obtained according to [6, 7]. Used in the experiments UPTFE, commercially available under the trade name "Forum" (Institute of Chemistry, Far East Branch, Russian).

Samples for studies of strength and tribological characteristics developed fluorocomposites prepared in accordance with the requirements of normative documents on materials such as "Flubon" (analogous to "Fluvis") [9, 10]. Defines the parameters of strength (σ_t , σ_{comp} , E_{comp} , HB) and tribological properties (wear intensity I, the coefficient of friction f) according to standard procedures or methods recommended in [9, 10], with the use of plants MR-200 ComTen 94c, P-0.5, HP-250, friction machines SMC-2, HTI-72. Analysis of physico-chemical and structural aspects of the modification of PTFE, technology acquisition and processing fluorocomposites and operating features of these products was carried out on the basis of IR spectroscopy (Tensor-27), nuclear power (NANOTOP-III), optical (Micro200T-01), scanning electron (LEO1455VP) microscopy and X-ray diffraction (DRON-2.0).

Samples were prepared for research on technological regimes recommended in [3, 11] and by original technologies, realizing the possibility of multi-level modification.

3. Results and discussion

Analysis of the literature devoted to materials science and technology of functional fluorocomposites [1-13], suggests that the main provisions of the traditional technology, component paradigm is the use of classical methods of regulating the supramolecular structure of the matrix polymer using fillers dispersed organic and inorganic nature and the introduction of PTFE fragments of reinforcing fibers dispersed using mechanical mixing operations of components of cold pressing and monolitizatsii preforms at temperatures above the crystalline melting point of the binder phase.

Using this technology, the various species, consisting in the introduction of fine fillers (carbonaceous, siliceous - UDD UDAG, zeolites, etc.), including nanoscale mechanoactivated [1, 4, 5], and the reinforcing fibers (carbon, glass, basalt, aramid), or mixtures thereof [3, 12], while maintaining the traditional process flow for obtaining blanks (products), not achieve a fundamentally new effects enhance the parameters of strength, thermal and tribological characteristics. Use of complex modifier comprising finely divided carbonaceous material fraction (cryptocrystalline graphite) in combination with dispersed reinforcing fibers of carbon fragments (HC) [2], the conventional technique of forming blanks not allowed to significantly increase the values of tensile strength, toughness and wear resistance, which is determined the potential for their use in the construction of machines and technological equipment with high demands on reliability and guaranteed life.

In some literature concluded impossible to maintain some of the initial parameters of the matrix polymer, polytetrafluoroethylene (σ_t example, specific toughness (NDC)) and increase their values upon administration of any composition and filler dispersibility, including high strength, especially at elevated levels of [8]. It is generally accepted structural paradox for fluorocomposites consisting in a significant decrease in the values of a number of important parameters (σ_t , f , density) with the introduction of high-strength reinforcing fillers (eg, HC). An analytical expression is capable of evaluating the expression of the structural paradox when creating fluorocomposites [11]:

$$\sigma_{tc} = \sigma_{tm} - 0,5i \quad (1)$$

where σ_{tc} - the composite tensile strength, MPa; σ_{tm} - Tensile strength of matrix polytetrafluoroethylene MPa; i - the filler content, % wt.

From this expression it follows that the introduction of the composite of more than 20% by weight. anyone, including high strength, the filler is impractical because there is a significant decrease in the values of σ_t parameter that determines the field of application of its products.

Confirmation of the validity of applying the proposed in [11] analytical expressions (1) to estimate the parameters of service characteristics of engineering fluorocomposites are parameter values for σ_t most effective brands that have found widespread application - Flubon-20LO, Fluvis-20 F4K20 significantly inferior to similar values of the source of polytetrafluoroethylene (30-36 MPa) [3, 6-11] and are close to the calculated values, defined by the formula (1) (Fig. 1).

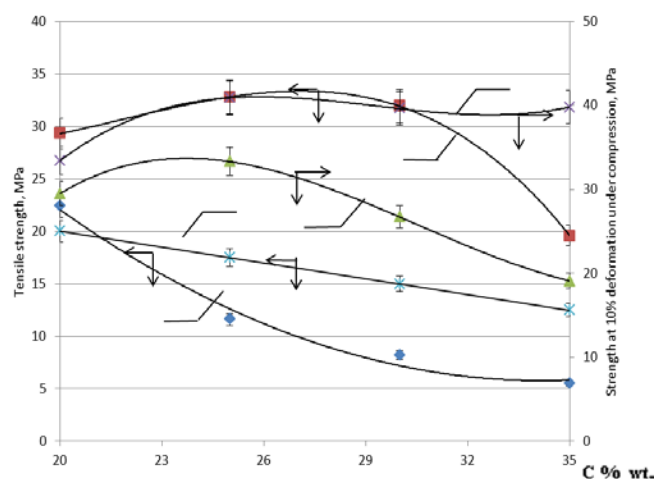


Fig. 1 Dependence σ_t parameters (1, 2, 4) and σ_{comp} at 10% deformation (3, 5) the content of carbon fiber in the composition (C % wt.). Depending 1, 3, 4, 5 - experimental dependence of 2 - calculated according to [11]

Several studies have analyzed the influence of the structure of the boundary layer at the interface level "matrix-filler" on the parameters of strength and tribological characteristics fluorocomposites sold under the brand name "Fluvis" (analogous to "Flubon") [2, 8]. Suggested the determining role of the bond strength at the interface in the implementation of the parameters specific σ_t and toughness, and the method of modification of carbon fibers by plasma treatment in an environment of fluorinated gases to increase the adhesion at the interface [8]. A similar approach was previously proposed in [3] the fibers during processing of low molecular weight fluorine compounds and methods of using the HC oxidation and etching. Achieved the effect of increasing the parameter σ_t using both the modified carbon [8, 9] and Arselon [12] confirms the validity of the fibers is not the hypothesis of the decisive influence of fluorine compounds on the surface of the reinforcing filler on the parameters of deformation and strength characteristics of composites based on PTFE. Thus, the parameter σ_t for materials such as "Flubon-LO", "Fluvis", "Superfluvis" does not exceed the values specified regulatory documents [8, 9], are, respectively, 9, 17 and 27 MPa, which is significantly inferior to the parameter value for the base σ_t polytetrafluoroethylene equal to 32 MPa [1, 6] (Table 1).

In addition, as the performances of arrangements of the process of polymerization of fluorine-containing monomers [2, 3, 6, 11], to form high molecular weight compounds from the gaseous medium must be compliance with the specific conditions that can not be realized to the extent required in the amount of vacuum in the process chamber modifying semifinished carbon fiber tape in

the form [8]. Information set forth in [8] et al., did not confirm the formation of polymer products of similar molecular weight, composition and structure of polytetrafluoroethylene to a macromolecule.

Table 1 - Parameters of service characteristics of highly fluorocomposites

Parameter	Value for the material							
	Flubon -LO	Fluvis		Superfluvis		Tech nology MA	Techn ology HC	Tech nology CM
σ_t , MPa	9	14	17*	18	27*	26	30	32
σ_{comp} 10% , MPa	27	30	-	33	-	35	40	45
$I \cdot 10^7$ mm ³ /H * m	5,0	5,0	3,5*	4,5	1,5*	2,4	2,3	1,5
ρ , kg/m ³	1830	1830	1930*	1850	1990*	1870	1920	1940
The content of CF,% by weight.	30	30	20*	30	20*	30	30	30

* - These regulatory documentation for materials "Fluvis", "Superfluvis" [9, 10].

Probable mechanism of manifestation of a technical effect of increasing values of the parameter σ_t , when introduced into the PTFE carbon fiber modified by plasma method [8], is to change the strength of interparticle friction between the components of the dispersed material (PTFE and HC), helping to reduce clustering processes that determine the prerequisites for the formation of structural defects [6].

Thus, the experimentally observed adverse effect of the values of a number of important parameters fluorocomposites with the introduction of the high-strength fillers can not be explained using classical ideas about the role of supramolecular structures at the interface and in the implementation of mechanisms of deformation and failure of these products under the influence of operational factors.

However, for any type fluorocomposites containing superfine as including nanoscale [1, 2, 5] and the fibrous reinforcing fillers (original and modified) [2, 3, 6, 8], and mixtures thereof, [2] realized the effect of multiple parameter is increased wear resistance in friction products for metal counterbody without external supply of lubricant. Obviously, this effect is a consequence of the mechanism of manifestation of the filler particles create any composition, structure and mechanical dispersion of obstacles to deformation and displacement of local areas of the binder matrix under the influence of tangential stresses and their own resistance to tribological factors - thermal and mechanical.

Systematic analysis of the impact on the structure fluorocomposites deformation mechanisms, fracture and wear products from them in various loading conditions and operation revealed the main factors influencing the expression of the structural paradox in the implementation of the traditional technology of their production at the molecular, supramolecular, phase and interphase levels (Fig. 2).

Imperfection fluorocomposites structure at the molecular level due to the specific structure of the macromolecule

polytetrafluoroethylene causes no plastic condition, characteristic of thermoplastics, which determines the ability of the matrix to the spreading over the surface of the filler and inert macromolecules expressed in the processes of physical and chemical interactions with components of any composition, structure, production technology.

The molecular structure of PTFE necessitates use of special procedures for the formation of products (semi-finished), providing interaction of individual particles of the dispersed matrix macromolecules by interdiffusion with the formation of boundary layers little defect structure at temperature influence on the compressed sample (mono politicization). This factor has caused the need for long exposure workpiece at temperatures exceeding crystalline melting temperature (330-350 ° C) to form a monolithic matrix with a minimum amount of defects, supermolecular structure which differs significantly from the structure of the starting powder particles semifinished. The surface layers of dispersed particles contained in mechanical contact of an external pressure at mono politicization play the role of active nucleating agent, resulting in the recrystallization process and the formation of supramolecular organization of a new type.

Therefore, the role of morphology and size of the dispersed particles of commercially available PTFE is very important for the formation of the structure of the matrix with the optimal combination of parameters of strength and tribological characteristics. Given that commercial grades of PTFE (F4, F4M et al.) Very significantly differ not only in dispersibility and morphology of individual particles [2, 11], but different mass macromolecules formed in the absence of regulatory documentation parameters characterizing the molecular weight distribution, and number-average molecular weight of the fractions with the highest specific gravity [2, 11], necessary to use special processing techniques to prepare the commercially available semi prior to processing.

Obviously, the most important aspect of the operation of preparation is approaching mass activity, the morphology of individual particles to optimize the values of the interparticle friction forces that have a significant effect on the kinetics of the process of cold pressing of the workpiece with a minimum of defects. Furthermore, it is necessary to ensure optimal mobility of macromolecules of different mass in the interparticle boundary layers formed during cold pressing, sintering the preform at the purpose of interdiffusion and formation of a monolithic structure. Obviously, for the implementation of this condition is an effective introduction to the interparticle boundary layer thermodynamically compatible modifiers in a controlled molecular weight distribution, acting as high-modifier.

On the supramolecular level of structure formation fluoro composite paradox manifested in the impossibility under the applicable process simultaneous production of a gradient structure with lamellar structure of the surface layer of the product provides a low shear resistance (low friction) in the operation of metal-supply system without external lubrication, and melkosferolitnym structure matrix in the amount of that raise the parameters of deformation and strength characteristics.

Processes of forming the optimal supramolecular structure in filled PTFE matrix during thermal exposure during mono politicization difficult due to the low mobility of macromolecules in the matrix binder. Therefore, an important role is played by the activity of the dispersed particles in the process of recrystallization of the original structure of the matrix of the PTFE particles. In the process of mixing the particulate filler particles are concentrated in the surface layer microroughnesses powdered binder particles that are able to supply industries have a significant range of size and morphological parameters.

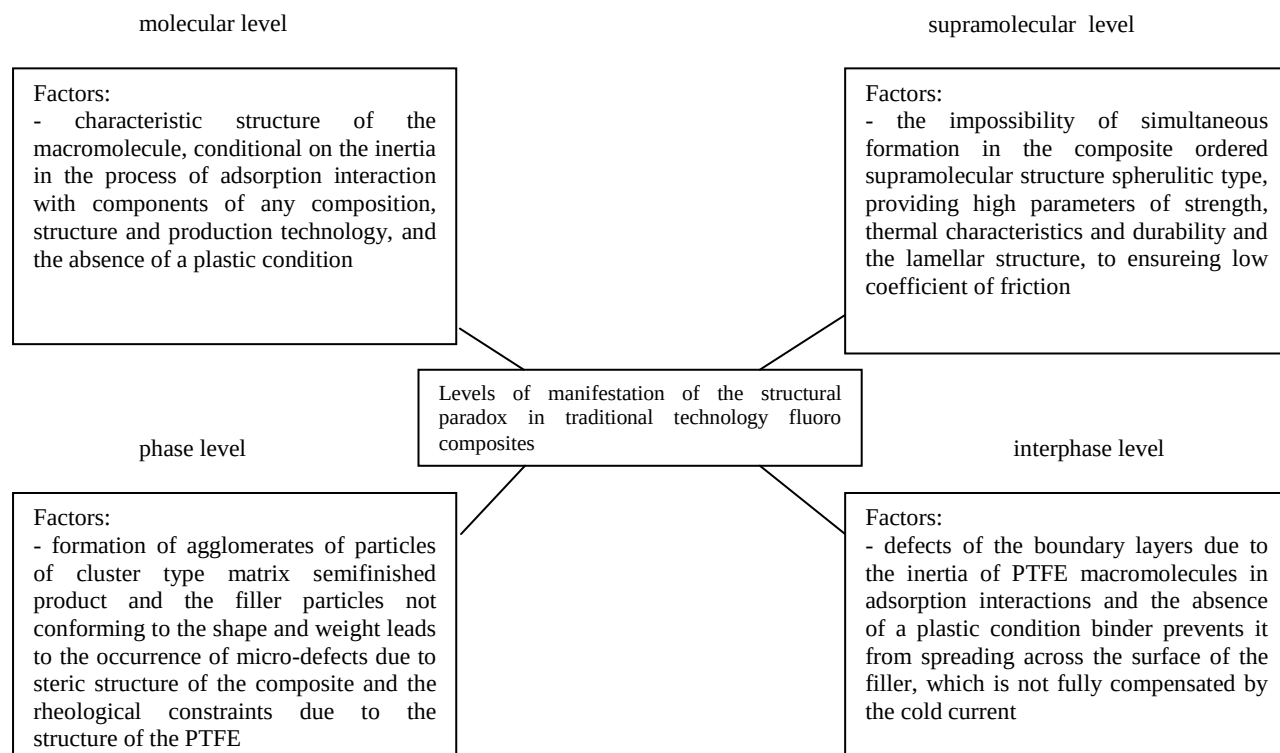


Fig. 2 The main factors influencing the expression of the structural paradox in the formation fluorocomposites according to the technological paradigm

This leads to the formation in step cold pressing the workpiece modifier concentration gradient and spatial grid formation, the shape and size of which depend primarily on the parameters of the particles in a state of an industrial semifinished product supply (Figure 4b). On stage mono politicization blank (hot sintering) dispersed particles modifier promote recrystallization of the matrix binder to form a supramolecular structure of a new type, size and morphological characteristics of which depend on the activity of the particles, the magnitude of its energy field, its impact on the mobility of macromolecules located in the periphery and their ability to spatial orientation to form ordered domains. Because of this factor to optimize the structure fluoro composite on supramolecular level sufficient doping [1, 3] content of dispersed components with sufficient activity in the range of values (0,001-1,0)% by weight. [1, 3, 6]. When an excess of the dispersed component in the composite formed cluster structures, impede the process of recrystallization of the matrix binder to form the optimal supramolecular structure and causing wear conjugated metal counterface. With the increase in the activity of single particles dispersed modifiers that can be achieved by using special technology education nanoscale fractions [1, 6], mechanical or thermal effect on the semi-finished product [1, 2, 4], the effectiveness of their actions on the supramolecular organization of the process increases, which provides modifying the desired effect at much lower concentrations [1, 7]. Therefore nanoscale modifiers (UDAG, zeolites, Sialons et al.), Subjected mechano-activated provide a pronounced effect of increasing the parameters of strength and tribological characteristics fluoro composites if they contain up to 1% by weight. [1, 4].

On the phase level education fluoro composite imperfect structure due to the formation in the mixing process of the particles of the matrix polymer and filler having a different shape, weight and electrical characteristics (Fig. 3a, b), the agglomerates of the cluster type (Fig. 3c), gives rise microdefects in the sample after cold pressing and remaining after sintering (mono politicization),

due to the forces of interparticle friction and rheological steric obstacles for filling cavities connecting clusters (Fig. 3d).

Interphase level of imperfection structure of composite materials based on polytetrafluoroethylene, which leads to a decrease in the parameters of service characteristics, realized as a result of defects in the boundary layers in the "matrix-filler", leads to low strength, which is predetermined inert PTFE macromolecules in adsorption interaction and lack of bonding a plastic condition that prevents its spreading over the surface of the filler and increase the contribution of mechanical component into force of the adhesive interaction between the components. Therefore, in the composites filled with dispersed fragments of carbon, glass and other fibers, not realized their strength parameters, which in other thermoplastic matrices lead to a substantial increase in the parameter values and σ_t, σ_{comp} . For example, the parameter for σ_t and fiberglass reinforced plastics based on polyamide 6 (PA6) is from 110 to 130 MPa at a filler content of 20% by weight. The initial value of σ_t for the matrix polymer 60-65 MPa.

Pooled analysis shown in Figure 2 the main factors leading to the manifestation of the adverse effect of the parameters of strength and tribological characteristics fluoro composites with increasing filler content, indicates the dominant role of factors caused by peculiarities of technology of matrix binder (PTFE powder) and a reinforcing filler (HC) that aggravate the adverse effects characteristic of the chemical structure of the main components of the processes of forming the optimal structure at various levels of the organization by using traditional methods of mixing the components, cold extrusion billets and hot sintering (mono politicization). Therefore, to increase the parameter values of strength and wear resistance of the composites with a filler content of 20 wt.%,

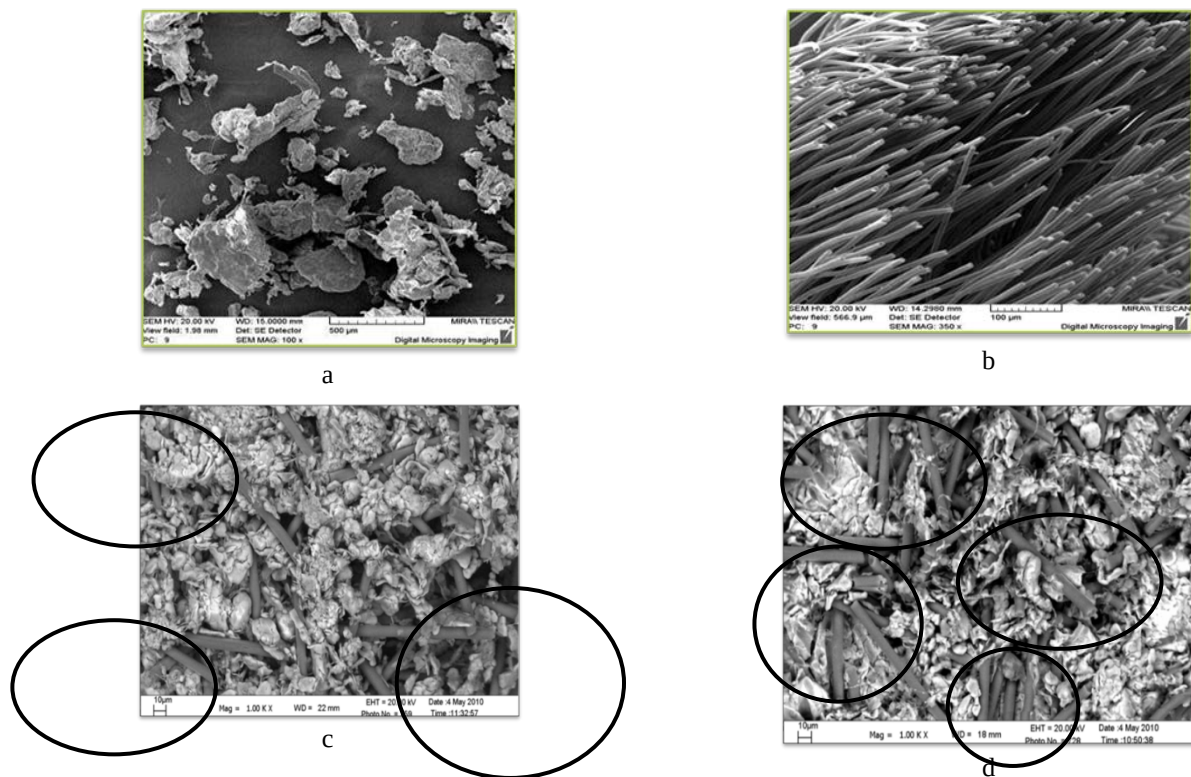


Fig. 3 Characteristic form a matrix of polytetrafluoroethylene particles (a), of carbon fibers (b) and in the composition of the cluster structures of PTFE + 20% by weight. HC after mixing the components (c) and the product formed by the conventional technology (d). Clusters are marked by circles

Related to the highly-fluoro composites, you must change traditional approaches technological paradigm, based on the features of the composition, structure and geometric parameters of the main components. The nature of these changes is as follows:

- it is necessary to carry out technological preparation components allow optimum parameters of geometrical characteristics of the dominant faction and reduce the negative impact of unstable molecular weight distribution of the polymer matrix on the parameters of strength, rheological properties and interparticle interaction;

- it is necessary to apply the technology of combining the components of the material to ensure destruction of the cluster structure formed by PTFE particles and hydrocarbons in the mixing process (Fig. 3, c);

- morphology characteristic matrix PTFE particles (Fig. 3, a) makes possible use as modifiers target components with high thermodynamic compatibility, which increases the ductility of the matrix in cold pressing and plasticizing effect due mono politicization. Effective modifier of this type are the synthetic products thermal gas dynamic polytetrafluoroethylene (UPTFE) containing oligomeric and polymeric fractions with similar molecular structure of the PTFE [6, 7];

- filling cavities cluster structures formed PTFE particles and hydrocarbons in the mixing process is possible through the use of fine particles UPTFE during the pre-modification tape semi-finished carbon fiber;

- cluster structure of the composite material is formed at the stage of mixing the components using a blade installations, allows it to implement the principle of multi-level modification of nanoscale components and micro-symmetric fractions with different forms of individual particles (carbon black, UPTFE, CF);

- when used as a modifier PTFE multi-dispersed carbon fiber role of morphological factors contributing to the possible formation of a concentration gradient of components of a heterogeneous system "PTFE-CF" prevails over the role of the intensity of the adsorption interaction at the interface "matrix modifier" providing education boundary layers optimum structure . Increased activity of the surface layer of hydrocarbons in interactions with PTFE by various technological factors (etching, oxidation treatment in the

medium fluorinated gases and liquids, and other chemical plasma processing. [3, 6-8]) to form an interfacial layer of increased strength while maintaining the traditional technological receptions leveled the negative effect of defects formed by clusters of fragments of HC. Necessary to use technological methods, reduces the probability of formation of cluster structures in the composite modifier on stages of preparation components, their combination, pressing and mono politicization blanks.

