

REGULARITIES AND MECHANISMS OF FORMATION OF SUBMICRO-, NANO-, AND ULTRAFINE-GRAINED STRUCTURES AND MECHANICAL PROPERTIES OF METALS AND ALLOYS UNDER DIFFERENT TREATMENTS

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An overview of our original studies and the results reported in the literature on the investigation of variations in structure, phase composition, mechanical and other properties of metallic materials under external impacts is made, including their high-pressure processing by large (severe) plastic and megaplastic deformation, explosion loading, and irradiation with ultra-short laser pulses.

Keywords: thermomechanical treatment, plastic deformation, titanium, alloys, structure, phase composition, mechanical properties, laser irradiation, explosion loading.

INTRODUCTION

Within the recent two decades, ultrafine-grained (UFG) (grain size 1–10 μm), submicrocrystalline (SMC) (grain size on the order of or less than 0.1–1 μm), and nanostructured (NS) (grain size on the order of or less than 0.1 μm) metals and alloys produced by large (mature) [1–4], severe plastic (SPD) [5], and megaplastic deformation (MPD) [6] have been intensively investigated and ever increasingly used in medical and engineering applications. In all these cases the process of deformation takes place under high applied pressures and degrees of the resulting plastic deformation. It should be emphasized that in addition to the above classification, in the foreign and partially domestic literature the term 'ultra-fine grained materials' has in the recent decade become quite common in describing the materials subjected to severe plastic deformation and having the microstructure elements measuring less than 1 μm . Unfortunately, without any discussion by the specialists the traditional term 'ultra-fine grain' (well-known to the Russian and Western researchers from the corresponding monograph [7]), which characterizes the structure with the grain sizes within 1–10 μm , has been replaced in many publications. The reason for a special definition of this size range back in the early 1970-s was the fact that the alloys with this particular structure exhibited the effect of structure superplasticity. In the present work the author adheres to this terminology well established in the Russian scientific literature.

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1. FORMATION OF STRUCTURE AND PROPERTIES OF METALS AND ALLOYS BY PLASTIC DEFORMATION UNDER DIFFERENT LOADING CONDITIONS

1.1. Thermomechanical treatment

It is well known that the technological processes of deforming materials to high degrees of plastic deformation are performed both at room and elevated temperatures (using heating of the processed specimens before deformation, heating of the tool sets to the specified temperature, heating by the heat released in the course of deformation, or using all these options simultaneously). In view of the fact that the deformation process is commonly carried out at essentially high speeds, marked heating of the deformed material is observed in the majority of the SPD experiments reported in the scientific literature. It seems unlikely to rule out heating in the local microvolumes of the experimental specimens even when using high strain degree deformation at cryogenic temperatures [8], since it is well known that deformation of ordinary and fine-grain materials (SMC and NC-metals and alloys) is accompanied by an active formation of slip bands and in the case of mesobands – by non-crystallographic shear. These bands are formed under conditions close to adiabatic ones, which corresponds to a real possibility of a considerable local heating in these regions of shear localization [9].