Based on the above concepts developed efficient processing methods of forming composites little defect fluorinated structure with a filler content of 25-35 wt.%, Which belong to the class of highly filled (Fig. 4).

Practical implementation of the developed approach will allow to change the activity of the surface layer of hydrocarbon fragments in interactions with the matrix due to the consolidation of particles UPTFE, fill in the blanks clusters of fragments of CF components thermodynamically compatible with the matrix polymer, to bring the geometric shape and size of the PTFE particles and CF, reduce the likelihood of formation of clusters, the step of mixing the components in a paddle mixer, to destroy the structure of the cluster in the volume of the composite material during sintering (mono politicization) preform and its subsequent processing by plastic deformation. Obtained highly filled composites little defective structure, surpassing its analogues in the homogeneity and the parameters of strength and tribological characteristics (Table 1, Figure 1).

It should be emphasized that the developed methodological approaches are effective in obtaining not only fluoro composites containing carbon fiber (CF), and basalt, glass, etc. oksalonovoe. Kinds of heat-resistant high-strength fibers or mixtures thereof [12].

Thus, our system of research, including materials science, structural and technological aspects, allowed the development of highly efficient technology of composite materials based on polytetrafluoroethylene, exceeding the parameters of strength and tribological characteristics of the best industrial analogues "Fluvis" and "Flubon" [6, 14 -16].

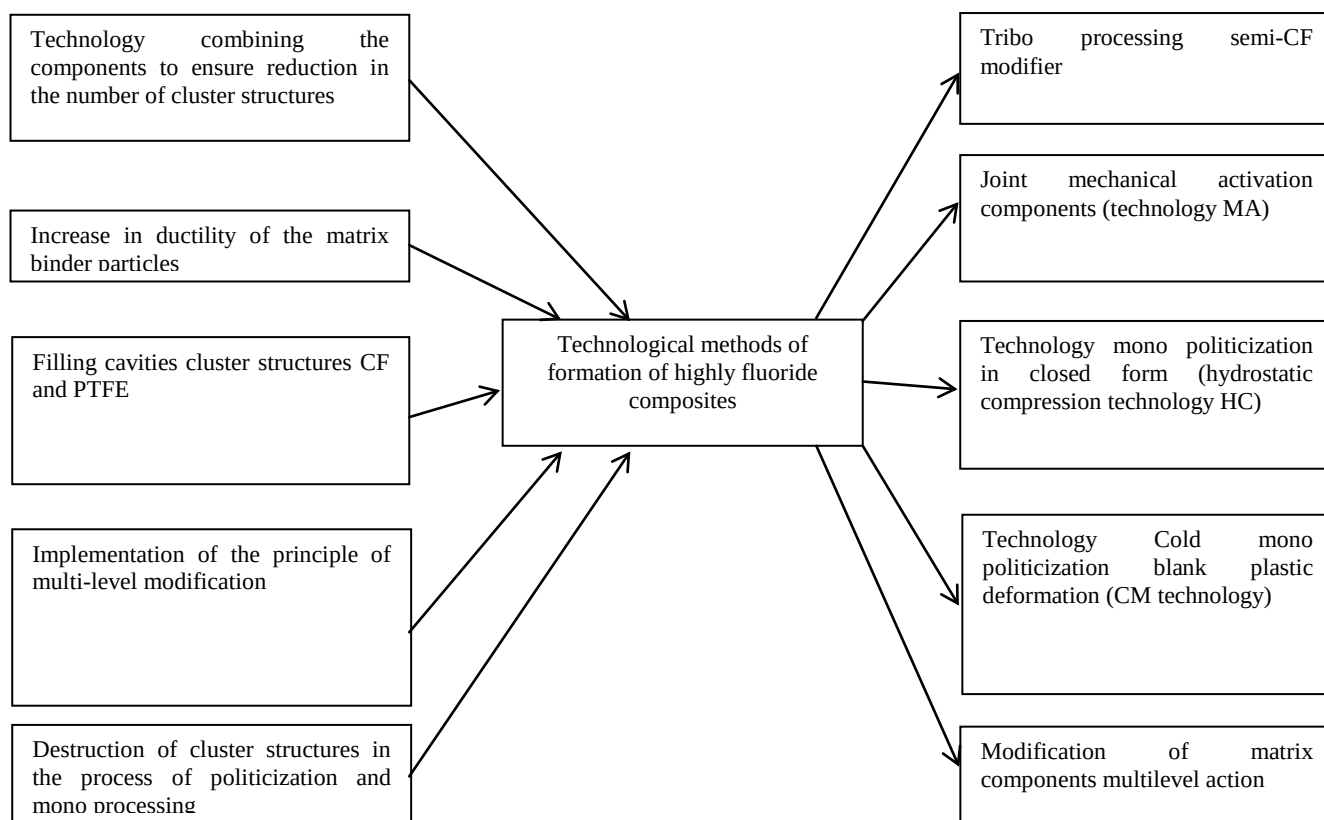


Fig. 4 Technological methods of producing high-strength wear-resistant fluoro composites with a high content of carbon filler (CF)

4. Conclusions

On the basis of studies:

- found that the main factor responsible for the manifestation of the structural paradox in traditional technology fluoride composites consisting in a proportional decrease in the values of parameters of strength and tribological characteristics with increasing degree of filling of the reinforcing filler is a discrepancy between the geometrical, dimensional and tribological parameters of the matrix particles (PTFE) and filler, leading to the formation of cluster structures in preparation of the composite, which is a prerequisite for the formation of macrodefects stages of cold pressing and subsequent sintering (mono politicization) products (billets);

- proposed effective technological methods to eliminate the structural paradox in highly composite materials based on polytetrafluoroethylene with a filler content of 20 wt.%, Based on the principle of multi-level modification implemented by the introduction of multi-component (UPTFE) [16] and reduce defects in the structure due to the destruction of clusters under the filler the influence of mechanical activation processes (technology MA), the thermal expansion of the components (technology HC) and the plastic flow of the matrix (CM technology) [13-15];

- The compositions of composite materials based on polytetrafluoroethylene, containing 25-35% by weight. reinforcing carbon fiber exceeding 1.5-2.0 times better analogy series "Flubon" and "Fluvis" the parameters of strength and tribological characteristics.

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STRUCTURAL EVOLUTION DURING MECHANICAL MILLING AND SUBSEQUENT ANNEALING OF HIGH-ENTROPY AlCuNiFeTi ALLOY

ЭВОЛЮЦИЯ СТРУКТУРЫ ВЫСОКОЭНТРОПИЙНОГО AlCuNiFeTi СПЛАВА В ПРОЦЕССЕ МЕХАНИЧЕСКОГО ЛЕГИРОВАНИЯ И ПОСЛЕДУЮЩЕГО ОТЖИГА

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This study reports the structural evolution of equiatomic AlCuNiFeTi high-entropy alloy (HEA) from elemental materials to solid solution during mechanical alloying (MA), and further, to equilibrium phases during subsequent thermal annealing. It was justified experimentally that MA of Al-Cu-Ni-Fe-Ti powder mixture during 15 hours resulted in a single-phase nanocrystalline HEA with a structure of BCC solid solution. During thermal annealing recovery and recrystallization of the BCC solid solution take place at temperatures ranging from 130 to 650 °C, and phase transformation, and grain growth of equilibrium phases occur at higher temperatures. The phase composition transforms to BCC and FCC solid solutions when the MA powder was annealed at 700 °C for 1 h. The BCC and FCC solid solution structure can be maintained even after the alloy was annealed at 1000 °C. The alloy powder was consolidated by pressure sintering at 800 °C with 5 GPa pressure for half an hour. The sintered sample exhibits 10.7±0.3 GPa in Vickers hardness.

KEYWORDS: HIGH-ENTROPY ALLOY, MECHANICAL ALLOYING, STRUCTURAL EVOLUTION, PHASE COMPOSITION, ANNEALING

1. Introduction

High entropy alloys (HAEs) are a new generation of alloys and are quite different from traditional alloys, which are based on one or two elements. Almost all conventional alloys have been designed to have a major element, such as ferrous, aluminium, copper, titanium, and magnesium alloys. As a new focus on materials research and a novel alloy design concept, high entropy alloys have been achieved successfully by changing or designing the component elements of metallic materials and have attracted great attentions of material researchers since it was proposed in 2004 by Yeh et al. [1, 2]. HEAs are typically defined as alloys whose principal elements are at least five, and the concentration of each constituent element is between 5 and 35 at.% [1- 4].

HEAs have been studied extensively in recent years, and they are expected to be plentiful in academic research and industrial applications. Some core effects in HEAs would be more pronounced than those in conventional alloys [5]: high entropy – it enhances the formation of simple solid solution phases, such as BCC and/or FCC structures, and thus simplifies the microstructures; severe lattice distortion – it arises from the atomic size difference among different elements in solid solution phases and might noticeably influence mechanical, physical and chemical properties; sluggish diffusion – it is due to the inefficient cooperative diffusion of various species and thus slow down phase transformations; and cocktail – it comes from the ideal mixing and inevitably excess interactions among the multi-principal elements in solid solution phases, and thus is a composite effect on properties.

HEAs have more excellent properties than conventional alloys and exhibit promising potential for engineering applications due to their good thermal stability [6], high hardness and high strength [7, 8], excellent wear resistance [9], superior oxidation and corrosion resistance [10], as well as many other exceptional properties [11]. The promising properties of HEAs offer the potential to be used in many applications, such as tools, molds, dies, mechanical parts and furnace parts which require high strength, thermal stability and wear and oxidation resistance. These alloys can be used for various applications that demand high temperature strength, oxidation, and corrosion and wear resistance.

Mechanical alloying (MA) is a widely used high-energy solid state processing route for the synthesis of advanced materials from elemental powders [12, 13]. The extension of solid solubility with good homogeneity and room-temperature processing are the main advantages of MA over the casting route, especially with multicomponent systems with large differences in the melting points. MA can easily lead to the formation of nanocrystalline and

will definitely increase the properties of high entropy alloys [13, 15]. In this paper, the AlCuNiFeTi high-entropy alloy powder was prepared by mechanical alloying and subsequent annealing to research the structural evolution. The as-milled powder was consolidated by pressure sintering and the structure and mechanical properties were investigated too.

2. Experimental procedure

Equiatomic elemental blend of Al, Cu, Ni, Fe, Ti powders with purity higher than 99.5 % and particle size of $\leq 45 \mu\text{m}$ was mechanically alloyed to synthesize quinary equiatomic AlCuNiFeTi high entropy alloy. Milling of elemental powders was carried out up to 15 h in high energy planetary ball mill at 580 rpm with ball to powder weight ratio of 10:1. Hardened steel vial and balls were used as a grinding media (balls of 10 mm in diameter) and petrol was used as a process controlling agent. In order to avoid a significant increase in the vial temperature the milling was periodically interrupted at 10 min for cooling after each milling cycle interval of 30 min. The powder samples were extracted at intervals of 1; 2; 5; 15 h during milling. The 15 h ball milled alloy powder was then heat treated 1 h at different temperatures (500; 600; 700; 800; 900; 1000 °C) under flowing high purity argon atmosphere. Then, ball milled alloy powder was consolidated by pressure sintering at 800 °C with 5 GPa pressure for half an hour in high purity argon atmosphere. The effects of milling duration (1; 2; 5; 15 hours), subsequent annealing at temperatures ranging from 500 to 1000 °C and consolidation of as-MA alloy on the structure and phase transformation were investigated by means of Rigaku Ultima IV X-ray diffractometer (XRD) with Cu K α ($\lambda=0,15409 \text{ nm}$) radiation. The range of scanning angle (2θ) was from 20° to 120° and the scanning rate was 2°/min. The crystallite size in the milled powders as well as after annealing and consolidation has been calculated from the XRD peak broadening using peak profile analysis after eliminating the instrumental and strain contributions. A scanning electron microscope with an energy dispersive spectrometer (EDS) was used to observe microstructures and measure the chemical composition of alloy powders. The thermal analysis in the temperature range of 30 – 1430 °C was carried out in a STA 449 F1 Jupiter (NETZCH Germany) differential scanning calorimeter (DSC) at a heating rate of 20 K/min under flowing purified argon atmosphere. Vickers hardness measurement of the consolidated samples was performed with a Digital Microhardness Tester MHV-1000 under a loading of 1,5N and a duration time of 15 s. 10-20 measurements were made on each sample for an average. The value

of Young modulus, E , was determined by instrumented indentation and calculated according to the Oliver-Pharr theory [14].

3. Results and discussion

3.1. Phase and structure evolution of elemental powders during MA

Fig. 1 shows the XRD patterns of the equiatomic AlCuNiFeTi MA powders prepared under different milling times.

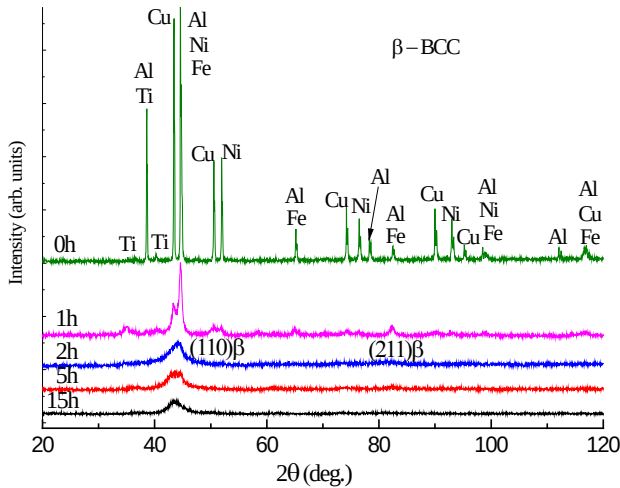


Fig. 1. XRD patterns of MA AlCuNiFeTi powders with different milling times

The pattern of 0 h exhibits peaks of all the pure elements in the initial mixture (blend). It can be seen that as milling time increases, drastic decrement of diffraction intensity and peak broadening are observed. The peak intensity decreases dramatically in the early stages of milling after the powder was grinded for 1 h. Obvious peak broadening can be observed and a lot of peaks become invisible as the alloy powder was milled for 2 h. The disappearance of diffraction peaks can be seen as the beginning of the solid solution formation. Only the most intense diffraction peaks can be clearly seen in the 5 h ball milled powder, which indicates the complete formation of the single phase solid solution with BCC structures (β -phase). As the milling time reaches up to 15 h, the diffraction peaks exhibit no change except for a minor broadening.

The intensity decrement and peak broadening in the diffraction can be attributed to the formation of nanocrystalline and high lattice strain induced by severe plastic deformation during the MA processing [15]. However, the cause of diffraction peak disappearance is complicated, which can be introduced by particle and crystal refinement together with high lattice strain, different atomic diffraction factor proportional to the atomic number, crystallinity decrement, formation of solid solution. For the X-ray diffraction peak intensity, the distorted atomic planes increase X-ray diffuse scattering effect and give smaller peak intensity [15]. Most of the diffraction peaks can hardly be seen after be ball milled for 2 h. Thus, the formation of nanocrystalline and high lattice strain are primary factors of the above-mentioned broadening and decrement of diffraction intensity of the diffraction peaks. Moreover, size mismatch effect between the constituents, increasing grain boundary fraction and increasing dislocation density produced by severe plastic deformation lead to the increment of lattice strain [16].

The crystal size of the alloy powders under different milling times have been calculated from the X-ray peak broadening using Scherrer's formula after eliminating the instrumental contribution.

The crystallite size of the alloy powders after 5 h of milling was nearly 40 nm. After 15 h of milling the crystallite size reduced below 20 nm. The crystal structure of the nanocrystalline AlCuNiFeTi HEA is identified as BCC with lattice parameter $a = 0.2914$ nm.

It is known that most of the binary metallic system in the AlCuNiFeTi high-entropy alloy system possesses limited solid solubility under equilibrium condition because of their positive heats of mixing [17]. However, the five components mechanically alloyed powders with milling duration higher than 2 h show simple solid solution structure, which can be attributed to the formation of supersaturated solid solution. The solid solubility extension is introduced by the effect of high mixing entropy and the non-equilibrium state of the MA process. As the component number increases, the random diffusion between different elements will be enhanced and thus the solid solubility is extended. In addition, the high-entropy of mixing can lower the tendency to order and segregate, and therefore makes the solid solution more easily formed and more stable than intermetallics and other ordered phases [5, 18]. On the other hand, the MA process can also extend the solid solubility limits [13]. Alloying occurs when the grain sizes of the elemental components decrease down to nanometer scale and then a substantial amount of enthalpy can be stored in nanocrystalline alloys due to the large grain boundary area. The energy stored in the grain boundaries serves as the driving force for the formation of solid solution [19]. Interdiffusion among the components occurs and the solid solubility is expected to increase with milling time increasing until it reaches a supersaturation level, beyond which no further extension of solid solubility will be achieved [13].

The entropy of fusion of all the elements in the present system is less than that of the configurational entropy of the five-component system ($\Delta S_{\text{mix}} = 13.38 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), which means the randomness due to the number of elements present in the system is higher than the randomness in the melting. This high configurational entropy (high randomness in the system) and also the large quantity of defects induced during MA process may lead to the formation of simple crystal structure in this HEA. The formation of amorphous phase at the equiatomic composition in the present system is not observed, possibly due to the smaller differences in the atomic sizes ($\delta = 4.9 \%$).

3.2. Microstructure and chemical composition characterization

The primitive powder exhibits a granular size of less than 45 μm . It's known that the ball to powder interaction during high-energy ball milling involves continuous plastic deformation, fracture, and welding of particles finally leading to the nanocrystallization or even amorphization [13]. In the early period of MA process the particles firstly cold weld together to form even larger particles. The cold welded agglomerations are crushed down to smaller particles when the milling is prolonged. This circulation leads the powder be refined gradually and facilitates the diffusion and alloying among different metallic elements. Equilibrium between the crushing and fragmentation is achieved at 15 h milling duration. The 15 h ball milled alloy powder shows refined morphology with average particle size of less than 5 μm as shown in Fig. 3.

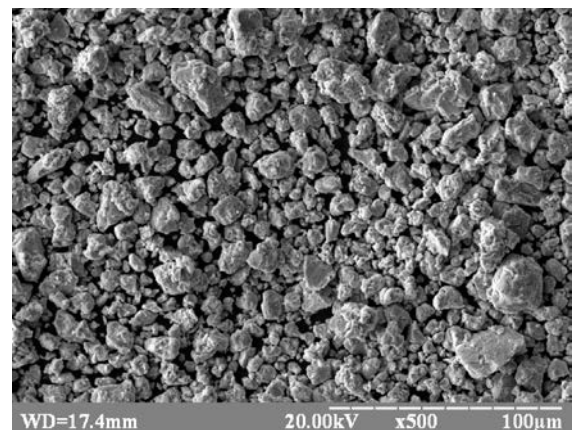


Fig. 3. SEM image of AlCuNiFeTi high-entropy alloy powder under 15 h milling durations

The quantitative elemental microanalysis results from the EDX spectrum (not listed in this paper) clearly indicates that the homogeneity and the equiatomic composition is maintained in each particle of the alloy after 15 h of MA.

3.3 Thermal analysis, annealing treatment and powder Consolidation

Fig. 3 depicts the differential scanning calorimetry (DSC) curve of the 15 h mechanically alloyed AlCuNiFeTi high-entropy powder.

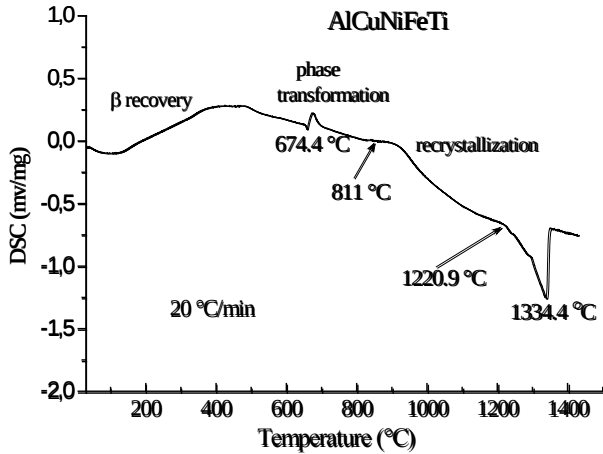


Fig. 3. DSC curve of the 15 h mechanically alloyed AlCuNiFeTi high-entropy alloy powder.

The 15 h mechanically alloyed powder exhibits exothermic/endothermic trends in the temperature range of 30–1430 °C. The endothermic peak at 95.6 °C is associated with energy absorption. This energy absorption can be related to the evaporation of process controlling agent (PCA) and gas. The long exothermic line in the temperature range of 130 to 350 °C and the broad exothermic peak with maximum at 400 °C in the DSC curve are associated with the release of internal stresses, such as structural deformation, lattice strain, etc. The exothermic peaks over 600 °C (at approximately 674.4 °C) is related to the energy release during the phase transformation process. The exothermic peak in the temperature range of 811 °C to 1075 °C can be attributed to the recrystallization of the BCC and FCC solid solutions. After heating to 1100 °C, an endothermic curve appears and it can be attributed to the gradual collapse of crystalline structure under high temperature. An endothermic peak appears at 1220 °C, indicating the beginning of melting. The endothermic peak at 1334.4 °C is designated as the alloy melting points.