In accordance with the terminology accepted in the Russian technical writing [10], the thermomechanical and/or mechanothermal treatments (TMT and MTT, respectively) have to be understood as a combination of the operations of deformation, heating and cooling (in different sequences), resulting in the situation where the formation of microstructure and properties of a metallic material in the final stage of deformation occurs under the conditions of a high density of crystal structure imperfections created by the plastic deformation. In other words, under the conditions of high-pressure metal processing in question there is a simultaneous impact by the applied external pressure and temperature. There are well-known industrially applied processes of structure refinement: the method of stepwise deformation, the high-temperature thermomechanical treatment (TMT) and other processes. According to these common features, all of the above-mentioned types of treatment (various modifications of SPD methods, impact by large (megaplastic) and other deformations (torsional shear, screw extrusion, etc.) in their physical conditions of affecting a material could be generally defined as thermomechanical or mechanothermal treatment. Major gains could be achieved in improving strength and sustaining plasticity not only by refining the material grain structure using the SPD methods (the principal processes are thought to be equal-channel angular pressing (ECAP) and high-pressure torsion), but in a number of cases – at a considerably lower cost using the traditional TMT and MTT treatments. For instance, earlier we observed that processing of titanium by a combination of radial-shear, cross-helical and profile rolling processes with controlled heating (in the current concepts of the SPD method, these processes are not classified as such; nevertheless, one of the conditions, specifically, high normal values of the stress tensor components are present in these deformation processes) it is possible, varying the TMT and MTT regimes, to form NC-, SMC-, or UFG-states ensuring an essential improvement of the strength and plasticity [1, 11, 12]. As a result of a simultaneous impact by plastic deformation and heating by the heat released in these processes, a high level of internal microstresses is sustained in unalloyed titanium after formation of nanocrystalline or submicrocrystalline state, which is due to the increased density of deformation-induced crystal structure defects. In order to release or rule out the microscopic internal stresses of the first kind, the material is subjected to post-deformation annealing at the temperatures lower than that of the onset of recrystallization, which allows sustaining an optimal combination of strength and plasticity of the SMC-titanium structure. In the cases where nanostructured state is formed after the postdeformation processing, then, given the above annealing (e.g., for VT1-0 titanium alloy) then this structure is transformed into submicrocrystalline structure stabilized with ultrafine titanium carbide particles [1].

By now, this line of research, associated with optimization of the technologies for refining the structure of metals and alloys, has been well developed both in Russia and in other countries. Numerous studies (see e.g., review papers and monographs [13–16]) report the principles and mechanisms of structure refinement using SPD influence on a number of mechanical properties (tensile strength and yield strength, plasticity characteristics, etc.) and on the fatigue fracture and corrosion resistance and, quite unexpectedly, on the surface bioactivity and other unique physical-chemical properties of SPD-materials. In this connection, it seems important to focus on the results obtained in the physics and mechanics of plastic deformation of metals and alloys preceding the recognition of this line of research in materials

science. In order to describe the features of plastic deformation causing qualitative changes in the structural state of a material compared to those after small deformation (e.g., near the yield strength), the author of [2] introduced a concept of mature deformation. Its distinguishing structural attribute is mass formation of deformation-induced high-angle boundaries of the fragments (grains) resulting from the structure fragmentation, which determines the process of subsequent microstructure refinement in the stages of deformation which comparatively recently have been proposed to classify as megaplastic deformation [6, 17]. By now, it has become evident that this process develops under certain condition and continues up to the formation of submicro- and nanocrystalline states in metals and alloys. It is therefore necessary to recall that the foundations of the present-day methods of formation of these structural states and the unique mechanical and other related properties achieved using plastic deformation of materials were developed back in the 1980-s, and their various aspects were reported in [2, 18–20].

On the other hand, according to the concepts of megaplastic deformation developed in [6, 17], the mechanism of structure fragmentation is not the sole possible scenario for forming SMC- and NC-states. These concepts imply that the stage of plastic deformation accompanied by fragmentation is preceded by megaplastic deformation. The transition from macroscopic to megaplastic deformation in its turn is due to the activation of one of possible additional energy dissipation channels, such as dynamic recrystallization, dislocation-disclination accommodation, phase transformations (including a transition into amorphous state), and other channels. Note that the structural changes in the stage of megaplastic deformation are characterized by a cyclic character and formation of grain-subgrain structures with a wide range of distributions of the structure elements over the mutual misorientations both during this process and in the stage of fragmentation.

In addition to the above-enumerated methods, other approaches to formation of grain-subgrain structures in metals and alloys are available. For instance, earlier we reported a possibility of forming structures with submicron dimensions of grain-subgrain elements via multiple (10–15 stages) mechanical-thermal treatment (MMTT) of dispersion-hardened nickel (Ni – 3 v.% HfO₂ alloy) at the strain rate 15 % over the specimen thickness, followed by annealing at 1373 K for 1 h in every MMTT stage [21]. We identified the structural mechanism of a gradual increase in the mutual misorientation of subgrains in every successive MMTT stage, whose action eventually resulted in the transformation of a certain fraction of subgrains into high-angle grain boundaries and the formation of a grain-subgrain mixture. At present, the principal method used by the majority of researchers is that of severe plastic deformation. Currently this term is most extensively used in the scientific publications to define the processes of superhigh deformations predominantly by the method of equal-channel pressing developed at the NAS of Belarus (Minsk) [22]. It was the use of this particular method (classical by now) which fostered the design and development of the scientific concepts and principles of practical application of severe plastic deformation, starting from the pioneering study reported in [5].