The 15 h mechanically alloyed AlCuNiFeTi high-entropy alloy powder was annealed 1 h at different temperatures and their XRD patterns are shown in Fig. 4. The powder shows thermal stability up to 600 °C. The XRD patterns of the MA AlCuNiFeTi powders after thermal annealing at 500 and 600 °C in Fig. 4 reveals that long exothermic curve and the broad exothermic peak at 400 °C in the DSC curve represents the recovery of the β -phase with stress releases. This is because the 500 and 600 °C-annealed XRD patterns in Fig. 4 show that the broad peaks (110) and (211) of the β -phase become sharper. This represents a BCC solid solution (β -phase) with fine grains of about 30–35 nm in diameter. Fig. 4 reveals that after annealing at 700 °C, the XRD pattern exhibits FCC peaks along with original BCC peaks. This indicates the phase transformation, which corresponds to the sharp exothermic peak at 674.4 °C in the DTA curve. The FCC structural phase shows as the major phase after the alloy is annealed at 700 °C for 1 h. Fig. 4 indicates that after annealing at 800, 900 and 1000 °C, the powders exhibit both BCC and FCC mixed phases but the intensity of diffraction peaks increase significantly. However, the major phase transforms to the BCC structure while the FCC phase shows as the minor phase when it is annealed at 1000 °C. The increasing of XRD

peak intensities of the BCC and FCC phases results from the crystal coarsening and internal energy release during the annealing process and corresponds to the broad exothermic line in the temperature range of 800–1000 °C in the DSC curve.

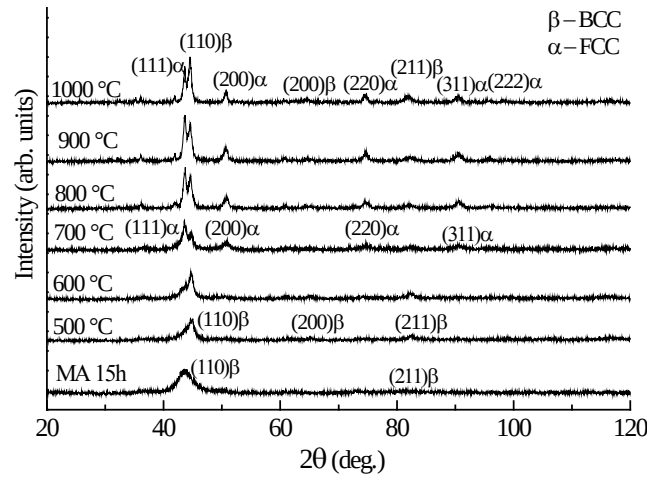


Fig. 4. XRD patterns of MA AlCuNiFeTi high-entropy alloy powders after thermal annealing at different temperatures

The phase transformation under annealing temperatures can be attributed to the metastable state of the supersaturated BCC solid solution. This metastable structure transforms to stable equilibrium phases in the final stage of annealing [16]. Both as-milled and as-annealed AlCuNiFeTi high-entropy alloy powders show simple solid solution structure, which indicates the successful synthesis of high-entropy solid solution alloy powder by mechanical alloying. The solid solution structure exhibits excellent thermal stability and will definitely facilitate its wide application in the future.

The XRD pattern of the 15 h mechanically alloyed AlCuNiFeTi high-entropy powder after consolidation by pressure sintering at 800 °C with 5 GPa pressure for 30 min is shown in Fig. 5, which evidences the phases formed in as-milled and as-consolidated conditions. The XRD pattern confirms that the as-consolidated alloy is composed of major BCC phase and the small volume fraction of FCC phase. Obvious peak broadening, shown in Fig. 5b, confirm the nanocrystalline nature of AlCuNiFeTi HEA with BCC and FCC structure.

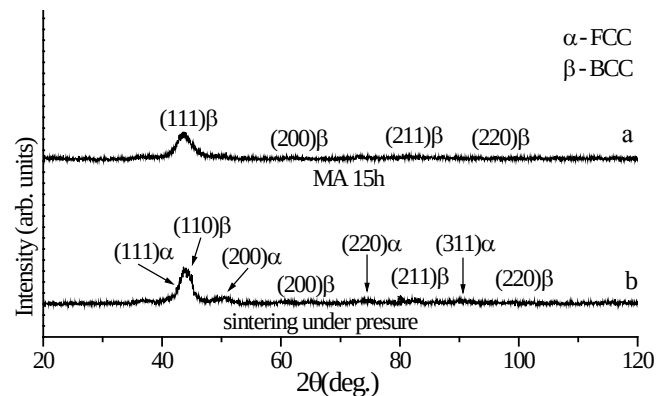


Fig. 5. XRD patterns of equiatomic AlCuNiFeTi HEA after MA (a) and consolidated at 800 °C with 5 GPa pressure for 0.5 h (b).

The crystallite size of the main BCC phase of the alloy is 50 nm and the lattice parameter of the phases present in the alloy are 0.2885 nm (BCC), 0.3573 nm (FCC), respectively.

SEM micrograph of bulk specimen is shown in Fig. 6, which reveals the presence of two phases. The SEM-EDX results are given in Table, which gives the compositions of the each phase present in the alloy. Grey phase (gray in Fig.6) has all the five elements and is rich in Al and Fe and depleted in Cu and Ni. Dark phase (dark in Fig. 6) is rich in Cu and Ni, and depleted in Fe and Ti. From the volume

fractions of the phases, it appears that the grey coloured phase is the BCC one and the dark one is the FCC phase.

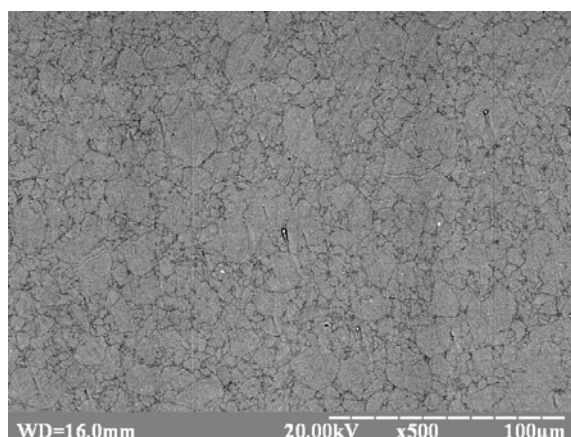


Fig. 6. SEM image of AlCuNiFeTi high-entropy alloy after sintering under pressure

Table 3. SEM-EDX results of nanocrystalline equiatomic AlCuNiFeTi sintering HEA

Phase	Al	Cu	Ni	Fe	Ti
Bulk	19.85	18.74	20.37	20.43	20.61
Gray	29.58	11.83	10.62	32.187	15.79
Dark	13.25	31.33	29.87	15.83	9.71

The Vickers's hardness of as-consolidated nanostructured equiatomic AlCuNiFeTi HEA has been found to be 10.7 ± 0.3 GPa. The Young modulus of the HEA is 127 GPa. The high hardness could be attributed to the nanocrystalline nature of the alloy, the solid solution strengthening equiatomic nature of the phases and the presence of two-phase structure [15, 18]. These AlCuNiFeTi HEA should also have good wear resistance according to the conclusion, that is, the wear resistance of materials is in general proportional to their Vickers hardness [20].

4. Conclusions

This study reports the preparation of quinary AlCuNiFeTi alloy by mechanical alloying (MA) processes. These alloy was then thermally annealed to investigate its structural evolution from elemental materials to non-equilibrium solid solution, and then to equilibrium phases at different temperatures.

The equiatomic high-entropy AlCuNiFeTi alloy has been successfully synthesised by mechanical alloying. Supersaturated single-phase solid solution of BCC crystal structure with crystal size less than 20 nm has been formed when the alloy is ball milled 15 h. In mechanically alloyed powders, recovery begins at 130 °C, and recrystallization occurs at higher temperatures approximately at 370 °C. The powder shows high thermal stability up to 600 °C. The solid solution structure transforms to BCC and FCC phases after annealing at 700 °C for 1 h. The phase transformation under annealing temperatures can be attributed to the supersaturated solid solution formation during the mechanical alloying process. Simple equilibrium phases obtained in the annealed state of mechanically alloyed powders confirm that the high-entropy effect enhances the formation of simple solid solution phases instead of complex compound phases.

The 800 °C sintered sample shows high Vickers hardness of 10.7 ± 0.3 GPa, indicating good sinterability and high strength of the mechanically alloyed AlCuNiFeTi high-entropy alloy.

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MECHANOCHEMICAL PROCESSES IN THE FORMATION OF ENGINEERING MATERIALS BASED ON POLYMERS

МЕХАНОХИМИЧЕСКИЕ ПРОЦЕССЫ ПРИ ФОРМИРОВАНИИ МАШИНОСТРОИТЕЛЬНЫХ МАТЕРИАЛОВ НА ОСНОВЕ ПОЛИМЕРОВ

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Abstract: *There were studied the mechanisms of interfacial processes when combining components of different composition, structure, and molecular weight in disintegrating type high-energy installations. The effects of formation of mechanochemical transformations products due to the flow of physical and chemical processes of interfacial interactions at the place of active centers of combined components were established. There were developed compositions and obtaining technology of composite materials and products containing mechanochemically combined components that cause the realization of synergies enhance the parameters of strength and tribological characteristics. The directions of the practical application of composites with mechanically activated components for the manufacture of tribological purpose products and coatings, which are used in metal-polymer constructions of vehicles and technological equipment.*

KEYWORDS: MECHANOCHEMICAL COMBINATION, ACTIVE CENTERS, INTERFACIAL INTERACTION, MODIFYING EFFECT, FUNCTIONAL COMPOSITES.

1. Introduction

According to the classical concepts of materials science of polymer composites most important factor determining the parameters of strength and tribological characteristics of the product, is the intensity of the interfacial interactions at the components interface. By controlling the mechanisms and kinetics of interfacial interactions in the composite on the basis of thermoplastics of different composition, structure and molecular weight, it is possible to achieve the optimal value of the strength of the boundary layer, which provides a maximum modification effect [1-5].

For industrial application of new approaches to the management of interfacial interactions is necessary to develop simple technologies based on the use of the equipment, the widespread practice - mixers, crushers, dismembrators, injection molding machines etc.

An analysis of the literature on the problems of creating high wear-resistant composite materials based on thermoplastic matrices, shows promising approach based on the directional change in the energy state of the particles of the components that determine the intensity of their interaction with the formation of the boundary layer of a determined composition, structure and strength. However, the range of engineering composites obtained using special energy impacts on the components in the manufacture and processing of the materials is extremely limited, which does not allow their widespread practical use for the development and manufacture of component parts of automotive components and the process equipment of various purposes increased resource [1 2, 6-11].

A special perspective on the management of the energy state of engineering materials components are mechano-chemical technology to carry out the synthesis of new products, thermodynamically compatible with the matrix polymer directly in the process of preparing a composition [1, 2, 5, 8, 12-14].

The purpose of the work was to establish the mechanisms of formation of the energy state of components in different types of technological impacts for the optimal structure of interphase boundary layers in filled thermoplastic matrix, which defines the parameters of service characteristics.

2. Methods of research

As binders for composites were used thermoplastic polymers - polyamide 6 (PA 6) and polyamide 11 (PA 11), high density polyethylene (HDPE), polypropylene (PP), polytetrafluoroethylene (PTFE) in the state of industrial supply (JSC "Grodno Azot" JSC

"Polymir", JSC "KhimvoloknoMogilev"). Some experiments were carried out with the regenerated thermoplastic (HDPE, PP, LDPE) obtained at JSC "Belytorpolimer" in accordance with the existing standard documentation. To form the coatings used thermoplastics dispersed particles obtained by granular semifinished products cryogenically dispersing.

For the formation of multilayer coatings and components modifying with different kinds of technological impact used fluorides - solutions of fluorinated oligomers "Epilam" and "Foleoks" with a molecular weight of 1000 - 2000 units (manufacturer - Institute of Synthetic Rubber, St. Petersburg, Russia) and products thermogas dynamic synthesis polytetrafluoroethylene produced under the brand name "Forum" (Institute of Chemistry FEB RAS, Vladivostok, Russia).

In order to control the parameters of the energy state and dispersion of components used technological methods based on mechanical dispersion, mechanochemical combination, the impact of energy flows in the heat treatment, exposure to corona discharge, microwave, laser beam, using original cryogenic plants dispersion, rolling shear (Yanka Kupala State University of Grodno), the installation of the planetary mixing AGO-2 (Institute of Solid State Chemistry and Mechanochemistry of the SB RAS) systems for the treatment of microwave radiation, laser QUANTUM-15, high-shredder dismembrator, installations for the electrostatic application of coatings (JSC "Grodno Mechanical Plant", JSC "Belcard", JSC "Lakokraska"). Selection of the type of energy impact and the conditions for the activation process has been driven by structural and chemical and dimensional parameters of components, the functionality of the coatings or products.

To obtain composite materials used highly dispersed, including nanoscale particles of carbonaceous (UDD, UDAG, nanotubes, colloidal graphite), siliceous (mica, clay, flint, shungite tripoli), fluorine (UPTFE) and metal-containing (oxides of Fe, Cu, Zn) compounds obtained by the original technology of manufacturer (JSC "Sinta", SSI "Lykov Institute of Heat and Mass Transfer", Institute of Chemistry FEB RAS), or as a result of special technological effects on the semi-finished product (mechanochemical dispersion, sublimation).

Physical and chemical processes at the interface "matrix-filler", "coating-substrate" in the preparation and processing of composites and coatings and use of the products were evaluated using the methods of IR-spectroscopy (Tensor-27), X-ray diffraction (DRON 2.0, DRON 3.0), DTA (Thermoscan-2) by conventional means. The morphological parameters of the particles and substrates subjected to different types of energy impact, examined using an atomic force

(NT-206), scanning electron (Mira, Tescan), optical (MDS) microscopes. Energy state of dispersed particles, samples of composites, coatings and substrates investigated by thermally stimulated currents (TSC-analysis) on the original installation (ODL "Microtestmachines").

3. Results and discussion

Used in materials science of composite materials based on polymeric, oligomeric and combined matrix dispersed modifiers differ not only in composition, crystal-chemical structure, dimensions (dispersion), and energy state, which determines their activity during interphase interactions [1, 3, 6 9-11].

Energy state of the dispersed particles or substrate is a multi-value, depending on the magnitude of the surface energy, the formation mechanism of uncompensated charge, its relaxation time under the impact of various physical and chemical, electro-physical, thermal, and others processes.

When substantiated choice of functional materials and metal-polymer systems is necessary not only to provide a given level of

activity in the processes of interfacial interaction between the components, but its expression in the formation of the composite (system) in the optimal range of parameters of technological factors. Therefore, in each process must be justification for the type and mechanism of energy impact on the components that determine the formation of the boundary layer with optimal parameters of adhesive tribological, deformation-strength, thermal and others parameters defining a given service life of product or design.

It was considered the effect of the common types of technological impacts - thermal, laser, mechanochemical, ultrasound on parameters on the morphology and the energy state of the dispersed particles and the coatings produced from natural and synthetic semi-finished products - clay, flint, schungite, tripoli, fragments of carbon fibers (CF), polyamide 6, polytetrafluoroethylene (PTFE) polyolefins (HDPE, PP, EVA), PET and other polyester.

Analysis of the morphology of the surface layer of single particles obtained by using various technological impacts and geochemical factors indicates the presence of nanoscale elements of spherical, whisker and plate habitus (figure 1).

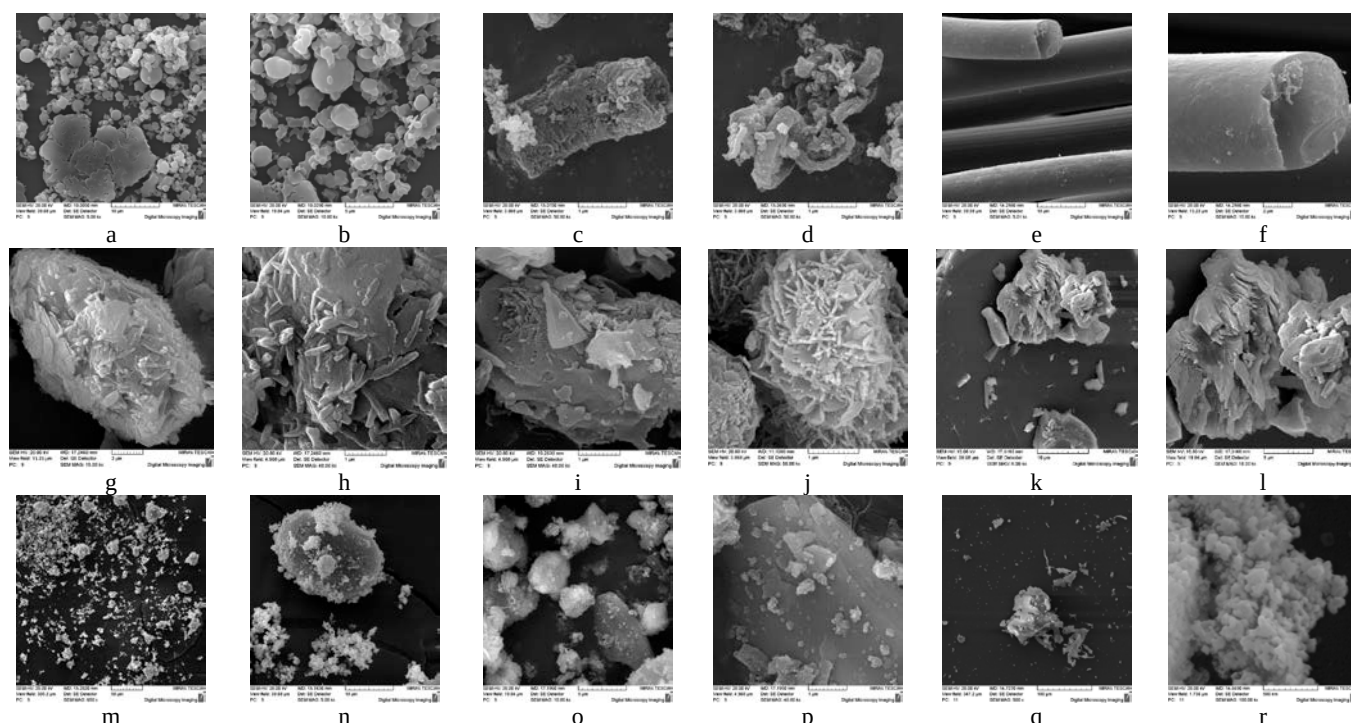


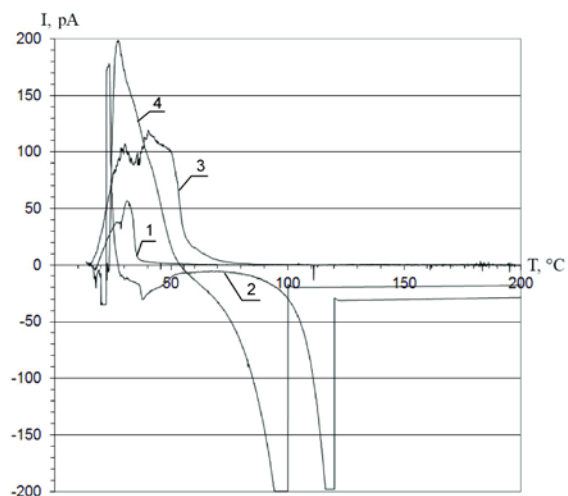
Figure 1 - The characteristic morphology of the dispersed polymer matrix modifiers: ultrafine polytetrafluoroethylene (a, b), carbon nanotubes (c, d), carbon fibers (e, f), clays (g, h), tripoli (i, j), glass (k, l), metallurgical products (m, n), schungite (o, p), cryogenic grinding PA 6 (q, r)

The presence of such nanoscale elements in accordance with modern concepts of condensed matter physics and quantum physics determines the particular energy state of the surface layer, characterized by the concept of "nanostate" [15-18]. It is obvious that the kinetics and mechanisms of interfacial processes in the high-molecular matrix, the modified active particles depend on the parameters of the energy state and its impact on the structure of the boundary layer under the influence of technological factors in the formation of the composite.

Analysis of the energy state of the dispersed particles of different composition, technological prehistory and structure under the criterion of thermally stimulated currents (TSC) indicates the presence of prerequisites of impact on the structure of the boundary layers, determined by temperature (figure 2), which manifests the effect of "nanostate" due to the presence of nanoscale elements on the modifier surface.

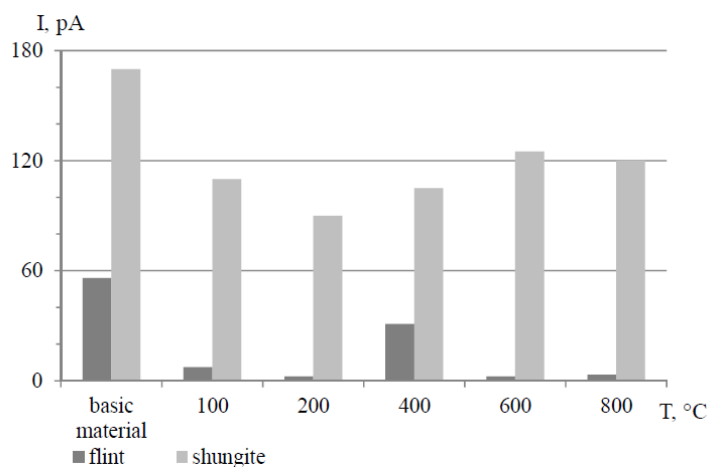
Another factor determining the activity of the particles, is the intensity of the impact energy (thermal, mechanical, laser, ionizing, etc.) to the semi-finished product or substrate, which defines mechanisms for desorption, dehydration, dehydroxylation,

oxidation, degradation and others processes, changing the concentration of charge carriers of different types. For example, in the pre-heat treatment of particles common modifiers of polymer matrix - schungite and flint, in the temperature range 100 - 800 °C changes significantly the value of the thermally stimulated current (figure 3). A characteristic feature of the energy impact is change of the initial morphology of the surface layer of the dispersed particles. Analysis of the morphology of the surface layer of dispersed particles obtained by dispersing a variety of semi-finished products by the energy impact of various types (thermal, mechanical, laser), indicates the presence of the characteristic features which determines interfacial interactions activity. For natural carbonaceous semis (oxidized graphite, schungite) is characteristically the formation of a relatively smooth surface layer with nanoscale roughness. Synthetic carbon particles (carbon nanotubes, carbon fibers (CF)) have a surface layer formed from globular fragments and sufficiently high defect. Silicate-containing particles (flint, glass, tripoli, clay) practically do not change the initial roughness after heat treatment (figure 4).