The results of numerous investigations demonstrated that the functional reliability of medical implants and structures used in orthopedic surgery, traumatology, dentistry, and other field of medicine is determined by a complex of mechanical properties (strength, plasticity, resistance to cyclic loading, wear resistance, etc.), which a material demonstrates under real conditions of its service life in the living organism, and by its action on the surrounding living tissues, biological fluids, and the entire organism. The issue of designing functional inorganic medical materials is one of the key challenges in the modern biomaterials science [1, 23–26].

A possible solution to this problem could rely on the idea of replacing the titanium alloys widely used in medical applications by high-strength, nanostructured unalloyed titanium (VT1-0 alloy), which has been pursued for the recent two decades [1]. In particular, the formation of the above-mentioned states in high-purity titanium (VT1-0) using the methods of plastic deformation in question allows achieving high uniformity of grain-size distribution in contrast to the inhomogeneous stripy fine-grain structure formed by rolling titanium under ordinary conditions. Moreover, strain localization at the macrolevel is suppressed in such structure and, as a result, the level of strength is increased, with the high plasticity sustained, and so does the durability limit under cyclic loading [1, 3, 27–30]. Among other things, this makes it possible to manufacture super-thin, high-strength titanium foils measuring less than 10 μm in thickness, which are in great demand in medical and engineering articles [31].

Unfortunately, these methods for refining the structure of metallic materials using SPD, equal-channel angular pressing and high-pressure torsion being the most common, which are actively investigated and applied both in Russia and beyond, demonstrate low production efficiency and considerably increase the cost of the processed materials.

Moreover, the resulting NC metals and alloys generally have low thermal stability, high strength and hence lower plasticity without any specialized processing. This limits or rules out their high-pressure treatment during the production of the required commercial range of semi-finished products and increases the labor costs of manufacturing final products in the turning-milling automated machine tools under their serial production. In this connection, within the recent decade together with the co-workers we continued the development of the well-known technological principles of forming NC-, SMC-, and UFG-states in metals and alloys (using titanium and its alloys as an example). This pressing necessity stems from the fact that the practical application of the results of R&D works on achieving marginal grain refinement in metallic materials, using SPD among other methods, has faced serious difficulties. The major bottlenecks are the following: considerable cost increase due to a necessity of additional treatments of the resulting nanostructured product and low efficiency of the manufacturing process. The most urgent issues are the economic and production efficiency of SPD-methods in the cases where the task is to manufacture the required range of commercial products. Together with co-workers the author organized a low-cost, high-efficiency low-tonnage production of the VT1-0 alloy grades in different structural states using traditional methods of high-pressure treatment of metals, which did not belong to SPD processes. To this aim, a combination of radial-shear and torsion-profile rolling processes adapted earlier for rolling tungsten- and molybdenum-based difficult-to-deform alloys was used [32]. These methods are very common; they have been investigated in great detail [32–35]. Nevertheless, prior to the work of the author's research team they had not been considered from the perspective of a possibility of determining the trajectories and temperature-rate intervals of deformation, identifying the sequence of using these methods for target formation of inhomogeneities on the cross-sections of semi-finished products followed by removing this workover defect during the formation of NC-, SMC-, and UFG-states in the bars with relatively small cross-sections (e.g., as it was done for titanium-based alloys [36–38]).

One of the traditionally 'negative' effects of the cross-helical rolling (CHR) on the material structure is the so-called 'loosening' of the central zone of the bar, which occupies up to 20% of the material cross section. The investigations of the structure of this zone and the calculations of the material plastic flow under the conditions in question demonstrated that in the center of the rod the deformation occurs as a simple tension resulting in a banded structure (under critical conditions) and the formation of pores and metal rupture [35]. Note however that the pores and other discontinuities are formed only at large (higher than a certain critical value) degrees of deformation within a single pass. A selection of reasonable deformation regimes (trajectories and temperature-rate intervals) individually for every material and its intermediate structure allows not only successfully realize forming without development of internal and external defects of semi-finished products, but also to use the advantages of torsional rolling due to the structure workover via realizing the intensive shear component of deformation [37, 38]. These principles, well known in their general form, are successfully used in metallurgical production of rolled sectional bars from titanium alloys.

Several principal schemes of manufacturing NS-, SMC-, and UFG-titanium were used at the pilot-production site of the BelSU Nanostructured Materials and Nanotechnologies Science, Education & Innovation Centre. For instance, the technology of manufacturing banded-structure rolled material is reduced to thermal cross-helical rolling followed by the lengthwise rolling in roller passes to achieve the required profile of the rolled product. Two technological schemes are available for manufacturing rolled metal bars. The essence of the manufacturing process consists in a preliminary warm cross-helical rolling followed by lengthwise rolling. In the former scheme, in the final stage cold cross-helical rolling is performed, followed by annealing to alleviate internal stresses. This scheme is most suitable for production of 6–8 mm bars (up to 3 m long, depending on the furnace dimensions) from the VT1-0 titanium. According to the second scheme, the warm lengthwise rolling in roller passes is replaced by cold rolling. In the final stage, the bars are calibrated, annealed, and reeled. Using this scheme, we can produce calibrated high-grade bars/rods (accuracy class up to h7) with the diameters from 3 to 5 mm and length up to 3 m.

By now these low-cost, high-efficiency technological processes for manufacturing bars/rods (of a variety of profiles) from titanium of the nanostructured VT1-0 grade have been successfully used in the technological cycle of the pilot production company OOO "Metal-deform" at the NR BelSU [1].

1.2. High-velocity deformation

It is well known that during dynamic loading, realized under high-power pressure pulses (with pulse durations of a few microseconds and shorter) whose value is a few or tens of gigapascals, accompanied by the formation of shock waves, the strain rates are on the order of 10^2 s^{-1} and higher [39]. Shock-wave loading is among the most effective high-energy methods for hardening metals and alloys, which occurs as a result of intensive multiplication of dislocations and formation of fine structures, including SMC- and NC-states. The main advantage of this impact consists in a possibility of achieving considerable hardening by a relatively small change of the initial specimen shape. The structure of metals and alloys subjected to shock-wave loading changes under a simultaneous action of several factors: high pressure, specific high-rate plastic strain, compressive stresses in the loading wave and tensile stresses under unloading. These processes are followed by considerable heating of the specimens. High pressure in the shock wave promotes phase transformations, resulting in the formation of phases with a smaller specific volume compared to the initial phase. On the other hand, tensile stresses in the unloading waves can initiate the formation of phases of a larger specific volume. In the conditions under study, there is grain structure refinement resulting in considerable hardening of the material [39, 40].

The plastic strain rates corresponding to dynamic conditions could be achieved not only by shock-wave impacts. Using SMC-titanium [4], it was shown that under ordinary quasi-static conditions of torsional deformation at room temperature the plastic strain rates could be comparable to those under dynamic loading ($\dot{\epsilon} \sim 10^2\text{--}10^3 \text{ s}^{-1}$). It was found in [41] that the plastic strain rate in the localized strain bands (measuring not more than $10 \text{ }\mu\text{m}$ in width) was about $8 \cdot 10^2 \text{ s}^{-1}$. It turned out that the above-described torsional deformation was realized only for SMC-titanium having the structure with lengthy non-equilibrium grain boundaries. This effect is not observed in the testing of coarse-grained or SMC-specimens, but with the grains elongated along the rolling direction rather than globular grains. This circumstance suggests that the above-described features are associated with the deformation via mutual displacements of the grains due to grain boundary sliding in the course of high-strain-rate deformation taking place under the conditions in question.