Particles size 100 - 200 microns

Figure 2 - The spectra of thermally stimulated currents (TSC) of dispersed particles of flint (1) shungite (2), tripoli (3), carbon nanotubes (4)



Particles size 50-100 microns

Figure 3 - Dependence of the thermally stimulated current maximum $I_{\max}$ from processing temperature of dispersed particles

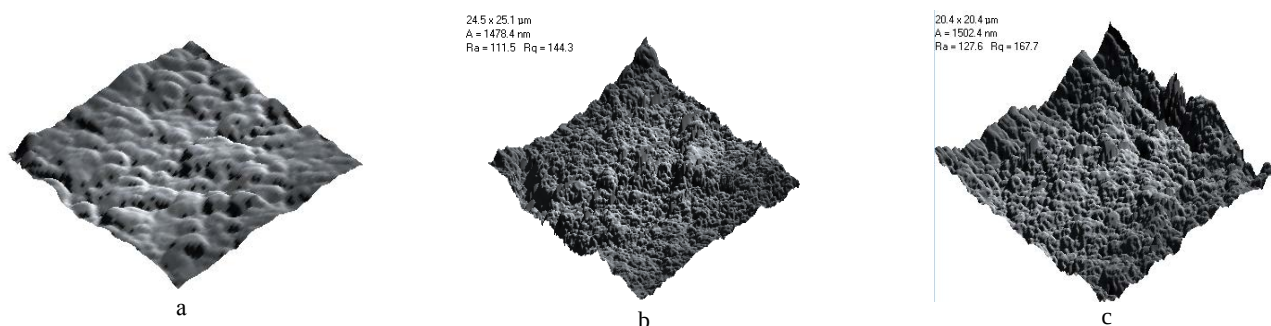


Figure 4 - A typical morphology of the dispersed particles of flint (a), clay (b), shungite (c), subjected to heat treatment in the 250 - 450 °C temperature range

Exposure to concentrated stream of the laser radiation allows to obtain particles with a developed relief as when using the organic polymer (PTFE, HDPE, PET) and carbonaceous (CF, shungite, electrode graphite) and silicon (flint, glass) intermediates. It was established the influence of the type of power influence on the energy state of the dispersed particles. The energy parameters, characterized by value of thermally stimulated currents, while volumetric thermal impact are reduced (figure 3), while the concentrated (local) impact - increase. This factor indicates the need in the justification of technological modes of manufacture of composite materials and their processing into products accounting factor morphology and energy state to optimize the conditions of intense interfacial interaction of components at different structural levels. There were established general regularities of formation of the active state of the modifiers-dispersed particles, which are caused by a combination of crystal-chemical premises and the morphology of the surface layer. The choice of the activating energy impact depends not only on the characteristics of the composition and structure of modifiers, but also on the existence of the most effective actions directly in the formation of a composite material (articles) for the given parameters of the impact of technological factors. Therefore, the optimal of modifying effect have components with developed morphology of the surface layer in which the energy parameters depend not only on the structure but also the geometry of the fragments, causing the possibility of implementing nanostate.

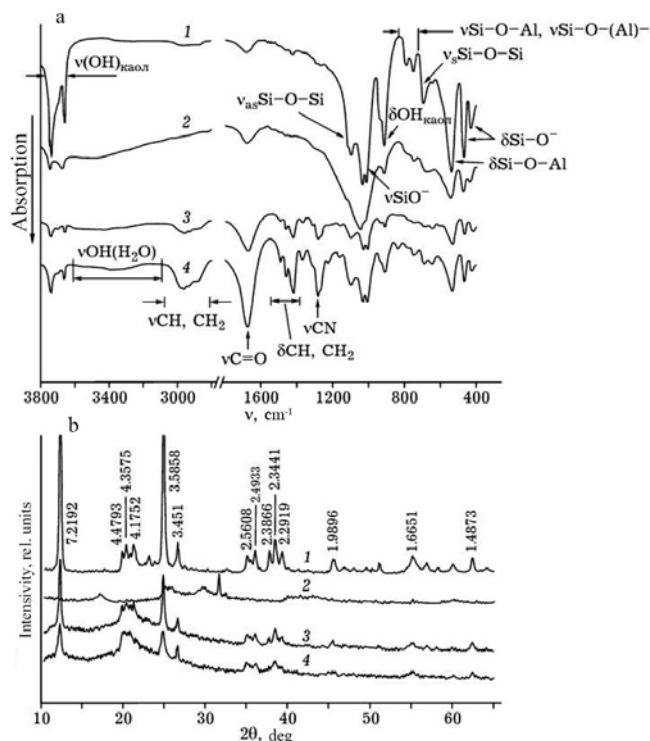
As previously noted, one of the most effective directions of realization of the energy factor to optimize the structure of polymer composites technology applies mechanochemical (tribochemical) effects, during which can be formed foods of interfacial interaction with the boundary layer formed by active fragments of the polymer matrix and modifier [1, 3-6, 8 12-14].

Properties of mechanical activation consists in the fact that regardless of the initial structure of the components, of their crystal structure and energy state, while exposure to a different type of mechanical stresses (compression, shear, torsion), conditions are created not only to change the morphology of the surface layer of both components to form the most developed layer but for the adsorption, including chemisorption, interaction of active fragments of various types and structures (quantum dots, radical products mechanodegradation, lattice defects, defects of the composition (impurities), etc.). At the same time in a joint mechanical activation becomes a secondary factor of stability of the active state stipulated by the presence of an electret charge, uncompensated electrons of the radical fragments of juvenile surfaces and other assumptions and the time of relaxation. Simultaneous exposure of different mechanical stresses on the components of the mixture allows for mechanisms of solid-phase interaction with the formation of non-stoichiometric products, which can not be formed by the reactions of the classical exchange and connection.

Classic understanding of condensed matter mechanochemistry and research in the field of tribochemistry of metal-polymer systems can justify the use of joint mechanical activation technology for the preparation of the components of functional materials based on thermoplastic matrices (PA 6, HDPE, PP, EVA, PTFE) [1, 12-14]. In conventional milling of thermoplastic semi-finished by abrasion, crushing at ambient and cryogenic temperatures to form products with the active state characterized slight relaxation time due to leakage of adsorption processes components of the environment. Mechanochemical activation of a mixture of components in percussion or tangential action systems helps to ensure effective interfacial interaction of formed disperse products until the formation of the chemisorption bonds in the boundary layers.

Model studies of the effectiveness of mechanochemical activation (MA) of mixtures of components were carried out on dispersed

powders of thermoplastic polymers of different composition, structure, crystallinity and hygroscopic (ultrathene, polypropylene, polyamide 6, poly-N-vinylpyrrolidone PVP) and siliceous modifiers which have found wide application in materials science of polymer composites, including nanomaterials (kaolinite, flint, SiO_2). Treating the mixture of components was carried out in a high energy mill impactor AGO-2 at accelerating action in the range of 20 - 60 g in 1 - 4 minutes. By IR-spectroscopy and X-ray analysis (Figures 5 and 6) found that when the joint activation of ultrathene, PVP and kaolinite the interaction of the lone pair of electrons of the polymer and the active sites on the acidic nature of juvenile surfaces of kaolinite.



The polymer content in the mixture of 30 wt. % (1, 2) and 80 wt. % (3, 4)
Figure 5 - The IR spectra of (a) and a diffraction pattern (b) mixtures of kaolinite with PVP before (1, 3) and after MA for 4 minutes (2, 4)

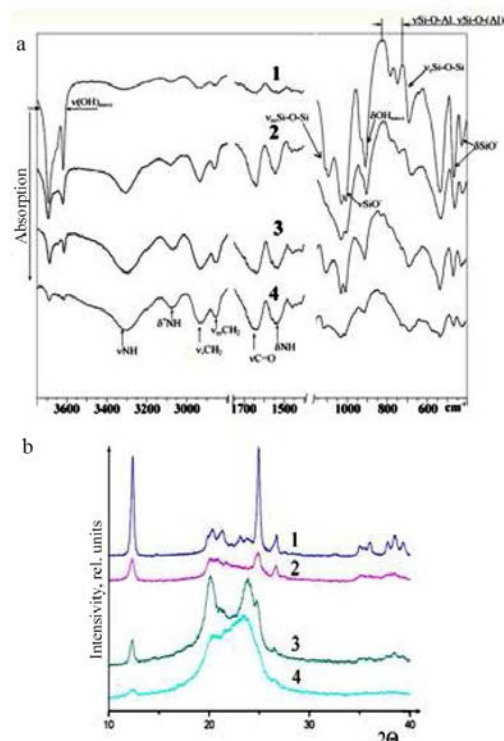
As objects of research used powdered polyamide 6 with the size of the individual particles of 80-200 microns. Used for modifying the layered silicate – kaolinite $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$. The mechanical activation was carried out in a planetary-type ball mill marks AGO-2 with water cooling.

In the process of mechanochemical combining components may flow interfacial processes leading to the formation of the boundary layer increased strength. Indeed, the IR spectra of the polyamide mixture (30 wt.% + kaolinite) after mechanical activation for 4 minutes, as in the case of pure mechanical activation kaolinite, decrease in intensity of bands and deformation vibrations of: ν , δ (Al)-OH; ν , δ Si-O-(Al), Si-O-Al respectively region 3800-3600 cm^{-1} , 950-850 cm^{-1} , 850-780 cm^{-1} with a maximum of 545 cm^{-1} (Figure 6, and).

In a polymer composite diffractogram kaolinite reflexes persist only decreases their intensity: $d_1 = 7,17$ ($I/I_s = 100$), $d_2 = 3,57$ ($I/I_s = 80$) and $d_3 = 3,37$ ($I/I_s = 35$). Polyamide reflexes imposed a series of reflections of kaolinite in the $d = 4,47$ - $3,74$, so we can not judge any change of polyamide reflexes settings (Figure 6b).

By increasing the content of the polyamide in the mixture, for example, up to 60%, the pattern of bands change the kaolinite and the polyamide in the IRS after mechanical activation for 4 minutes becomes completely different. After activation, fade bands corresponding to vibrations ν_{as} and ν_s Si-O-Si bonds of the silicon tetrahedra frame region 1150-1050 cm^{-1} and with a maximum

Similar results were also obtained when MA of other joint mixtures - HDPE, PP, PTFE and silicon-containing and carbonaceous components (flint, SiO_2 , CF), which indicates that common mechanisms interfacial of active fragments formed due to the mechanism of stress and leading to the destruction of the original structure and formation of active fragments capable to recombination. Of particular interest are the composites obtained by mechanochemical combining of polyamide 6 with the functional components that should be used for the manufacture of products with increased parameters of strength characteristics and tribological coatings.



The polymer content in the mixture of 30 wt. % (1, 2) and 80 wt. % (3, 4)
Figure 6 - The IR spectra of (a) and a diffraction pattern (b) mixtures of kaolinite with polyamide 6 before (1, 3) and after MA for 4 minutes (2, 4)

685 cm^{-1} . There is a decrease in the intensity and broadening of all bands of kaolinite. There has been no shift of the bands of the polymer, as well as the emergence of new bands. In this case there is, apparently, the gradual amorphization of kaolinite. However, in the presence of polymer failure of silicate structure occurs not so active. In the diffraction pattern of the sample are very weak but clear reflections from the basal planes of kaolinite: (001), $d_1 = 7,17$ and (002) $d_2 = 3,57$ (Figure 6b).

Polyamide reflexes broaden and merge into one with two peaks $d_1 = 4,4$ and $d_2 = 3,7$, indicating that certain changes in the structure of the polymer.

Mechanically activated particles of polyamide-kaolinite mixture are characterized by developed morphology that will likely be reflected in the activity of the system (Figure 7). Based obtained by scanning electron microscopy data is observed the presence of nanoscale fragments lateral size of 20-50 nm on the surface (Figure 7 c, d). The introduction of this mechanically activated mixture in a polyamide matrix should lead to a change in the parameters of physical and mechanical properties of the polymer matrix. This system has advantages over mechanically activated particles of metals, silicates, metal oxides, etc., as the presence of the boundary layer grafted to the silicate particles increases the thermodynamic compatibility with the base polyamide matrix.

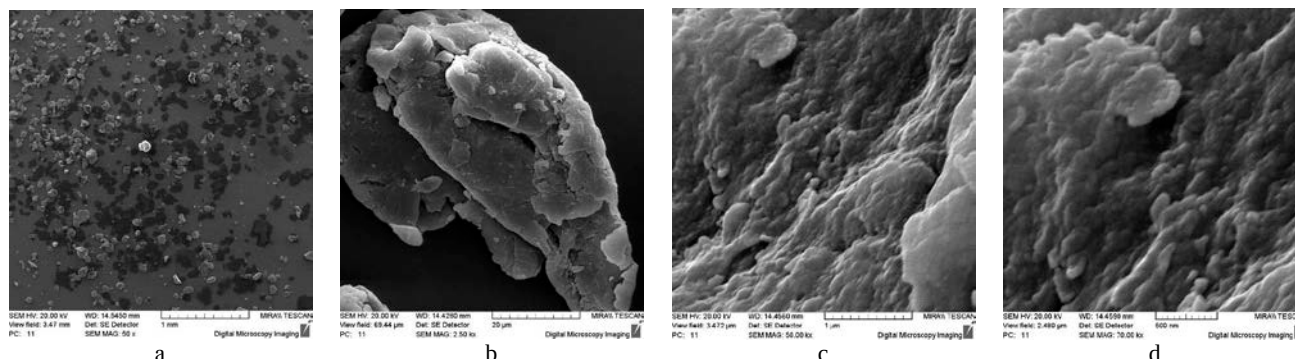


Figure 7 - The morphology of the particles of polyamide 6 and kaolinite: initial (a, b) and the mechanically activated for 4 min at 60g

Introduction to the polyamide matrix of mechanically activated particles leads to a change in the parameters of strength characteristics of the composite material. Table 1 shows the parameters of physical and mechanical properties of polyamide 6, modified by mechanically activated kaolinite-PA6 mixture.

Table 1 - Physical and mechanical properties of polyamide 6, modified mechanically activated particles "PA6-kaolinite"

Parameters	The concentration of modifier			
	initial material	0,5 %	2 %	5 %
Physical yield strength, MPa	30,6	49,5	28,3	16,2
Deformation under physical stress limit, %	19,85	6,9	4,2	4,9
Strength at maximum force, MPa	48,6	77,6	30,2	37,6
Deformation at maximum force, %	133,4	81,6	5,6	9,2
Strength at break, MPa	48,6	77,6	30,2	37,6
Strain at break, %	133,4	81,6	5,6	9,16

The obtained results allowed optimizing formulations of composite materials based on polyamide 6, modified by mechanically activated particles "polyamide-kaolinite" used for the application of tribological coatings.

Studies on the effect of the energy factor in the technology of functional composite materials based on thermoplastic matrices allowed us to develop formulations for use in the construction of machinery and technological equipment with high operational resources.

For the development of composite materials for the application of tribological coatings use polymer thermoplastic matrix produced tonnage, including domestic manufacturers – PA 6, HDPE, PP. Modifying the matrix polymers by functional components (tripoli, flint, kaolinite, UPTFE, HDPE) was performed by mechanochemical activation (MA), followed by grinding at cryogenic temperatures (-198 °C). The coatings are produced by fluidized bed. Comparative studies (Table 2) show that the developed compositions not only not inferior to imported analog PA 11 («Rilsan», France), but also significantly superior in its durability. This developed on the basis of the domestic polyamide 6 (JSC "Grodno Azot") compositions of composite materials have a value of 3 - 5 times lower than the imported counterpart. Compound of composites with mechanically activated components have been successfully tested in the construction of driveshafts trucks, lathe chucks, produced by JSC "Belcard" and JSC "BelTAPAZ".

Installed features of change of the energy state of the polymer particles and substrates subjected to various kinds of technological influences (thermal, laser), allowed to develop recommendations for their use as components of dietary supplements and bactericidal components of medical devices.

When using MA technology obtained layered composites in which natural silicate (talc) acts as a carrier and biologically active ingredient in the form of organic acids and salts (succinic acid, sodium succinate, chitosan succinate, sodium stearate, etc.) are chemically bound with bearer form. Compounds of mechanically activated components can be used in the preparation of

pharmaceuticals and dietary supplements of multifunctional actions using environmentally friendly way [14].

Table 2 - Characteristics of composite materials for tribological coatings

characteristics	The parameter for the material		
	PA 11 «Rilsan», France	PA 6, JSC "Grodno Azot"	Developed composition
Traction resistance, MPa, not less	43	50	67-78
The adhesion cm, not less than	20	15	27-32
Brinell hardness, MPa	90	100	89-94
friction coefficient	0,05-0,2	0,15-0,25	0,10-0,15

High-energy impact on the dispersion components (shungite) and plastic products (thermal or laser) provides formation of uncompensated charge with a long relaxation time, the presence of which prevents the development of pathogenic environment E. coli, Salm. enteridis, St. aureus. These results extend the range of processing methods to enhance microbicidal properties of articles made of polymeric materials based on particular components giving energy state, and can be used for the manufacture of composite materials used in medical practice.

Dispersed particles activity subjected to energy shocks, manifested in the developed morphology of the surface layer and the presence of uncompensated charge with a long relaxation time, allowed to develop effective compounds of lubricants and greases for heavy-duty friction units on the basis of industrial products. With the introduction of fine particles, activated by thermal, laser or mechanochemical action in the lubricating composition are formed charge clusters that improve the load-carrying capacity and thermal stability of the separating layer in the area of frictional contact. The compositions of lubricating oils, hydraulic fluids and greases for use in the construction of automotive components (brake chambers, driveshafts), lathe chucks for metalworking equipment and friction belt conveyors were developed. The compositions have been testing at the leading enterprises of the Grodno region (JSC "Belcard", JSC "BelTAPAZ") and recommended for implementation.

In the developed compounds of composite materials and lubricant medium developed regulatory and technical documentation, regulating their use in friction, automotive components and designs of belt conveyors.

4. Conclusion

There were studied peculiarities of the morphology and the energy state of the dispersed particles of silicon and carbon-containing semi-finished products (shungite, tripoli, flint, electrode graphite, polytetrafluoroethylene, polyethylene, etc.), obtained in the technological impact of different energy. The fact of the formation of the predominant active form and dispersed state of the particles due to the occurrence of crystal-lattice or destruction of the

molecular structure, which leads to the localization of the charge carriers in the surface layers of particles with a strong structure and enhance its ability to adsorption react with polymeric, oligomeric matrices and their degradation fragments, formed under the influence of energy factors (thermal, laser, mechanical) is established.

There was established the mechanism of interfacial interactions at the joint mechanical activation of dispersed particles of thermoplastic polymers (PA 6, PP, EVA, PTFE) and silicate modifiers by complex influence of mechanical stresses, which consists in the formation of the chemisorption bond in place of the active centers of polymer radicals and the surface layer of silicate particles (kaolinite, silica, flint). There was established possibility of mechanochemical interactions of dispersed particles of layered silicates, organic acids or their salts (succinic acid, benzoic acid, sodium benzoate, and stearates, etc.) during MA to form layered composites in which natural silicate is carrier of grafted an organic component. Expediency of mechanically activated components for obtaining of composite materials with enhanced service performance parameters is shown.

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ENERGY ASPECTS OF STRUCTURE FORMATION OF NANOCOMPOSITES BASED ON THERMOPLASTIC

ЭНЕРГЕТИЧЕСКИЕ АСПЕКТЫ ФОРМИРОВАНИЯ СТРУКТУРЫ НАНОКОМПОЗИТОВ НА ОСНОВЕ ТЕРМОПЛАСТОВ

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Abstract: *Using methods of spectroscopy of thermally stimulated currents (TSC spectroscopy), atomic force microscopy (AFM) and scanning electron microscopy (SEM) analysis was done of the energy state of dispersed particles of different composition and structure - mineral (tripoli, shungit, clay, mica, silica) and synthetic (ultra dispersed polytetrafluoroethylene, nanodiamonds, silicate glass, metal oxides). There was established the effect of occurrence of the special energy state of dispersed particles, due to the presence of nanoscale components of the structure. There were studied parameters of the energy characteristics of the modifier (value and density of the residual charge, activation energy of the relaxation, time of charge relaxation et al.) depending on the action of technological factors - temperature, mechanical stress, energy flows. The optimal ranges of occurrence of effective modifying action in macromolecular matrices of various types - polymeric, oligomeric, combined. There were proposed technological principles formation of mechanical engineering nanocomposite materials with improved parameters of deformation and strength and tribological characteristics.*

KEYWORDS: ENERGY STATE, DISPERSED PARTICLE, TECHNOLOGICAL IMPACT, MODIFYING EFFECT, NANOCOMPOSITE MATERIAL.

1. Introduction

In a wide range of engineering materials occupy a special place composite materials for various purposes, which are obtained by modifying the matrix polymer, oligomeric and combined components of the target on the basis of silicon, carbon, metal-containing compounds with a given dispersion and form [1-22].

Acting in materials science of polymer composites based on commercially available thermoplastics paradigm based on three main approaches of structure parameters management:

a. on the supramolecular level by introducing in binding matrix modifiers providing the prevailing mechanism of formation of the supramolecular structure of the given type and geometric parameters, or the use of special types of thermal processing on products, semi-finished or functional structures [8, 12];

b. on the interfacial level by introducing reinforcing components mainly fiber-like fragments of a predetermined length of fragments into the polymer, oligomeric and combined matrixes [1-7, 10-22];

c. on the intermolecular level by forming a three-dimensional crosslinked structure under the action of high-energy radiation. [19] Without considering the features of mechanism of modifying action of the dispersed particles of different composition, structure and dispersion, we note the common criteria for their informed choice:

- 1) prevalence, availability and cost of raw semi-finished;
- 2) adaptability to the dispersion process in obtaining a stable output optimal size fraction;
- 3) processability of combination of dispersed particles with a matrix binder;
- 4) required activity in the modifying processes on the molecular, supramolecular and intermolecular levels;
- 5) technological time of active state relaxation;
- 6) ecological compatibility and safety of application in traditional technology of composite materials;
- 7) ability to secure recycling of technologically justified waste products and amortized articles made of composite materials.

The implementation of the entire set of selected criteria in a specific composition modifier for a particular type of composite material, is generally difficult to achieve the solution of which depends on many factors, primarily on the established methodological approaches in a regional or national industry caused by the material, human, technological, organizational maintenance of existing facilities.

However, in all cases the use of high-matrix modifiers, generalizing (basic) criteria of their choice is given the effectiveness of action

necessitates technically significant effect of improving the parameters of strength, tribological, thermal, adhesive and others service characteristics with minimal economic costs, taking into account the material and energy intensity and staffing processes of production and consumption target.

The obvious is the condition for the implementation of this criterion, suggesting the achievement of optimal structural state at a given level of organization of the composite material at a particular combination of matrix binder, a kind of modifier and combining and processing technologies.

An analysis of the literature devoted to materials science and technology of composite materials based on high molecular matrices [1-22], indicates a lack of unified methodological approaches to the selection of functional modifiers to create a composite of a particular functional purpose.

As a rule, is implemented the traditional labor-intensive approach based on the use of results of experimental studies to determine the mechanisms of modifying action of various components of the composition, structure, and technology for dispersion. The practical implementation of this approach is not only costly, but also tends to not achieving an optimal technical effect. Moreover, in some cases are formed the conditions of manifestation of "structural paradox", the essence of which is inadequate change the service characteristics of composite materials, even when using high-efficiency, including high strength and heat resistance, components. An example of such a manifestation of the structural paradox is given in [23].

The obvious is the need to develop criteria for informed choice of components to create functional materials that take into account the most common features, common to all types of condensed matter, which form the physical paradigm of modern materials.

The objective of this work was to analyze the possibility of evaluating the effectiveness of modifiers in high-molecular matrix on the criteria of energy state.

2. Methods of research

As binders for composites using thermoplastic polymers - polyamide 6 (PA 6) and polyamide 11 (PA 11), high density polyethylene (HDPE), polypropylene (PP), polytetrafluoroethylene (PTFE) in the state of industrial supply (JSC "Grodno Azot" JSC "Polymir", JSC "HimvoloknoMogilev"). Some experiments were carried out with the regenerated thermoplastic (HDPE, PP, LDPE)

obtained at JSC "Belvtorpolimer" in accordance with the existing standard documentation.

In order to control the parameters of the energy state and dispersion components were used technological methods based on mechanical dispersion, mechanochemical combination, the impact of energy flows in the heat treatment, exposure to corona discharge, microwave, laser beam, using original cryogenic plants dispersion, rolling shear (Yanka Kupala State University of Grodno), the installation of the planetary mixing AGO-2 (Institute of Solid State Chemistry and Mechanochemistry of the SB RAS) systems for the treatment of microwave radiation, laser QUANTUM-15, high-shredder - dismembrator, installations for the electrostatic application of coatings (JSC "Grodno Mechanical Plant", JSC "Belcard", JSC "Lakokraska"). Select the type of energy and the impact of the conditions for the activation process was driven by the composition, structure and chemical and dimensional parameters of components, the functionality of the coatings or products.

To obtain composite materials used highly dispersed, including nanoscale particles of carbonaceous (UDD, UDAG, nanotubes, colloidal graphite), siliceous (mica, clay, flint, shungite tripoli), fluorine (UPTFE) and metal-containing (oxides of Fe, Cu, Zn) compounds obtained by the original technology of manufacturer (JSC "Sinta", SSI "Lykov Institute of Heat and Mass Transfer", Institute of Chemistry FEB RAS), or as a result of special technological effects on the semi-finished product (mechanochemical dispersion, sublimation).

Physical and chemical processes at the interface "matrix-filler", "coating-substrate" in the preparation and processing of composites and coatings and use of the products were evaluated using the methods of IR-spectroscopy (Tensor-27), X-ray diffraction (DRON 2.0, DRON 3.0), DTA (Thermoscan-2) by conventional means. The morphological parameters of the particles and substrates subjected to different types of energy impact, examined using an atomic force (NT-206), scanning electron (Mira, Tescan), optical (MDS) microscopes. Energy state of dispersed particles, samples of composites, coatings and substrates investigated by thermally stimulated currents (TSC-analysis) on the original installation (ODL "MICROTESTMACHINES").

3. Results and discussion

An analysis of the literature devoted to materials science and technology of polymeric composites [1-23] suggest that the use of modifiers that are in the nanometer range, the so-called nano-sized particles of different composition, structure and technology of. In the presence of a large number of studies on the mechanisms of modifying action of the nanoparticles in the polymer, oligomer and combined matrices, it is necessary to emphasize the ambiguity of the results and the lack of a unified view of determining the dimensions and the concentration range of the optimal effective action of dispersed particles in the matrix binders, differing in molecular weight, chemical structure macromolecules, structural features of the organization under the influence of technological factors - temperature, pressure, exposure time and others. The most effective multi-purpose modifiers appeared natural compounds of silicon - zeolites [21, 22], fine products of detonation [14, 18], termogas dynamic and plasma [20, 23] synthesis - nanoceramics Sialons, nanodiamonds (UDD), diamond-charge (UDAG) nanoceramics, fullerenes, nanotubes, thermally split graphite, mica, clay, as well as nano-sized particles of metals and oxides obtained by thermolysis of metal precursors in molten thermoplastics [25]. This set a number features of modifying action of nanoparticles of different composition, structure and technology which determine the efficiency of use. These features can be systematized by characteristic criterions:

- 1) increasing the degree of dispersion nonlinear effect on the energy state of the particles, and efficiency of their modifying action [24];
- 2) increase the degree of dispersion of the particles increases the tendency to the formation of cluster structures of different structures [21];

- 3) the activity of modifying action nonlinear depends not only on the composition, structure and technology of fine particles, but also on external, including technological, factors acting on components during their production, storage, manufacturing and processing of composite materials [24];

- 4) an increase in the degree of dispersion of the particles determines the non-linearity of the economic costs of their production, storage and practical use;

- 5) dispersed modifiers particles of high-molecular matrix are usually necessitated the development of special technologies and equipment for their practical application [15, 20, 22];

- 6) superfine (including nano-sized) particles have a negative impact on the environment and require special measures to comply with the conditions for their safe production and use [26];

- 7) long-term (long-acting) effects of superfine (including nano-sized) particles on the mechanisms and kinetics of physical and chemical (including biochemical) processes studied not fully [24, 26];

- 8) the effectiveness of modifying action of superfine (including nano-sized) particles in some cases inadequate to prognosis due to technological constraints of the optimal (settlement) conditions of interfacial interactions at various levels of the structural organization of the composite material [14-24].

Distinctive features of the practical application of nanoscale modifiers indicate the need for systematic analysis of the mechanism of their action, which will determine the most characteristic features of their effective action and conditions for their manifestation in practical technology of polymer nanocomposites.

In order to establish these common characteristic features studied the morphology of the dispersed particles of different composition, structure and technology which have found wide application in practical materials science. SEM and AFM methods found that, regardless of individual characteristics of the dispersed particles are characterized by their tendency to agglomerate and form cluster structures of different structure and the presence of micro-particles in the range of components that belong to the nanoscale. Such nanoscale components have a plate (Figure 1b, 2b, 3b), spherical (Figure 1 d, 2 f, 3, d, e, f), needle (whisker) (Figure 1, f) habitus.

The presence of such nanoscale components in the structure of the dispersed particles causes the expression of characteristic energy state of the surface layer, which causes a structuring of the surrounding macromolecular binder to form a quasi-crystalline structure [14, 15, 24]. Experimental confirmation of a particular energy state of the surface layer of dispersed particles is the spectroscopic data of thermally stimulated currents (TSC) (Figure 4). Regardless of the individual characteristics of dispersed particles (composition, structure, dispersion, obtaining technology), there are typical temperature ranges in which noted the movement of charge carriers of different nature. In other words, all the dispersed particles, irrespective of their individual composition, structure and preparation technology, a certain contribution to the mechanisms and kinetics of the formation of the boundary layer in the composite material making energy state due to the presence of nanoscale fragments in the surface layer of the particle.

This contribution depends not only on the individual characteristics of the particles - the composition, structure, technology of obtaining, but also on the technological parameters of processing. For example, heat treatment of the dispersed particles of natural modifiers flint and shungite in the temperature range 100 - 800 °C is ambiguous effect on their energy state, as measured by the value of the maximum value of TSC (Figure 5). The observed effects of increasing and decreasing the value of the parameter I, depending on the treatment temperature due to the occurrence of physical and chemical processes that change the original structure of the particles - dehydration, dehydroxilation, oxidation, thermal oxidative degradation et al. [2, 14-18].

The characteristic features of the structure of the investigated particles cause multiple destinations their activity management through the use of technological operations specified destination. For example, the layered minerals such as clay, mica is effective

pre-treatment of the components, the ability to penetrate into the interlayer space and destroy the original structure of the particles to form nanoscale platelets [16]. As a result, the impact of processing technology factors intercalated composite with filler particles

occurs percolation macromolecular binder in the interlayer space to form a reinforced nanostructure with high parameters of strength characteristics [15, 16].

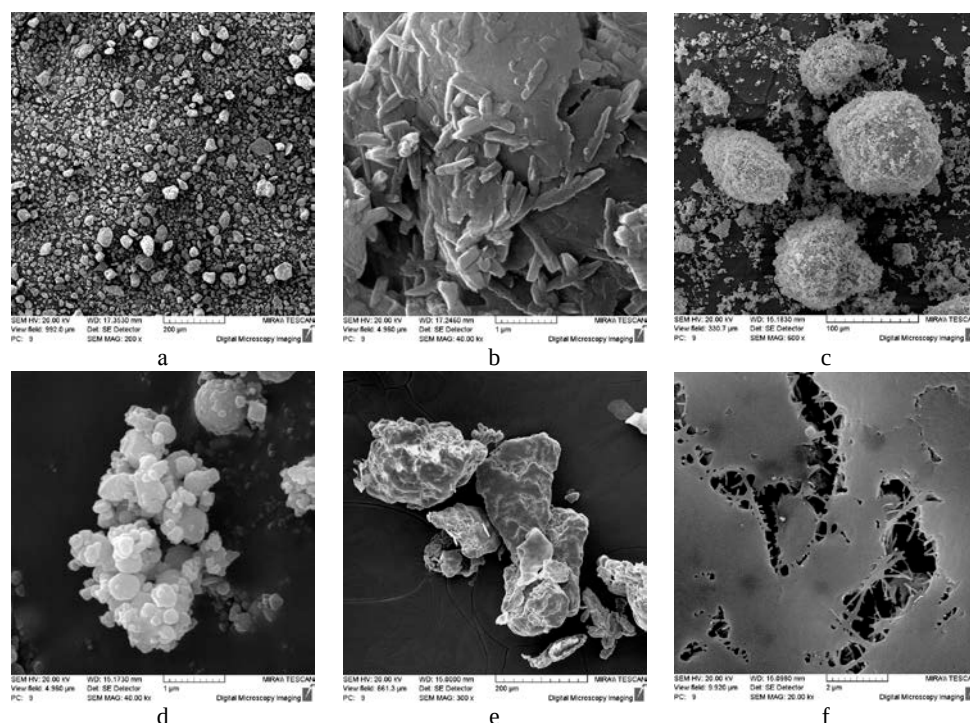


Figure 1 - The typical morphology of dispersed clay particles (a, b), metal oxides (c, d), polytetrafluoroethylene (e, f)

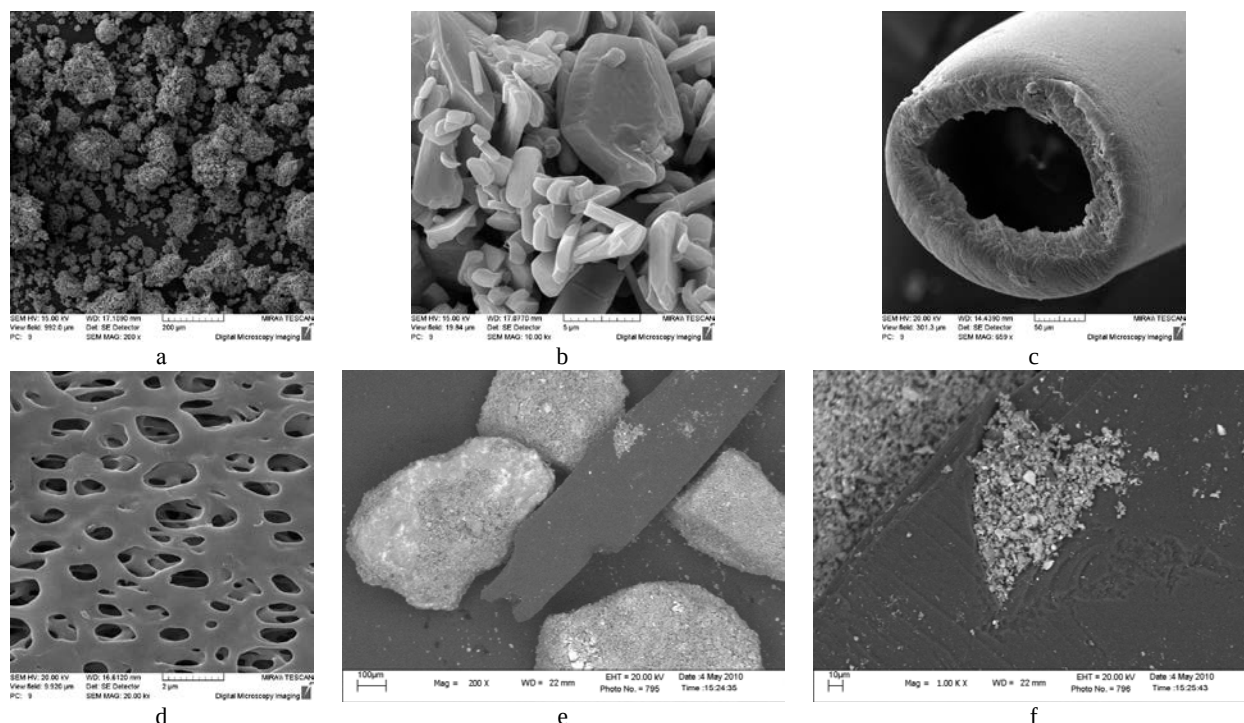


Figure 2 - Particles morphology characteristic: copper formate (a, b), polysulfone fibers (c, d), shungite (e, f)

When used as a modifier precursors of metal salt formic acid (formate) type, it is necessary to take into account the morphology of the precursor particles, which contribute to the formation during thermolysis not single particles of metals (Cu, Fe, Ni, Co), and their cluster formations providing nexus the structure of a nanocomposite [2, 14].

A particular importance in nanocomposites creating have a high energy state and morphology of the surface layer of high-strength

reinforcing fillers - fragments of a fiber given composition and size [4, 27, 28].

When using carbon fiber (CF), despite the presence of characteristic nanorelief (Figure 3 d), fails to provide the required level of interfacial interaction in composites based on thermoplastic matrices and crosslinking. Therefore, in some cases, the introduction into the polymer matrix (e.g., PTFE), high-strength carbon filler (CF) leads to the appearance of the structural paradox [21, 23, 28]. An effective way to increase the efficiency of

modifying action of carbon nanofibers is a modification of the surface layer with the use of fluorine-containing compounds, such as PTFE particles. Mechanochemical treatment of CF by UPTFE promotes the formation of a specific structure of the boundary layer

(Figure 3b), which increases the compatibility of the filler with a PTFE matrix [28].

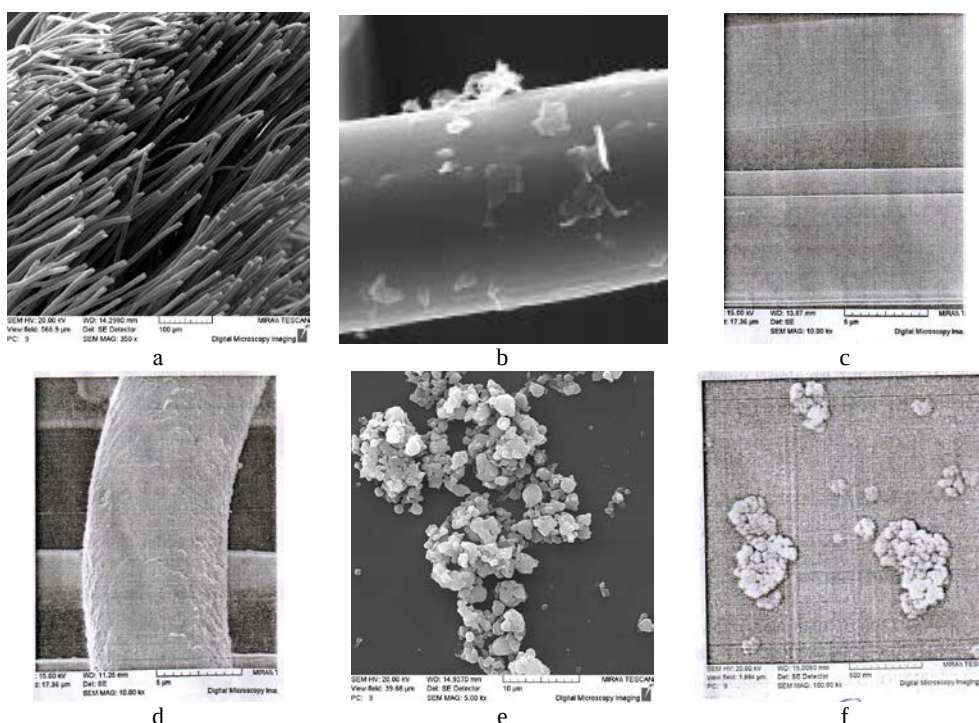
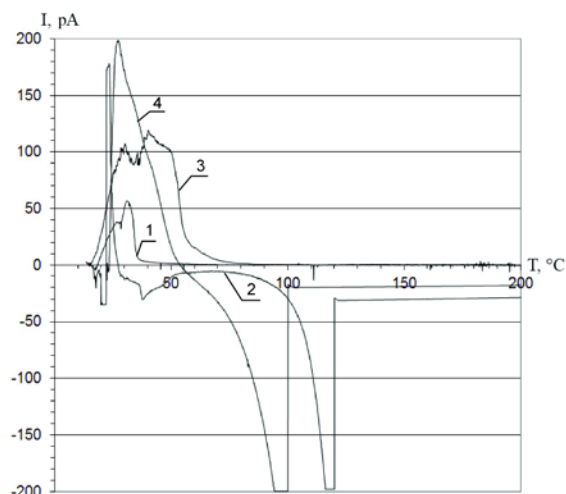
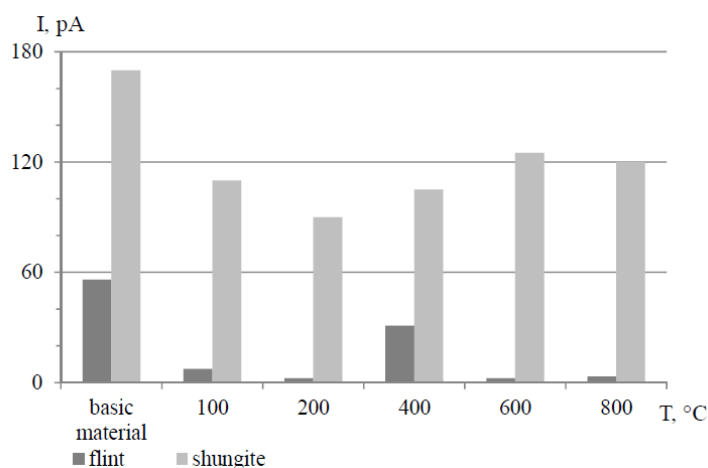


Figure 3 - The characteristic morphology of source carbon fiber (a, b, c), and treated with ultrafine particles of polytetrafluoroethylene (d), ultrafine particles UPTFE (e), ultrafine diamond (f)



Particle size 100 - 200 microns

Figure 4 - The spectra of thermally stimulated currents of dispersed particles of flint (1), shungite (2), tripoli (3), carbon nanotubes (4)



Particle size 50-100 microns

Figure 5 - The dependence of the maximum current $I_{\max}$ by thermally treating temperature of dispersed particles

Specific nanorelief reinforcing particles may be formed and by introducing into the polymer matrix of pore formers. For example, the structure of polysulfone fibers with porogen fragments comprises nano- and micro-sized range, which promote infiltration of the matrix binder and increase the proportion of the mechanical component adhesive interaction at the interface [4, 9, 12]. Thus, driving technological factors in the preparation of the dispersed particles and the direction of the modification, realization of special morphology and the energy state of the surface layer defining the mechanisms and kinetics of interfacial processes in composite materials for various applications. Obviously, the choice of technology activation of dispersed particles of modifiers is a multifactorial problem, including not only the materials science, but also economic and environmental aspects.

Of particular interest are technologies that combine several mechanisms for modifying the surface layer of the dispersed particles, ensuring the simultaneous effects of both mechanical (thanks to effect of flowing in the micro-nano-relief of the surface layer) and adsorption (due to the intensification of physical and chemical processes of interfacial interactions) and structured (by forming special structure of the boundary layer) factors on the mechanism and kinetics of interfacial processes in composite materials. However, these factors can occur at different stages of the process - the preparation of components, mixing them, during processing of the composite article while modifying special treatment products to impart the specific parameters of service characteristics.

For a reasonable choice of composition, size modifying particles with sizes microrange values, it is necessary not only to evaluate the energy activity in the parameter maximum thermally stimulated current (TSC) in a certain temperature range, the corresponding technological modes of production and processing of the composite, but to optimize the process conditions create a surface nanorelief layer, which will generate a boundary layer with mechanical and adsorptive implemented components adhesion strength. Estimates of the dimension of the parameter surface morphology L_0 providing the necessary action activity modifying particles, it is advisable to carry out using the expression $L_0 = 230 \cdot \theta_D^{-1/2}$,

where θ_D - the Debye temperature of the sample material for the semi-finished product, which is obtained from modifying particles. Experimental studies carried out with the various components of the composition, structure and technology of show the adequacy of the size parameter L_0 obtained using the proposed analytical expression, literature data [23-26].

Among the promising areas of particular target modification components is their mechanochemical activation under specified conditions the energy impact [1, 2, 19-34]. Due to mechanical stress certain intensity is ensured not only the formation of the active sites of the surface layers of the matrix and modifying components, and their interaction with the formation of the boundary layer of the combined product of optimal structure.

The research allowed to offer effective approaches to optimal selection of dispersed particles of high-matrix modifiers:

1. It is advisable to use fine particles of micron range mainly developed morphology of the surface layer formed nanoscale components of different composition and structure;
2. The ratio of geometrical parameters of the components of the surface layer and the amount of fine particles must be determined using physical criteria characterizing nanostate selected material objects (matrix modifier);
3. In order to ensure effective action modifying fine particles need to give particular energy state due to the combined effect of the structural and chemical, dimensional and technological factors. Choosing the prevailing factor determined by a combination of operational, energy, economic and environmental parameters that determine the effectiveness and appropriateness of industrial application in accordance with the terms of reference;
4. When choosing a method of activation of superfine particles, provides an optimum modification, it is necessary to establish the prevailing mechanism of formation of the transition (boundary) layer of a given structure and parameters of strength and adhesion characteristics and unconditional implementation of the principle of "reasonable sufficiency" in relation to a particular combination of material science, environmental and economic factors;
5. The greatest prospects to create functional composite materials and their production tonnage based on macromolecular matrices have dispersed particles derived from natural compounds laminate, the frame, the chain-like fibrous structure and natural, synthetic and semi-finished artificial using conventional and special technologies for the formation of the morphology surface layer with nanoscale components with an optimum level of energy activity;
6. For composites based on high viscosity and high melting matrix preferably using technology joint mechano-chemical activation of components and multi-level modification using particles of different composition, structure and dispersion.