In [42], an investigation of the influence of defects, which had formed as a result of preliminary severe plastic deformation, on the resistance to quasi-static and dynamic deformation of VT1-0 titanium was performed. This alloy grade was tested in two grades: coarse-grained with the grains measuring $10\text{--}15 \text{ }\mu\text{m}$ and submicrocrystalline states, formed by ECAP with the grain-subgrain structure element dimensions (termed as grain size in what follows) on the order of $0.3 \text{ }\mu\text{m}$. It was found out that at room temperature the value of the dynamic yield strength of the coarse-grained VT1-0 titanium is higher than that subjected to ECAP. Thus we can conclude that as the strain rate increases (within the range $4 \cdot 10^5\text{--}10^6 \text{ s}^{-1}$), the grain size influence on the yield strength of titanium decreases to such an extent that the hardening effect due to the SMC-grain refinement is practically eliminated. A different situation is observed in the case of quasi-static deformation: the strength of SMC-titanium is much higher than that of coarse-grained (CG) state of this material, which is illustrated in Fig. 1.

The authors of [42] assumed this effect to be associated with the crystal structure imperfections weakening the dependence of the yield strength on the strain rate. To put it differently, the same defects can determine an increased resistance to deformation under quasi-static conditions and be the sources of dislocations at high strain rates, thus reducing the resistance to plastic deformation. The origin of this effect could also be associated with other reasons. In a number of works we put forward an assumption that the earlier observed increased plasticity of NC (SMC)-materials could result from the grain-boundary sliding – a high-temperature deformation mechanism manifested under ordinary conditions (quasistatic loading at room temperature) [1]. Generally, the development of grain-boundary sliding in ordinary CG-materials is typical only for the region of elevated and homological temperatures ($T \sim 0.4 T_{\text{melt}}$ and higher), since under the above-mentioned conditions this is a diffusion-controlled process. As the grain size is decreased and the volume fraction of the material belonging to grain boundaries is increased, the role of the latter in implementing such deformation mechanisms as grain-boundary sliding (GBS) and diffusion-induced creep increases [1, 21]. Note that the role of intra-grain dislocation slip decreases, since the nucleation and evolution of the dislocation structures is energetically unfavorable for total dislocations in nanograins. Thus, in nanostructured materials (including those manufactured by large plastic deformations) grain-boundary sliding (and one of its versions – cooperative GBS [43]) can effectively compete with the motion of lattice dislocations in the value of its contribution into the total deformation

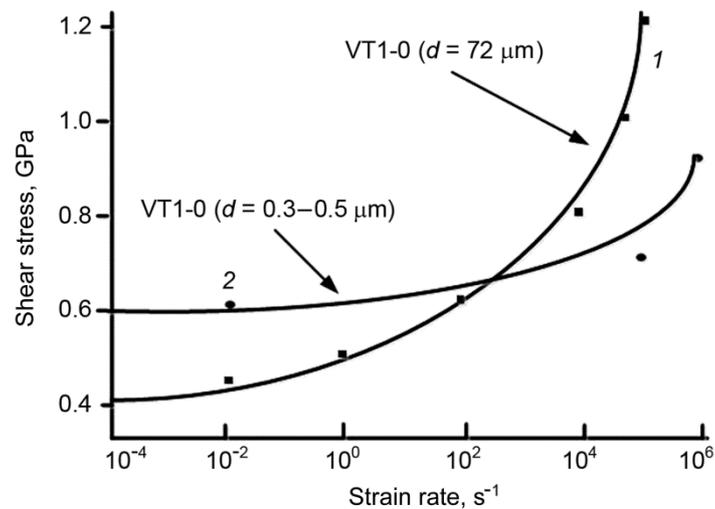


Fig. 1. Schematic representation of the dependence of shear stresses in VT1-0 titanium on the strain rate: Curve 1 – coarse-grained (Curve 1) and submicrocrystalline (Curve 2) states [44].

even at room temperature. This could be due to the non-equilibrium state of the grain boundaries, which results in the considerably increased coefficients of diffusion along these boundaries [1, 21, 44–47]. In a number of studies [3, 5, 47, 48] we demonstrated experimentally that the diffusion coefficients in NC-materials manufactured by plastic deformation are much higher (by 2–3 orders of magnitude) than that for individual grains of bicrystals, which is due to the non-equilibrium state of GBs [3, 44]. It is well known that activation of slip in nanostructured materials represents the physical reason for manifestation of the structure superplasticity at relatively low temperatures (the effect of low-temperature superplasticity) [49].

The development of viscoelastic deformation was investigated in [50] along with the study of the variations in structure, levels of microstress and microhardness under the conditions of dynamic loading of VT1-0 titanium in different initial structural states (coarse-grained and submicrocrystalline) at the strain $\sim 10^3$ – 10^4 s $^{-1}$. The dynamic compression tests were performed in an RSG-20 machine by the Kolsky traditional method using a Hopkinson pressure bar 20 mm in diameter. It was shown that in the initial SMC-titanium no changes in the average size of the structure elements had been observed, unlike the case with the initially coarse-grained material, where the structure after the deformation was essentially refined. The value of microstresses after dynamic deformation was found to remain at an approximately constant level. The value of microhardness after dynamic deformation compared to the initial state increases with an increase in the grain size. A comparison of the curves of dynamic loading of the coarse-grained and SMC-titanium of the VT1-0 grade demonstrated that the patterns of deformation behavior of this material in the states under study were different. A characteristic feature of the deformation behavior of SMC-titanium is the presence of a short strain hardening stage in the dynamic loading curve and its succession by sharp softening, which is not observed in the CG-state. At sufficiently high strain rates, the softening stage can transit into a stage of plastic deformation accompanied by cyclic variation in the plastic flow stress. It is assumed that the reason for this peculiar behavior is a high tendency of nanostructured titanium towards plastic strain localization at the mesoscale level, which is thought to be due to grain-boundary sliding.

It is known that the use of shockwave impact on solids gives rise to numerous phase transformations – shock-induced polymorphism [51]. Shock-induced phase transitions generally follow the martensitic type of transformations resulting from shear strains in the matter. The martensitic, diffusion-free rearrangements ensure superfast transformation of one lattice type into another on the basis of cooperative displacement of a large number of atoms by short distances at supersonic velocities of individual grain growth within the time as short as $\sim 10^{-8}$ s. The martensitic character of shock-wave transformations was determined by the crystal orientations in the titanium specimens survived after the $\alpha \rightarrow \omega$ -transition [52]. Under normal conditions, titanium crystallizes in the close-packed hexagonal lattice of

the α -phase. High pressure initiates a transition into a denser hexagonal structure of the ω -phase with three atoms in a unit cell, which is followed by a slight volume change. The equilibrium pressure of the $\alpha \rightarrow \omega$ -transition at room temperature is found to be ~ 2 GPa, and the starting transition pressure, depending on the material purity and loading conditions, exhibits a marked scatter from 3 to 9 GPa [53, 54].

A modern phase diagram of titanium at high pressures was constructed in [55], where using the method of synchrotron X-ray diffraction the behavior of titanium was investigated under the conditions of continuous loading up to the pressures ~ 200 GPa and laser heating to 3500 K in a diamond anvil. An experiment similar to [55] was performed in [56], where using the method of synchrotron X-ray diffractometry a sequence of phase transformations was studied in nanostructured technically pure titanium with the grain size ~ 200 nm, manufactured by cold rolling followed by equal channel angular pressing, and in coarse-grained titanium within the range of pressures up to 161 GPa in the diamond anvil at room temperature. It was found out that three phase transformations occurred in NC-titanium at high pressures, starting from an $\alpha \rightarrow \omega$ transformation at 10 GPa, which is succeeded by an $\omega \rightarrow \gamma$ transformation at 127 GPa and a $\gamma \rightarrow \delta$ transformation at 140 GPa. The results obtained are consistent with the data on the sequence of phase transformations published earlier for the experiments with coarse-grained titanium. The authors of [56] demonstrated that the $\alpha \rightarrow \omega$ -transition in NC-titanium takes place at 10 GPa both under the hydrostatic conditions and after their change to the non-hydrostatic mode, in contrast to CG-titanium, where the onset of the phase transformation is shifted from 10 to 4 GPa. This could be accounted for by the fact that an increase in the fraction of internal surfaces in the material with respect to its bulk as a result of nanostructuring gives rise to an increase in resistance to shear deformation and stabilization of the α -phase up to higher pressures. Furthermore, an increased concentration of impurities near the grain boundaries delays the $\alpha \rightarrow \omega$ -transition, increasing its energy barrier.