Practical testing of the proposed methodological approach was implemented to create composite materials based on thermoplastic matrices and greases for heavy-duty friction units of machines and technological equipment used at the enterprises of mechanical engineering, building industry, chemical and mining industries.

For the development of composite materials for the application of tribological coatings used primary and recycled thermoplastic polymer matrix produced tonnage, including domestic manufacturers - PA 6, HDPE, PP. Modifying the matrix polymers functional components (tripoli, flint, kaolinite, UPTFE, HDPE) was

performed by mechanochemical activation (MA), followed by grinding at cryogenic temperatures (-198 ° C). The coatings are produced by fluidized bed. Comparative studies have shown that compounds designed not only inferior to similar imported PA 11 («Rilsan», France), but also significantly superior in its durability. This developed on the basis of the domestic polyamide 6 (JSC "Grodno Azot") compositions of composite materials have a value of 3 - 5 times lower than the imported counterpart. Composition of mechanically activated composites components have been successfully tested in the construction of driveshafts trucks, lathe chucks, produced by JSC "Belcard" and JSC "BelTAPAZ."

Compositions and technology of multilayer coatings on the basis of solid and highly rigid substrate formed by deposition from the gas phase active. In order to optimize the parameters of strength characteristics of the sub-layers of diamond-like carbon (APT) and the titanium compound (TiCN, TiAlN) proposed treatment of microwave radiation (microwave) with a wavelength $\lambda=12,25$ cm, the frequency of 2450 MHz. On the sub-layers with high hardness settings applied by dipping and rubbing (rotaprintny method) layers of fluorinated oligomers ("Foleoks") and polymer-oligomeric products termogazodinamicheskikh synthesis (UPTFE). Composite multi-layer coatings with activated substrates based on APT, TiCN, TiAlN effective for use as an anti-antirazgarnykh and in the construction of the friction units of precision tooling (lathe chucks) and molds for the manufacture of non-ferrous metals produced at UP "Tsvetlit". The compositions of multilayer composite coatings based on titanium compounds (TiN, TiCN, TiAlN) and fluorinated oligomers for use on metal working tools (drills, taps, milling cutters, broaches, etc.), Used in the manufacture of automotive components, lathe chucks and mining equipment at JSC "Belcard", JSC "BelTAPAZ", JSC "SIPR with OP".

Activity dispersed particles subjected to energy shocks, manifested in the developed morphology of the surface layer and the presence of uncompensated charge with a long relaxation time, allowed to develop effective formulations of lubricants and greases for heavy-duty friction units on the basis of industrial products.

With the introduction of fine particles, activated by thermal, laser or mechanochemical action, in the lubricating composition of the charge formed clusters that improve the load-carrying capacity and thermal stability of the separating layer in the area of frictional contact. The compositions of lubricating oils, hydraulic fluids and greases for use in the construction of automotive components (brake chambers, drive shafts), and lathe chucks for metalworking equipment. Introduction to the base composition of nanoscale products obtained laser or thermal ablation of PTFE in combination with activated silicate-containing particles (SiO₂, flint) to stabilize the viscosity of the damping fluid based on mineral oil in the temperature range 25 - 80 ° C, increases resistance to galling lathe chuck drive unit 1.5 - 2.0 times and resource needle bearing crosses the propshaft trucks MAZ, BelAZ, KAMAZ. The compositions have been testing at the leading enterprises of the Grodno region (JSC "Belcard", JSC "BelTAPAZ") and recommended for implementation.

4. Conclusion

The features of the selection modifiers disperse macromolecular matrix composite materials to create the specified functionality. The role of the energy state due to the peculiarities of the composition, crystal-chemical structure and morphology of the surface layer of dispersed particles used as a modifier to achieve the desired technical effect is significant.

Methodological approaches to the process of selecting the components and functional materials and methods of activation, based on the provision of prevailing flow mechanism of interfacial interactions and the formation of the optimal structure of the boundary layer.

We consider the practical application of methodological approaches designed to create composite materials for the manufacture of products used in engineering, construction industry and mining.

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SINTERING OF FILTERING MATERIALS BASED ON METAL POWDERS AND FIBERS BY ELECTROCUTION

СПЕКАНИЕ ФИЛЬТРУЮЩИХ МАТЕРИАЛОВ НА ОСНОВЕ МЕТАЛЛИЧЕСКИХ ПОРОШКОВ И ВОЛОКОН ЭЛЕКТРИЧЕСКИМ ТОКОМ

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Abstract The paper shows the results of testing the obtaining process of filtering material based on metal powders and fibers by electrocution sintering. The equipment design and manufacturing techniques of test samples are presented; experimental samples of filtering materials based on powders of tin-phosphor bronze BrO10F1 and stainless steel 12X18H10T fibers have been manufactured. Method implementation requires no special equipment: a common spot welding machine has been used. Photographs of appearance and structure of the samples and the results of studying their properties have been presented: porosity, permeability coefficient, pore sizes. It has been shown that the materials manufactured by electrocution sintering possess a satisfactory complex of filtering properties and may be used for purification of liquids and gases.

KEYWORDS: FILTERING MATERIAL, ELECTROCUTION SINTERING, MANUFACTURING TECHNIQUES, PROPERTIES

1. Introduction

Electric current assisted sintering of metal powders is famous for its efficiency, low power consumption, possibility of automation and high productivity. In comparison with the classical methods of powder metallurgy this technique doesn't require expensive equipment and/or shielding atmosphere that provides significant energy savings. Besides, with the help of electric current assisted sintering we can adjust technological conditions while manufacturing each and every product in the lot. After the analysis of known techniques in electric current assisted sintering of porous powder materials we have outlined the most promising ones for manufacturing porous materials from metal powders. These are electromagnetic pulse sintering (EPS) and electric discharge sintering (EDS) [1-5]. However in the known sources electric current assisted sintering is described as a preliminary or intermediate processing of powdered materials. The matters of obtaining filtering materials in a single step of electric current assisted sintering were not considered therein.

The purpose of this paper is testing the process of obtaining filtering materials based on metal powders by the example of tin-phosphor bronze powder BrO10F1 and stainless steel 12X18H10T fibers by electric current assisted sintering.

2. Results and Discussion

The process of obtaining filtering materials by electric current assisted sintering was carried out on the spot welding machine MT 2201 UHL4 (Figure 1). Samples were manufactured using the developed equipment consisting of special conductive copper electrodes and punches, and a graphite matrix [6, 7]. This matrix allows obtaining discoid samples of 12 mm in diameter and 20 mm thick. The appearance and drawing of the equipment are shown in Figures 2 and 3. As mentioned above, the initial materials were: tin-phosphor bronze powder BrO10F1 (own production) and stainless steel 12X18H10T fibers (wire cuts). The powder particle sizes were $(-1.0 + 0.63)$ mm. Its surface morphology is shown in Figure 4. The fibers had a diameter of 0.2 and a length of 2 to 7 mm. Their surface morphology is shown in Figure 5. Metallographic studies of the initial materials were performed using a scanning electron microscope CamScan (England).

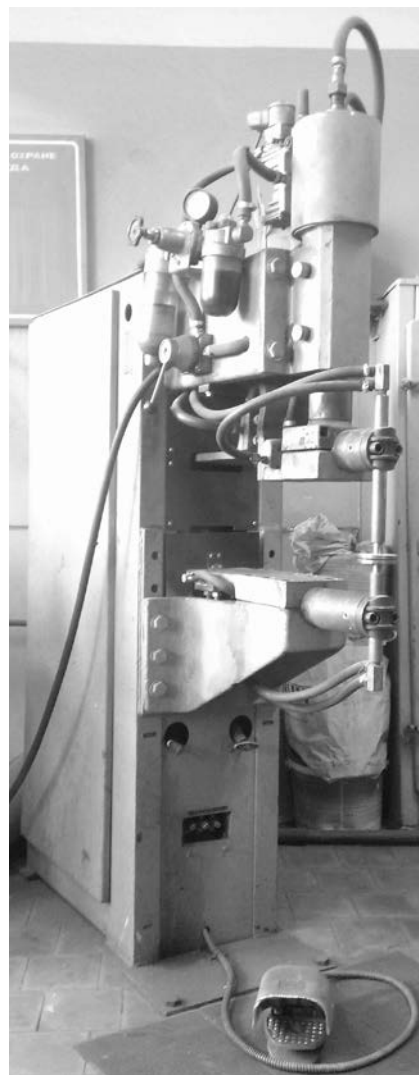


Fig. 1 Spot welding machine MT-2201 UHL4



Fig. 2. Accessories for manufacturing test specimens

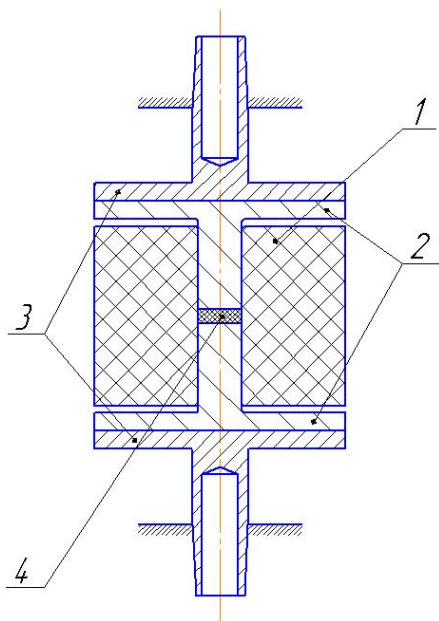


Fig. 3. Equipment

- 1 - matrix;
- 2 - punches;
- 3 - conductive electrodes;
- 4 - sintered material

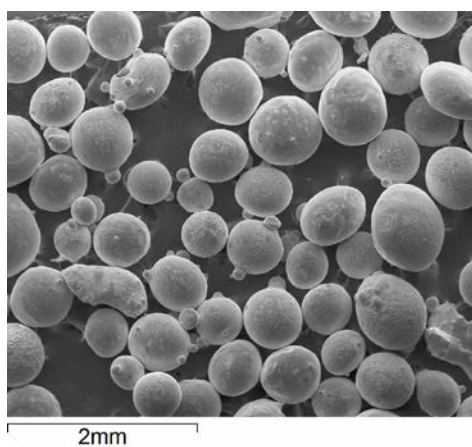


Fig. 4. Surface morphology of the particles in the tin-phosphorous bronze powder fractions (-1.0 ± 0.63) mm obtained by atomization of the melt with a gas flow

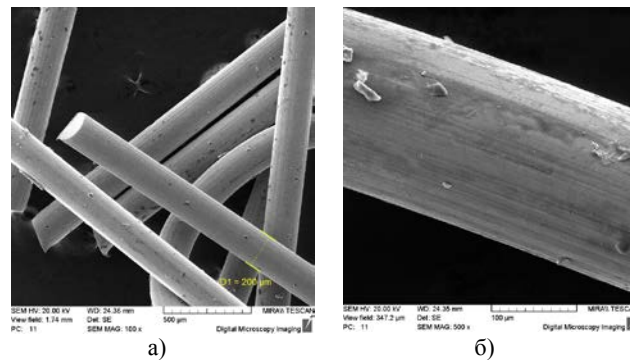


Fig. 5. Morphology of stainless steel 12X18H10T fibers

- a) $\times 100$;
- b) $\times 500$

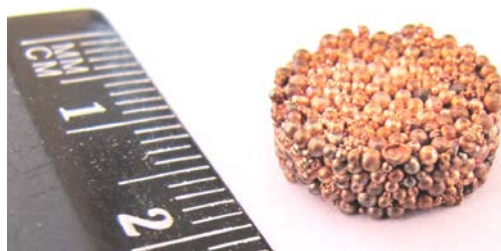
The manufacturing technology for producing the samples was as follows. The lower punch was inserted into the graphite matrix. A portion of powder or fibers was poured into the die cavity. Then the upper punch was mounted between the conductive electrodes of the spot welding machine (Figure 6). A pressure of 5-20 MPa was applied to the punches through the electrodes. Sintering was performed by passing an electric current through the matrix.



Fig. 6. Accessories for electric current assisted sintering in the spot welding machine

Sintering of the powder samples was performed under the following conditions: current 7.5-12.3 kA; passage of current from 0.4 to 3.6 seconds; effective current 8.9 kA, current density 7.87 kA/cm^2 , number of welding current pulses 120, heating time 2.4 seconds. Sintering of fiber samples was performed at the current of 7.5 - 11.6 kA and passage of current duration from 0.4 to 3.6 seconds. The effective current was 8.9 kA, the current density was 7.87 kA/cm^2 , the number of welding current pulses was 60, and the heating time was 1.2 seconds.

The appearance of the obtained samples is shown in Figure 7. Their structure is presented in Figure 8. Metallurgical study of the structures was performed using the light microscope MeF-3 from Reichert (Austria).



a)



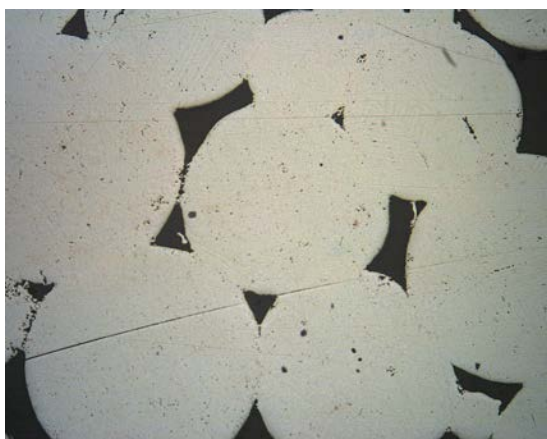
b)



c)

Fig. 7. The appearance of samples of filter materials, sintered using electric current:

a, b) - a sample on the basis of bronze powder;
c) - a sample of fiber-based stainless steel 12X18H10T



a)



b)

Fig. 8. Sample structure

a) Bronze powder, $\times 50$;
b) Stainless steel fiber, $\times 50$

accordance with GOST 25283-82) and pore sizes (according to GOST 26849-93). The research results are as follows. The samples of tin-phosphor bronze BrO10F1 powders: porosity 28-36 %; permeability coefficient $(250-1850) \cdot 10^{-13} \text{ m}^2$; pore size 150-250 μm . The samples of stainless steel 12X18H10T fibers: porosity 30-39 %; permeability coefficient $(40-51) \cdot 10^{-13} \text{ m}^2$; pore size 80-164 μm . The analysis of the results leads to the conclusion that the samples of permeable materials obtained with the help of electric current assisted sintering have a satisfactory set of filtering properties and can be used for clarification of liquids and gases.

3. Conclusion

We tried the process of manufacturing permeable materials based on metal powders through the example of tin-phosphor bronze BrO10F1 powder and stainless steel 12X18H10T fibers with the help of single-step electric current assisted sintering. We studied the structure and properties of the samples made of spherical dispersed bronze BrO10F1 powder and stainless steel 12X18H10T fibers. We found out that the samples have a satisfactory package of filtering properties. The samples made of tin-phosphorous bronze powders have porosity of 28-36 %, permeability coefficient is $(250-1850) \cdot 10^{-13} \text{ m}^2$, pore size is 150-250 μm . The experimental samples of stainless steel fibers possess porosity of 30-39 %, permeability coefficient is $(40-51) \cdot 10^{-13} \text{ m}^2$, pore size is 80-164 μm . We proved the possibility of electric current assisted sintering for bronze powder-based materials and stainless steel fibers within a single-sinter treatment.

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We examined the obtained samples and determined their porosity (according to GOST 18898-89), permeability coefficient (in

LASER TECHNOLOGY IN MATERIALS SCIENCE NANOCOMPOSITE MATERIALS BASED ON THERMOPLASTICS

ЛАЗЕРНЫЕ ТЕХНОЛОГИИ В МАТЕРИАЛОВЕДЕНИИ НАНОКОМПОЗИЦИОННЫХ МАТЕРИАЛОВ НА ОСНОВЕ ТЕРМОПЛАСТОВ

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Abstract: *The physicochemical and structural aspects of the modification of polymeric materials and fillers, laser exposure to a given intensity. Installed effects transform the morphology of the surface layers of dispersed, semi-finished fiber and membrane to form nano-sized components with increased vigour. Modification of certain process parameters laser that achieve predetermined functional characteristics. It sets the parameters of the effect of a significant increase of strength characteristics of film semi-finished products made of thermoplastic (HDPE, LDPE, PP, PA, PET, PTFE), due to the formation of spherulitic supramolecular structures. The energy parameters of the surface layers of composites, subjected to modification of a short-pulse laser exposure. Installed effect forming electrets structures and nano-relief, providing suppression of unfavorable biochemical processes in the application of products in practice. The results of the use of materials and products subjected to laser modification, engineering and medical practice.*

KEYWORDS: LASER INFLUENCE, TRANSFORMING THE STRUCTURE, FORMATION CHARGE, ACTIVE STATE, STRENGTHENING EFFECT

1. Introduction

The use of laser radiation (LR) as a modifying factor in the structure and parameters of physical and mechanical properties of semi-finished metal and polymer materials treated with the middle of the last century [1-4]. In this area there has been significant progress in creating a variety of devices store information, antifriction materials, adhesives. However, in most publications, focuses on the process of structuring, ablation, changes in the optical characteristics, improving the parameters of physical and mechanical properties of polymeric and metallic materials [1; 3-10].

There is currently no established theory that uniquely describes the structural changes occurring in thin surface layers of semi-finished products of different structure, composition and production technology, under the action of laser radiation. It is obvious that this is largely due to various methodological terms of sample processing, differing pulse duration LEE, ego, energy, angle of incidence of the beam on the substrate LR, geometric parameters of the samples, and so on. D. Therefore, the available data in the literature are often not correlated c determine the effect of changing the topography of the surface layers of the treated samples, the parameters of the supramolecular structure, hardening et al. [1-11].

For example, in [3] the main factor change the supramolecular structure under the action we consider thermal degradation of particles of various impurities that are present in the polymer intermediates. In [6], the authors established that the formation of ordered structures in the volume of non-crystalline polymer sample under the influence of short-pulse radiation. A number of studies indicated a characteristic change in the surface topography of semi-finished polymer exposed to LR, who is characterized by the formation of specific relief, geometrical parameters which depend on the processing conditions [3; 11; 14].

It is obvious that the effects of transformation of the structure and physico-mechanical characteristics of the polymer intermediates, due primarily change the energy state of the polymer molecules and the components included in the technical intermediates, m. K. Is known that, even with a relatively small power fluxes (with the point of view of industrial technology and engineering used in geometrical parameters of components), you can change the state of the polymer and oligomer macromolecules, resulting in structuring, degradation, ablation and supramolecular ordering [10-14]. This fact necessitates a systematic study of the mechanism of action of modifying LR polymeric semi-finished products of varying composition, structure and production technology, t. To. In connection with the intensive development of

the technological base of this type of functional processing can be effectively used in the process of preparation of ingredients in the preparation of composite materials in order to increase their deformation and strength characteristics for surface activation in the form of semi-finished films and block blanks for coating and control tribological parameters for the formation of electrophysical state with a given relaxation time of polymer and composite products used in sealing, tribological systems and practices, and so on implantation etc.

The specific advantages of the method of modifying the laser allow controlling radiation parameters (energy and pulse duration, wavelength) and the local impact on the surface of the product or semi-finished with minimal energy loss. In addition, the short duration of the pulse Lee and the ability to control the flow of geometric parameters determine the possibility for significant portions of energy in the local area semi without causing the formation of macroscopic defects caused by melting, destruction, burning, ablation, and others. Processes for traditional forms of technological energy impacts.

The aim of this work was to evaluate the possibility of using short-pulse laser (s) to modify the semi-finished products from a variety of thermoplastic materials.

2. Preconditions and means for resolving the problem

The theoretical calculations of the engine heat cycle were made for three For studies used semi-finished foil in a state of industrial supplies thickness of 120 to 200 microns, obtained by extrusion blow molding or extrusion through a flat head, polyethylene (HDPE), high density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET). Before processing LEE foil samples purified from mechanical impurities by treatment with ethyl alcohol. For modifying the samples of polymer materials used laser installation "Quantum-15" and the PRP-100N, generating laser light with a wavelength $\lambda_0 = 1,06$ microns, $\lambda_0 = 0,69342$ microns and a pulse duration of $1,2 \cdot 10^{-6}$ sec. The number of pulses in the treatment ranged from 1 to 10. The substrates on which the samples were placed foil was used as the light-scattering (reflecting) and light-absorbing materials. The energy of a single pulse was 0,6-6 J.

As a parameter for evaluating the charge state of a sample of the polymer material used values of thermally stimulated currents (TSC), resulting in a sample by heating it and change its size when exposed to external factors, in particular laser radiation.

The method of thermally stimulated depolarization (TSD) is to measure the thermally stimulated current electret sample. Heating the sample at a constant rate of 10^0 C/min to thermally fix current values at different temperatures were performed using an instrument ST-1. Device management and processing programs are designed ODO "MICROTESTMACHINES" (Gomel).

Study of the morphology of the surface layers of film samples was carried out using an optical complex that includes a microscope and image processing software Autoscan Areas, and by atomic force microscopy (AFM Nanotop-3). Structural changes in the polymer matrix after exposure to laser radiation was evaluated by IR-ATR spectroscopy using the IR Fourier spectrometer Tensor 27.

3. Results and discussion

Compliance with the optimal parameters of supramolecular polymer matrices is very challenging [15], so most industrial plastics have sufficient variation in service characteristics due to, inter alia, differences in the structure and content of supramolecular structures in the bulk polymer matrix. For example, wear resistance of polytetrafluoroethylene, polyamide, and others. Quite polymeric materials depends substantially on the ratio of the ordered (crystalline) phase and disordered, which varies significantly even within the same batch of material depending on its processing process parameters - temperature, time of exposure, the time and intensity heat removal from making out the form elements, the heat treatment temperature of finished products and so on. Therefore, the most important task of practical polymeric materials science is - provide stable performance of service characteristics of industrial materials using relatively simple technological methods based on the management of processes of formation of the supramolecular structure of the energy flows of different nature and intensity.

Of particular relevance in the manifestation of the operating parameters of the product polymer or composite material has a surface layer structure that defines and tribological, protective, fatigue and others. Characteristic. In this aspect of laser technology are particularly effective modification and prospects for practical application.

The modification of the surface layers of polymer films (HDPE, LDPE, PP, PET) short-pulse ruby laser GORE-100N, operating in free-running mode with a pulse duration $\tau = 1,2$ ms and with a wavelength $\lambda = 0,69342$ microns Characteristic changes in the structure, topography and structure of polymeric materials. Investigation of the physicochemical characteristics of the films indicates a significant impact on the density of irradiation parameters tensile strength and elongation (Figure 1). Hardening effect is especially significant for PET film which is in non-crystalline state as a result of the technological features of preparation. Noteworthy nonmonotonic dependence $\sigma_t = f(P)$, which indicates the specific restructuring of the supramolecular structure of materials by laser radiation.

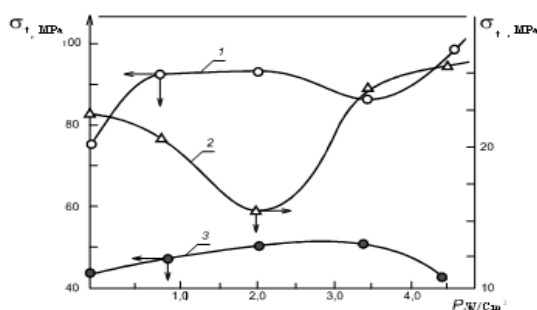


Fig. 1 Dependence of tensile strength of the laser power density for samples of film of PET (1) LDPE (2) PP (3)

IR spectroscopic studies confirm the fact of changing the structure of the investigated materials. The IR spectra of the samples irradiated LDPE LR, new absorption bands in the 600-800, 1600-1750 cm^{-1} and the redistribution of the intensities of bands in

the 1360 cm^{-1} which characterize the ratio of crystalline and noncrystalline phases.

These assumptions are confirmed by the study of the morphology of the surface of the polymer samples subjected to laser irradiation of different capacities. With increasing doses there is a total increase in the number of characteristic fragments of the tapered surface of the sample is likely due to the recrystallization process under the action of the laser beam. Given that the input power is relatively small and the radiation does not exceed 3.5 W / cm^2 , and the processing time of 1.2 ms, it can be assumed that the process of degradation with deep entrainment noncrystalline component from the surface layer, such [10] does not occur and the change in elevation is due to the formation of local quasi-crystalline formations, due to changes in the energy state of macromolecules. This assumption is supported by the fact smooth relief in excess of the power density of 4.5 W / cm^2 , which is probably due to thermal destruction of the crystal irregularities on the mechanism of fusion. Dimensions formations on the surface of the irradiated films are in the range 30-40 nm and cross section 10-150 nm in height (Fig. 2).

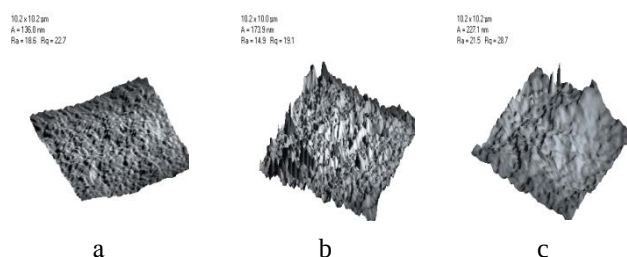


Fig. 2 The characteristic surface morphology of the film sample of high-density polyethylene (LDPE) initial (a) and after a single exposure to laser radiation energy of 30 joules (b) and 2 J (c)

Similar changes in the surface topography of film samples are observed during their processing laser source "Quantum-15" with a wavelength $\lambda = 1,06$ mm and pulse duration with $2 \cdot 10^{-6}$ sec.

The typical form of PET films treated with different doses of LR, is shown in Fig. 3, 4.

Attention is drawn to the fact of the active influence of the type of the substrate on which the treated samples, the characteristics of the topography. On the reflective substrate same dose if the caller significantly less change in the parameters of the surface topography (Fig. 2) than the light-absorbing (Fig. 3).

This effect is probably due to the peculiarities of the processes of energy redistribution in a foil sample LR: reflective substrate leads to almost total reflection of the flow and efficiency of its influence on the process of structuring is substantially lower than the irradiation on the light-absorbing substrate. In the latter case, almost all the energy of the incident flux is redistributed between the macromolecules of the sample, causing a change in their spatial orientation.

As shown in [6], the impact of LR can cause the formation of ordered ("quasicrystalline") areas, even in a sample of polymethyl methacrylate (PMMA). Moreover, the size of these areas are large enough and are determined by Wray structural analysis. It seems more reasonable representation of the authors of [5; 6] on the mechanism of ordering macromolecules in polymer matrices, based on the occurrence of acoustic waves under the influence of short-pulse Lee.

Controversial, and, in our opinion, is not proven hypothesis proposed in [3], according to which the supposed presence in the volume of semi-finished polymer significant number of contaminants ("dust" in the terminology of the authors) and low molecular weight products of synthesis. Obviously, if we assume that pollution is indeed present in large enough quantities in the polymer semi-finished products (which is doubtful, t. To. the modern synthesis technology require thorough cleaning of components in the reaction volume, because contamination can lead to a breach of polymerization reactions and the formation of polydisperse product), they are predominantly inorganic nature

(mostly silicate particles), and can not decompose to gaseous state, due to the "swelling" of the surface layer of the sample, due to its high temperature resistance, reaching values above 973 K [16].

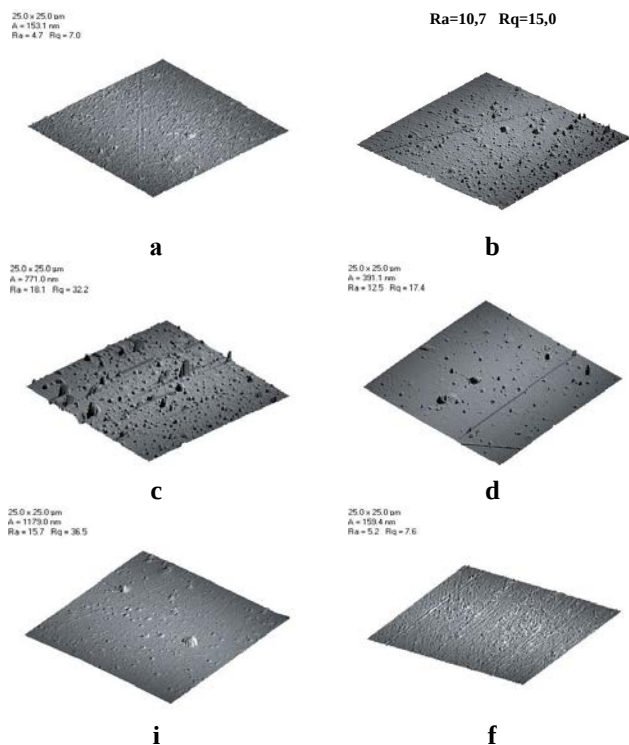


Fig. 3 The topography of the surface layer 3 of polyethylene terephthalate film (PET) of the original (a) and once treated with the laser beam voltage heater 500 (b) 600 (c), 700 (d), 800 (e) 900 (f). Field scanning 25x25 microns. Flocked substrate

The content of significant amounts of low molecular weight fractions in industrial films also unlikely because modern production technologies based on the removal of these products at the various stages, as they may cause adverse effects on the composition of products, including edible products that are packaged in a semi-finished product of film.

Intensive energy impact on the foil samples causes not only a change in the spatial arrangement of macromolecules, but their energy state. Prerequisites for change in the energy state of the polymer sample by laser irradiation can be - the flow of localized degradation processes the most stressful parts of macromolecules to form makroradikalnyh products, the formation of traps charge carriers through the cleaning of the surface layers of samples from contamination and adsorbed gaseous and liquid phase product of the environment, the flow of the secondary processes of synthesis between components of the surface layer and the polymeric components of the sample (in Vol. h. makroradikalnymi with food) that may cause formation of polar groups (for example, C=O , -OH).

Change in the energy state of the surface layer of polymer semis after Lee can be effectively used in the technology of composites during the deposition of functional layers on the semi-finished product, when creating components tribosystems and a number of other practical applications. For example, it is known that the energy state of the filler particles leads to hardening of polymer composites due to the formation of the boundary layer quasicrystal [16; 17], and the management of its parameters is an effective way to improve the tribological parameters tribosystems (stents) [17] and sound passage [18].

Fig. 4 shows a typical dependence of the values of thermally stimulated currents I on the temperature of the unmodified polyethylene sample. TSC spectrum of the original polyethylene is characterized by three intense peaks in 17-55 °C; 80-113 °C; 195-

219 °C. According to the data [17] in the polymeric electret charge pattern is formed by capturing structural carrier traps, localized areas of imperfections in the polymer structure and interfaces "polymer-metal particle." The presence of metal particles in the samples in the samples due to the fact that the electrode layers may be formed of metal compounds, in particular, salts of carboxylic acids, which are then decomposed to release the metal particles. The presence of the peak I in 17-55 °C obviously related to the removal of moisture contained in the polymer film by adsorption from the environment. The presence of a second peak in the spectrum in 80-113 °C probably due to the phase transition type I - the melting of the crystalline portion of polyethylene sample and release of charge carriers of structural traps and, as a consequence, increase the values of the thermally stimulated current. The third peak in 195 °C above apparently associated with the appearance of additional charge carriers as a result of oxidizing processes occurring in polyethylene at elevated temperatures.

A single laser treatment of the polymer sample, located on the light-absorbing substrate (graphite), low-energy radiation ($E \sim 0.6$ J) leads to a noticeable change in the spectrum of TSC in the studied temperature range (Fig. 5).

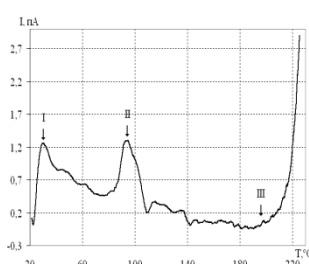


Fig. 5 Dependence of the thermally currents I of the temperature T in the original sample HDPE

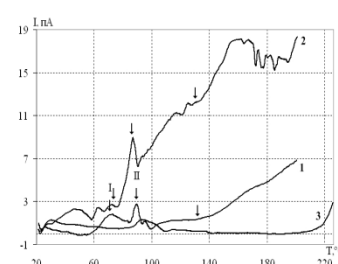


Fig. 6 The dependence of thermally currents I of the temperature T in the sample LDPE subjected to a single treatment with laser radiation with an energy $E \sim 0.6$ J
1 – reflective; 2 – light-absorbing substrate; 3 – initial sample

The value of thermally stimulated currents in the temperature range studied increases in ~ 2 times. In the spectrum there are additional peaks of thermally stimulated currents in the temperature range 55 °C-80 °C; 84 °C-95 °C; 95 °C-100 °C. The appearance of additional peaks in the spectrum of TSC obviously indicates the formation of a surface layer of a different type of charge carriers when exposed to laser radiation. This is due to the processes of degradation of macromolecules of the polymer, the intensification of oxidative processes in the surface layers of the polymer sample by laser radiation. This assumption is confirmed by the fact that the beginning of the third peak TSC exposed to laser radiation is shifted to 130 °C and is more intense compared to baseline TSC spectra for polyethylene.

Processing of polyethylene sample by laser radiation on the reflective substrate (paper) leads to the formation of such a spectrum of TSC. However, it should be noted the formation of a series of intense peaks in the temperature 140-185 °C, which may indicate structural changes in the polymer matrix under the influence of laser radiation. The values of the current in the temperature range from 60-180 °C 2.5-3 times higher for the sample of polyethylene irradiated on the reflective substrate than for the same sample, irradiated on the light-absorbing substrate, ceteris paribus.

Increasing the number of treatments of the polymer sample, which is located on the light-absorbing substrate, up to 10 times increases the values of thermally stimulated currents 1.5-2 times and the emergence of a sufficiently intense peak in the spectrum of TSC in 120-180 °C. Repeated exposure of laser radiation on polymer sample, located on the light-scattering substrate, resulting

in a decrease in the values of thermally stimulated currents in 17-115 °C. At temperatures observed 116-195°S thermally stimulated current sign inversion, the absolute value of the thermally stimulated current ~ 2 fold lower than the single exposure of polymer sample, for a given type of substrate.

Increasing the values of the energy of the laser radiation exposure to 5 J irradiation of polymer light-absorbing substrate leads to the degeneration of the peaks of thermally stimulated currents in the range from 17 °C to 80 °C.

Thus, the laser irradiation on the surface layers of products (semi-finished products) of thermoplastic polymer or composite materials with specific energy parameters allows you to change the settings of various characteristics - of strength, energy, morphological. By varying the parameters LR, you can achieve the necessary parameters microroughness providing optimal adhesion and tribological [19, 20].

Under the influence of laser radiation on the thin-film coating of fluorine-containing compounds, possibly modifying the surface layer of carbonaceous filler (carbon fiber), provides a significant strengthening effect of composite materials based on polytetrafluoroethylene.

Effective is the use of laser irradiation on the surface layer of polymeric implants used in ossikuloplastike, thanks to the implementation of synergies resulting from the formation of optimal morphology close to that of natural bone morphology, and energy state with a long relaxation time, which has a beneficial effect on the suppression or inhibition of postoperative complications [18].

Thus, controlling the process parameters laser treatment of semi-finished polymer can change the parameters of different characteristics: structural, of strength, electro and others. The use of laser technology in the composite polymer materials science, and applied fields tribotechnology allows purposefully change the kinetics of interfacial processes in order to form the structure of a given composition and structure.

4. Conclusions

Analysis of the literature and the results of the study indicate the prospects of using laser technology in the formation of functional materials and systems. Laser radiation has a complex effect on the polymer intermediates, changing its structure, deformation-strength and electrical characteristics. Probably a synergistic effect of laser radiation due to the change of the energy parameters of polymeric macromolecules, which causes secondary processes of structural transformations that modify the settings of service characteristics.

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ION-PLASMA HARDENING OF A TITANIUM ALLOY OT4-1

ИОННО-ПЛАЗМЕННОЕ УПРОЧНЕНИЕ ТИТАНОВОГО СПЛАВА ОТ4-1

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Abstract: The paper is devoted to studying the influence of technological process parameters of deposition on the composition, structure and strength characteristics of TiN coatings on titanium alloy OT4-1. The TiN coatings were deposited by a vacuum-arc evaporator. In addition, the influence of the type of layers formation on microhardness and wear resistance of TiN layers and a metal substrate is presented.

KEYWORDS: ARC EVAPORATOR, LAYERS, TIN, ALLOY, MICROHARDNESS, WEAR RESISTANCE

1. Introduction

A vacuum and plasma technology of hard coating deposition on different details of machines and parts of constructions allows to strengthen their surface. Protective and decorative titanium nitride layers are applied on various materials and alloys. The most widely used is wear-resistant coating of metal-cutting tools [1, 2]. Decorative coatings with high anticorrosive and wear-resistant properties are formed on the surface of various steels, such as 12X18H10T for example [3]. The properties of coatings are determined by technological process parameters since the operating properties of deposited layers depend on the degree of crystal structure's perfection. The paper is devoted to studying the influence of these parameters on the composition, structure and strength characteristics of TiN coatings made of OT4-1 titanium alloys.

2. The experimental part

Initial materials.

The sheets of titanium alloy OT4-1 were used as a material on which wear-resistant titanium nitride coatings were formed. OT4-1 titanium alloy (Ti—Al—Mn system) with a tensile strength of $\sigma_b < 700$ MPa relates to alloys of low strength and high plasticity. It is a pseudo α - alloy with a small amount of β - phases ($K\beta < 0,25$) due to insignificant alloying of α - (Al) and β - (Mn) - stabilizers. It is characterized by high ductility both hot and cold that allows to receive all types of semi-finished products: foil, tape, sheets, plates, forgings, stampings, profiles, pipes and so on.

Methods of forming a coating.

In fig.1 a VU-1M vacuum installation's scheme is illustrated. To form a coating a solid (cathode) 7 is evaporated in vacuum by a low-voltage DC electric arc. By evaporation of the substance in a vacuum chamber 1 its highly ionized plasma is formed there. Between the cathode 7 and an electrode 8 a controlled potential difference appears. In the electric field charged plasma particles have been accelerated to achieve the energy proportional to the potential difference and run towards the auxiliary electrode 8, on which the processed details 2 are located, forming on a surface of dense and uniform coating thickness. The cathode material was "VT-1-0" titanium with a diameter of 60mm. Nitrogen gas of high purity had been used as reaction gas. Limiting residual pressure in the vacuum chamber was 6.6×10^{-3} Pa. The coating mode provided uniform layers with thickness in the range of 1,0-4,5 mcm. Studies were conducted on the samples made of titanic alloy OT4-1. Pre-ionic surface treatment of the samples was carried out in a glow nitrogen discharge.

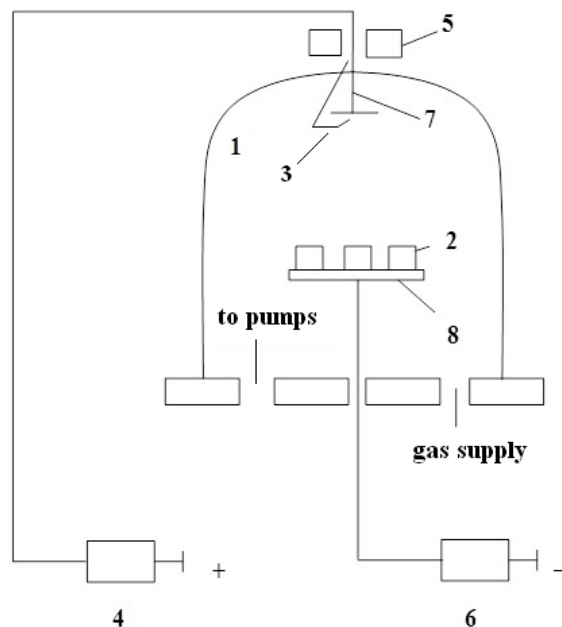


Fig.1. Schematic illustration of installation VU-1M:
1-vacuum chamber, 2- processed details, 3- igniter electrode, 4- power supply, 5- focusing coil, 6- power supply, 7- cathode, 8- auxiliary electrode

Research methods.

Microhardness of the created layers had been determined by microhardness tester PMT-3. The load on a diamond pyramid was 50 or 20 g.

Microstructure and thickness of the samples were examined also by microhardness tester PMT-3 with increase x130 and x500.

Wear resistance in abrasion was conducted with MI-2 machine according to GOST 11626-75 by repeated multiple sliding of the sample on one and the same track of the counter body plane on an abrasive cloth under the load of 68,6 N (7kgs). The sliding speed of the samples on the sandpaper's plane was 40 rpm or 0.28 ± 0.05 m/sec. The loss of the sample's mass or the time of removing the cover during testing is a criterion of wear depreciation. The weight loss of the samples when sliding on Abrasive was evaluated by weighing the samples on analytical balance VLA-200. The weighing error was $\pm 0,0002$. Abrasive on a fabric basis with electro corundum and granularity numbers 40, 10 GOST 6456-79, GOST 5009-76 was used in the work

3. Results and discussion

The process of forming a coating may be divided into three steps. The first step is making a plasma stream of evaporated substance's particles, herewith the electrode 3 ignites the arc and evaporating of the cathode material starts (fig. 1). The peculiarity of

the arc with cathode spots is that the current at the cathode is concentrated on one or a few merging, rapidly disappearing and randomly moving spots. a cathode zone the emission process is occurring which ensure the value of the electron current from the cathode which is close to the total discharge current. In addition, the thermal, auto- and thermoautoelectronic emission processes are prevailing. When the cathodes receive a large amount of energy from current, cathodes strongly heat up and evaporate, and most often there is their erosion - destruction of an electrode to ablation of weight. Therefore, arc discharges usually to burn in the vapor of the evaporated metal [4]. Feature of arc with cathode spots is seen in the fact that the current at the cathode is concentrated in one or more emerging, the fast disappearing and randomly moving spots. The current density in those cathode spots reaches 10^7 A/cm². The second step is ionic bombing or ionic cleaning of the surface and has a very important role in the formation. As a result of the bombardment physical and chemical cleaning of the surface in high vacuum and significant warming of the surface occur while the bulk sample remains relatively cold. In turn, this causes considerable compressive stress that heals surface micro-cracks and improves the working characteristics of the surface. Finally, the bombing causes grasping the sprayed particles by the purified and heated surface and the thinnest layer between the substrate and the coating is formed. The third step is in coating a predetermined thickness onto the surface - this is carried out with a small U bias potential between the cathode and the auxiliary electrode (not more than 200 V). During the coating process, the surface is periodically short-ionic cleaned to maintain the desired temperature.

Microhardness layers of TiN.

Due to anisotropy of mechanical properties of titanium nitride TiN in different crystallographic directions one should expect increase in operating properties of coating along one of them. If the layer is texturised along the direction [111], the strength characteristics will be maximal as the plane (111) in a face-centered cubic unit cell is the most populated with atoms. The spatial group is Fm3m, parameters of crystal cell are: $a=0,422-0,424$ nm. The lattice type is NaCl.

Figure 2 shows the influence of technological parameters (the potential bias) and the type of layers formation on the microhardness of TiN layers and a metal basis.

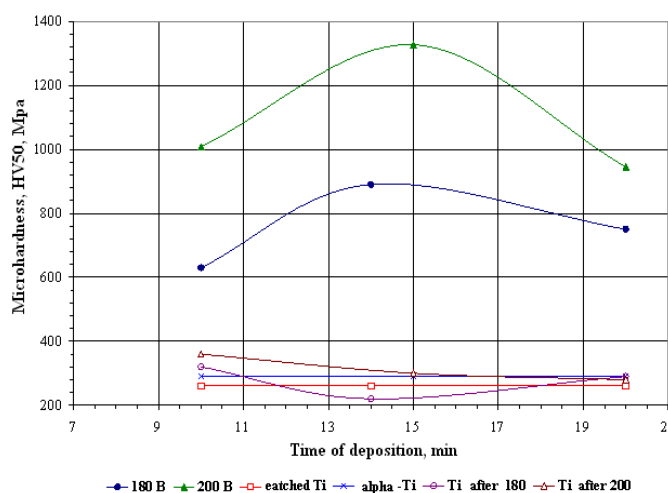


Рис.2. Influence of the potential of displacement on microhardness of TiN layers

The initial microhardness of titanic alloy OT4-1 varied from HV₅₀=150 to HV₅₀=290 MPa in accordance with the surface preparation before spraying. Such considerable difference in values of HV₅₀ is explained by different composition of surface layers. The initial sample was not heat-treated or alpha case. Heat-treatment was made to increase the alloy plasticity and to protect from oxidation. The samples' etching (removing of the alpha case

layer) was carried out traditionally in water solution containing 100-120 g/l of sulfuric (H₂SO₄), 120-130 g/l of nitric (HNO₃) and 30-40 g/l of hydrofluoric (HF) acids.

The sample with the maximum microhardness of 1330 N/mm² was textured by a plane (111). The X-ray phase analysis of the coverings deposited at various nitrogen pressures showed that the maximum value of microhardness corresponds to the smallest width of diffraction lines. As appears from fig. 2, microhardness along with the influence of potential bias depends on spraying duration. Increasing the thickness of coating (spraying duration) causes an increase in microhardness. This fact is not new. We have observed a decrease in microhardness with increasing the duration from 15 to 20 minutes. It may be connected with the fact that a TiN film begins to pulverize having reached thickness of 5-6 microns under the influence of the plasma column, and its surface becomes more defective. As a consequence there is a decrease in microhardness.

Fig. 3 shows the dependence of coating thickness on the time of deposition. The results were obtained by processing the X-ray pattern of system "substrate-film" in view of the X-ray absorption coefficient calculated for the stoichiometric composition of titanium nitride.

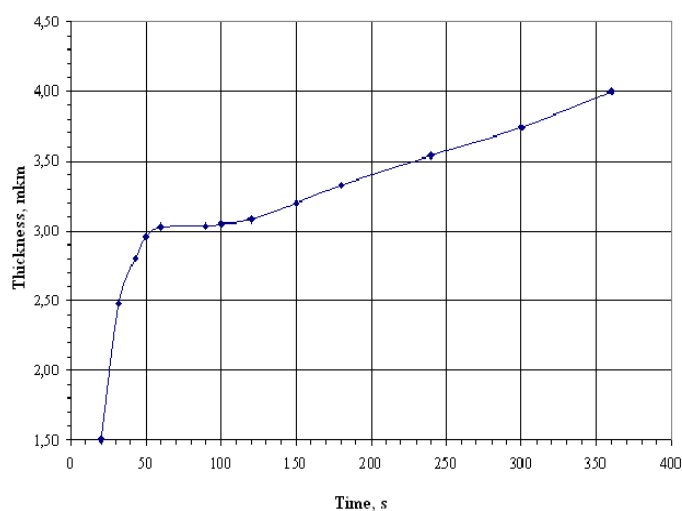


Fig.3. The thickness of film as a function of the time deposition ($p_{N_2}=10^{-2}$ Pa)

The dependence course of "thickness-time of deposition" may be explained on the basis of the island model of films' growth. At the initial moment of growth the film is formed in the form of islands while the X-ray diffraction intensity of the reflection from the substrate is weakening slightly. With a further growth the islands begin to merge, and the proportion part of the coated surface is greatly increased. This causes sharp changes in the intensity ratio of diffraction peaks on the substrate material before and after coating. The growth can occur up to several layers of a film, and then the dependence of coating thickness on the application time varies slightly. One of possible reasons for this are equally probable processes of deposition and sputtering. Thus, according to X-ray investigations under these conditions the coating thickness intensively increases during the first 1.5-2 min.

Since the microhardness of a metal base depended on the type of training the original surface (fig. 2), we tried to do a comparative analysis of microhardness according to the conditions of layer formation (tab. 1).

The greatest microhardness of HV₅₀=2000 MPa was observed in the double-layer sample formed in conditions of maximum HV₅₀ of TiN monolayer (current of the arc discharge 80A, time of deposition 15 min, potential of displacement 200V). On the etched surface of a titanium alloy a layer of the titan then titanium nitride were put. TiN layer upon gas-saturated surface of alloy OT4-1 had HV₅₀=1080 MPa, but was more rough.

Table 1

Microhardness of TiN layers depending
on the type of layer formation

Formation conditions of TiN layer	HV ₅₀ , MPa
etched Ti	150
alpha Ti	290
alpha Ti/ Ti layer /TiN	2000
alpha Ti./TiN	1080
etch.Ti /TiN/Ti layer	440
12X18H10T	250

Wear resistance of TiN coatings.

In this work we used an accelerated method of wear resistance tests. An abrasive grain rotating at a speed of 0.285 m/s cuts the coating layer from the sample surface. Therefore in this case grinding should be considered as super-fast cutting (scratching) surface layers of the sample by a large number of the smallest grinding grains (cutters) cemented into one sheaf [5]. We have found that TiN coating's wear resistance in conditions of accelerated sliding on an abrasive cloth doesn't depend on the size of grains while the wear pattern is rather complex. One can see on the wear curves the first (lapping) wear of the sample, then there comes a time the TiN film slips on the electrocorundum's abrasive grain (90-95% Al₂O₃) and after the film destruction the loss of metal substrate's mass takes place. Fig. 4 shows the wear resistance of titanium alloy samples OT4-1. For comparison here is the wear of steel 12X18H10T.

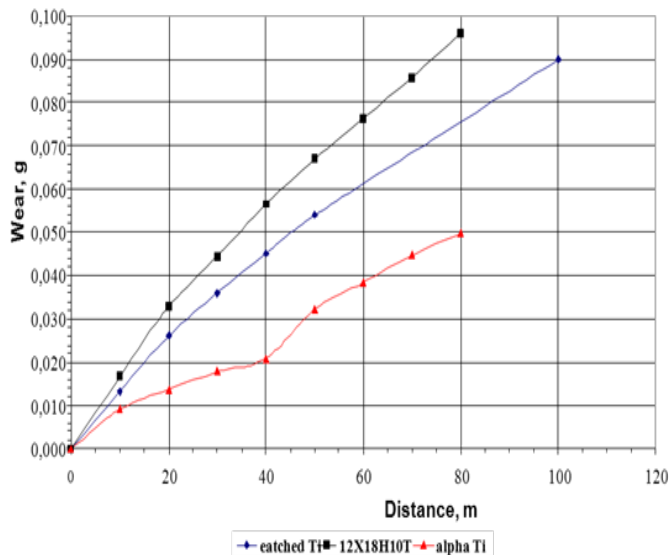


Fig. 4. Wear resistance of initial samples

As follows from fig. 4, replacement of steel 12X18H10T with the titanium alloy OT4-1 allows to reduce the wear almost twice (At $l=30$ m the wear of $m = 0,044$ g (12X18H10T), for gas-saturated OT4-1, $m=0,023$ g). As well as in a case with a microhardness, a wear of a titanium alloy depends on the surface state. A gas-saturated (alpha) layer protects a titanic alloy against abrasion. The alpha layer's wear pattern is complex because the layer on the sheet's surface is uneven, friable and has a large surface roughness.

Investigation of wear resistance of TiN layers revealed its increase in comparison with a metal substrate in all the studied samples. The TiN layer's wear pattern depends on microhardness, an original surface state and the method the coating is formed.

Figure 5 shows changes in the wear pattern according to technological parameters of the coating process (time-thickness, the potential bias). With increase in the layer's thickness (spraying duration) the wear resistance and microhardness also increase.

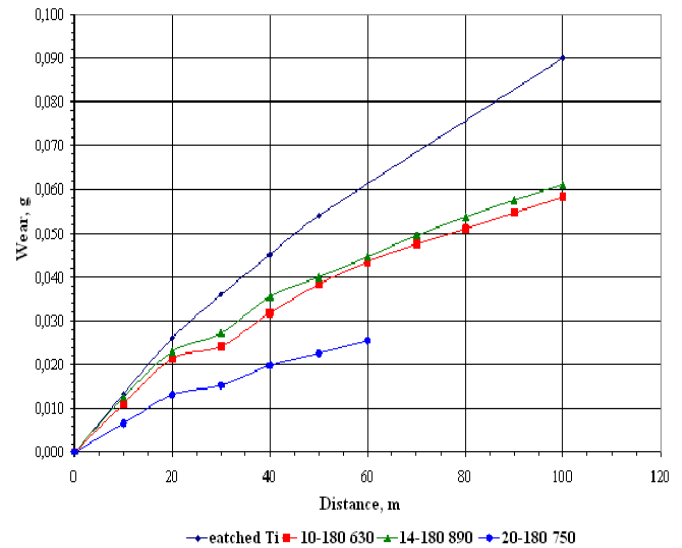


Fig. 5. Wear resistance of TiN layer

But the most interesting is the wear resistance of multilayer coatings (fig. 6). TiN layers were formed either on etched or on alpha surface. Microhardness of these layers is presented in table 1. In all the samples studied an increase in the wear resistance was observed. The greatest wear was seen in etch. Ti/Ti/TiN sample with the maximum microhardness of HV₅₀=2000 MPa. The sample was double-layer: the first layer contained plastic Ti and the second layer had solid TiN. The layer thickness was 9,5 microns, however the wear of this layer was observed at the first meters when it was sliding on a grinding skin number 10.

Considerable wear was also observed for the layer TiN, formed on an alpha case surface. The sliding distance was not more than 20 m. For a double-layer coating of etch.Ti/TiN/Ti we recorded the lowest point of microhardness HV₅₀=440 MPa, but the wear (0,018 g) and destruction were found while sliding 36 meters. An alpha case layer on a titanium plate has the maximum stability (40 m slip) and thus the greatest wear (0,020 g).

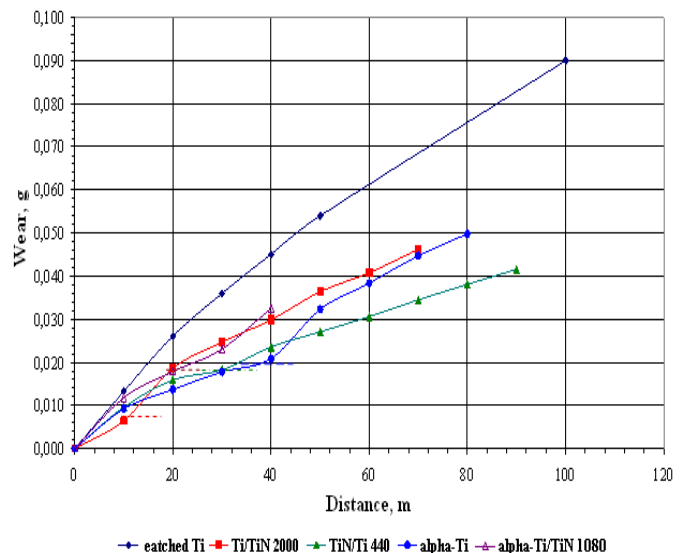


Fig. 6. Wear resistance of TiN layer

The results of abrasive wear of the samples for which we have found the maximum wear resistance are given in fig. 7.

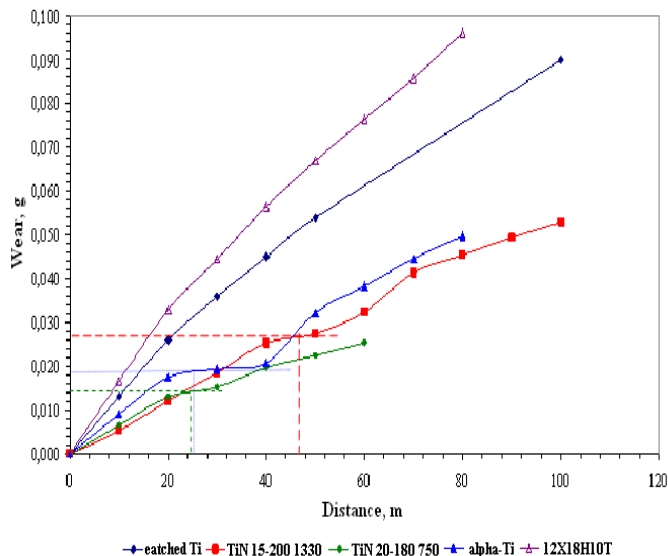


Рис.7. Wear resistance of TiN layer

For performing a comparative analysis it is necessary, in our view, to analyze the region of the «shelf» though even the grinding area indicates various wear patterns of a TiN layer, an alpha case layer and an etched surface of the titan. The calculated coefficients of friction also show different wear patterns of nitride layers formed under different conditions.

Type of material	Coefficients of friction
12X18H10T	0,87
etch. Ti	0,57
alpha condition Ti	0,52
TiN (15-200-1330)	0,51
TiN (20-180-750)	0,50

4. Conclusion

The samples of OT4-1 alloy both in etched and in an alpha states are more abrasive wear- resistant as compared with the steel alloy 12X18H10T. Alpha layers's wearing out starts at a distance of 24 m while sliding on Abrasive number 10. TiN layer's destruction with the maximum microhardness starts when it is sliding for 23 m, but its wear is less than for alpha titanium alloy's case layer. A TiN layer having microhardness $HV_{50} > 1330$ MPa starts to break down when sliding distance is 45 m and has the same wear as the titanium alloy the sliding distance of which gets 20 m. Thus as a result of ion-plasma deposition of TiN layers on a titanium alloy OT4-1 is observed surface hardening, reducing wear and friction coefficient.

5. Acknowledgments

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NEW GENERATION ELECTRIC-WELDED PIPES FOR METALLIC BUILDING STRUCTURES

ЭЛЕКТРОСВАРНЫЕ ТРУБЫ НОВОГО ПОКОЛЕНИЯ ДЛЯ МЕТАЛЛИЧЕСКИХ СТРОИТЕЛЬНЫХ КОНСТРУКЦИЙ

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Abstract:

Investigation of low carbon microalloyed API 5L X80 steels for electric-welded pipes applied in building of metallic structures of different complexity. Problems of weldability of these steels and effect of technological and structural factors on mechanical properties of weld seams have been considered. Also mechanical characteristics at cyclic loading of the steels are considered.

KEY WORDS: LOW CARBON MICROALLOYED API 5L X80 PIPE STEELS, WELDABILITY, WELD SEAMS, MICROSTRUCTURE, IMPACT TOUGHNESS, FRACTURE RESISTANCE.

1. Introduction

Circular section pipes as a building structure element has several essential advantages compared with shaped or thick sheet rolled metal both in reduction of steel intensity of building structure and in the case of such specific actions to building structure as corrosion, high temperature at fire and wind [1-3]. Moreover constructions made of pipes have high architectural expression. Pipes of large diameters milled on metallic construction works were applied in erection of unique constructions for a long time [4]. Roof structures of covered skating center in Moscow are supported by pipe $\wedge$ -bearing with height 50 m and outer diameter 2,5 m and pipe wall thickness 20-50 mm with cable-stayed structure. The pipe was made of 0.1C-Cr-Si-Ni-Cu steel, contained low concentrations of S and P (0.010 and 0.012%, respectively) and had $\sigma_{0.2} = 390\text{MPa}$ and $KCV^{-60} = 60\text{J/sm}^2$.

Wide usage of pipes in building industry appeared to be possible due to adoption of technology of massive pipe production.

At building of stadiums and the other unique constructions pipes with large diameters (530-1420mm) and high strength grade are widely used (table 1).

Table 1 – Mechanical properties of steels for building structures

Mechanical properties	Strength grade		Temperature, °C
	C390	C440	
σ_b , MPa	540-730	590-770	+25
$\sigma_{0.2}$, MPa	390	480	+25
δ_5 , %	20	20	+25
KCV, J/sm ²	34	34	-40

2. Preconditions and means for resolving the problem

For building of stadium in Kazan pipes $\varnothing 1420 \times 45,8$ mm (1) with $\sigma_{0.2} = 480\text{MPa}$, $\varnothing 1220 \times 30\text{mm}$ (2) with $\sigma_{0.2} = 390\text{MPa}$, $\varnothing 820 \times 40\text{mm}$ (3) with $\sigma_{0.2} = 480\text{MPa}$ were investigated. Table 2 presents chemical composition of steels under the study.

Table 2 – Chemical composition pipe steels according to the results of control tests

Pipe	Element content, %						
	C	Mn	Mo	Nb	V	S	P
1	0.07	1.55	0.1	0.05	0.08	0.002	0.01
2	0.08	1.51	0.01	0.04	0.05	0.003	0.01
3	0.07	1.39	0.22	0.05	0.03	0.004	0.01

It should be noticed that hydrogen content was on snowflake nonhazardous level. Table 3 presents mechanical properties of steels under the study.

Table 3 – Mechanical properties of pipe steels under the study

#	Mechanical properties						
	$\sigma_{0.2}$	σ_b	δ_5	ψ_z	KCV-40	KCV-60	HV
	MPa		%		J/sm ²		
1	520-670	610-700	20-28	60-70	>300	175-300	219-254
2	480-560	570-620	20-30	70-81	>300	275-300	138-183
3	520-600	610-710	22-27	72-76	>300	180-325	193-230

Investigation of mechanical properties of pipe steels under cyclic elastic-plastic deformation has been conducted with cylindrical samples with size $\varnothing 12 \times 60$ mm under tension-compression on "soft" cycle (at constant swing of stress) at asymmetry coefficient $R = -1$. Extremely high impact toughness of the steels is caused by thermo-mechanical treatment during rolling in γ -area near A_{r3} -point with accelerated cooling to $(\gamma + \alpha)$ – area, low concentrations of harmful impurities and gas elements that provide formation of fine microstructure evaluated by transmission electron microscopy [5]. Microstructure represents grains of quasipolygonal ferrite with size $1-2\mu\text{m}$ possessing developed substructure and lathlike bainite (fig. 1, 2) [6].

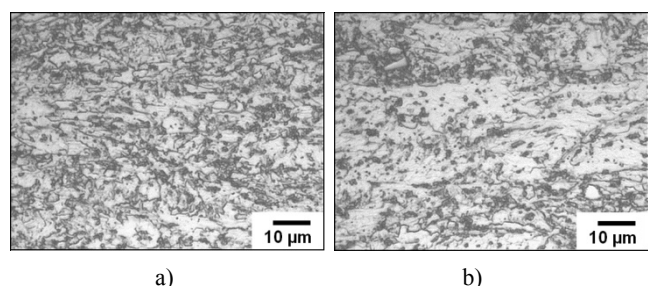


Figure 1 – Microstructure of the steels under the study: quasipolygonal ferrite (a) and lathlike bainite (b) (light microscopy)

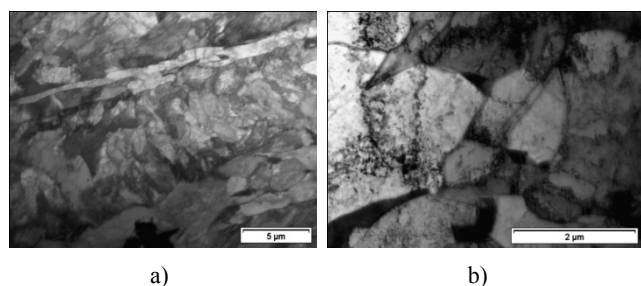


Figure 2 – Images of lathlike bainite (a) and quasipolygonal ferrite (b) obtained by transmission electron microscopy

Weldability of the C440 steels has been investigated in details. Analysis of heat-affected zone, seam zone has been conducted where seam structure has lowest properties. Kinetics of phase transformation of austenite in a range of cooling rates, mechanical properties of seam zone material, propensity to forming of cold cracks have been studied. At making of TTT-diagram simulated structure of seam zone has been obtained by induction heating of billets $6 \times 10 \times 55$ mm up to temperature 1300°C and subsequent cooling with rates $0.1-300^\circ\text{C/s}$.

Hard martensite constituent responsible for formation of cold cracks, appears at the cooling rate after $> 100^\circ\text{C/s}$, which is higher than cooling rate at welding of root technological seams and essentially higher than cooling rate of seam zone at construction welding. Criterion of exclusion of cold cracks is hardness $\leq 320\text{HV}$.

In this case absence of cold cracks can be guaranteed at any type of welding applied in making of steel constructions including welding of root seam without of preliminary, accompanying and sequential heating.

Dependence of impact toughness on considered cooling conditions has been studied. The results of tests showed that in cooling rate range $2-8^\circ\text{C/s}$ dip of impact toughness happened, associated with formation of ferrite and bainite mixture.

Strength of welds at testing of the samples cut from joint has been evaluated. At tension testing the samples were fractured on base metal, out of heat affected zone, showing typical mechanical properties for base metal. Bending test showed that on expanded side there was no cracks up to 180° bending angle.

Results of impact bending test are presented in table 4.

Table 4 – Results of impact bending test

	Impact toughness, J/sm^2 at $t^\circ\text{C}$		
	-20	-40	-60
KCV	97	55	28
KCU	-	69	76

Next aspect which we investigated in this work was behavior of pipe steel at cyclic loading. After first cycle of loading hysteresis loop is disconnected that is associated with Bauschinger effect i.e. action of compressing loading induces decreasing of resistance to small plastic deformation, so reaching of stress level corresponding to tension stress deformation value has to exceed value reached at a tension (fig.3).

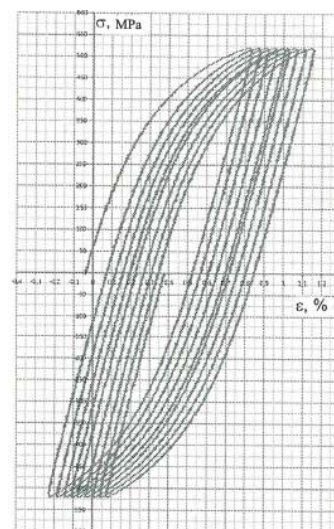


Figure 3 – Typical mechanical hysteresis loop of the steels under cyclic loading "tension-compression"

Analysis of tests results under repetitive "soft" loading showed that width of plastic hysteresis loop stabilizes in first loading cycles i.e. materials under the study are cyclically stable. Cyclic stability of the materials is caused by firstly developed subgrain structure. Effect of disordered dislocation nets is nonessential since such

material is normally cyclically softened. Secondly cyclic ductility of these materials and particularly plastic hysteresis loop width are twice higher than plastic steels for building structures have. This effect can be explained by not only high ductility but microstructure and properties inhomogeneity which enhance damping ability of these steels.

3. Conclusion

The steel under the study possesses wide favorable range of cooling rates, in which high resistance of brittle fracture at electric welding is provided.

Weldability completely corresponds to standard requirements. Considered steels have very good weldability that making of constructions has confirmed.

Application of steels under the study is reasonable in seismic active regions building since seismic oscillations are naturally low frequent.

4. Literature

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