The features of formation and structure of the ω -phase in titanium were reported in [57]. The metastable ω -phase of titanium, having nanocrystalline structure (crystallite size about 50 nm), was formed by the method of severe plastic deformation, specifically, by high-pressure torsion (hydrostatic pressure 6 GPa). It was shown that at the pressure 6 GPa more than 90% of α -titanium within a short period of time (300 s) is transformed into the ω -phase, while a similar static load (zero number of rotation, exposure time 5 min, which is equal to the time of five completed rotations) within the same length of time did not result in any phase transformation. An investigation of the microstructure by the TEM method demonstrated that the ω -phase was formed near the grain boundaries of the primary phase. This prompts a hypothesis that the martensitic $\alpha \rightarrow \omega$ -transformation occurs as a result of an increase in the internal stresses near the GB, which considerably exceed the external loading stress, and is a channel for the free internal energy dissipation. The microhardness for the specimens after torsion at the pressure 7 GPa is ~ 450 HV, which exceeds the respective value ~ 350 HV for the specimens predominately consisting of the α -phase. It is believed that the higher microhardness of the ω -phase could be due to both its structure refinement and physical properties. The authors of [57] note that the microhardness values obtained in their study are higher than those reported earlier but within the admissible measurement error.

The authors of [58] investigated the microstructure and texture evolution in the high-purity recrystallized titanium with the grain size ~ 10 μm under the conditions of dynamic loading within the range of strain 10^2 – 10^3 s^{-1} at room temperature. Using the methods of optical microscopy and electron backscatter diffraction, they found out that at low and moderate strain values ($e = 0.05$ – 0.40) the changes in microstructure predominately occur via fragmentation of certain grains, wherein deformation follows the twinning mechanism; at the same time other grains, deformed due to the glide of dislocations, are elongated. The number of the twin structure elements is reported to increase with the applied stress. The initial grains are noticeably elongated, with the lamellar structure formed inside them; the lamella thickness is within the size range ~ 0.5 – 2 μm . When the level of strain increases to $e = 0.5$ – 0.8 , the microstructure of titanium becomes more inhomogeneous and the grain thickness is observed to decrease to 1 μm . After the initial grains get fragmented and a certain critical grain size is attained, the twins prevent further structure refinement and the deformation mechanism changes for that of slip. This implies that at low values of applied deformation the slip systems play only a secondary role in strain accommodation, while at moderate and high values their role prevails. The slip bands are observed at the strain values higher than $e = 0.6$.

The influence of shock-wave loading and post-deformation annealing on the process of structure refinement in titanium was also addressed in [59, 60]. In [59], the titanium specimens with different initial grain sizes were loaded by the plane and sliding shock waves with the amplitudes 15 and 7 GPa, respectively, and then subjected to low-

temperature annealing at $T = 0.27 T_{\text{melt}}$ and natural aging for one year. After the plane-wave loading, the structure with a high level of microdeformations was observed in titanium and no block-structure features. The loading by a sliding shock wave resulted in the development of shear deformation mechanisms, active twinning along one or several slip systems, accompanied by grain refinement due to twinning. For instance, in the specimen with the initial grain size 140 μm , after shock-wave loading and heat treatment the grain size decreased to 40 μm . After repeated loading and heat treatment, the grain size further decreased to 2–5 μm . In the specimens with the initial grain size 25 μm , the formation of new grain boundaries resulted in refinement of the substructure inside the grains to 0.5–1 μm , while the outer contours of the initial grains remained the same.

In [60], using unalloyed polycrystalline titanium (VT1-0) with different initial average grain sizes (from 0.2 to 40 μm), the variations in the structural-phase state were investigated under shock-wave impact (SWI) by compressive loading to the pressures 40 GPa, followed by cooling to room temperature together with the rigging. Using the methods of transmission (including high-resolution microscopy) and scanning electron microscopy and microdiffraction, and also by X-ray diffraction analysis it was found out that under the SWI the effect of grain structure refinement takes place only in the specimens with the average grain size more than 0.3 μm . The value of this effect, characterized by the ratio of the average grain size in the initial state to that after SWI, increases with the increasing initial grain size (d) and for $d \sim 40 \mu\text{m}$ is a factor of 150. After SWI, elements of twinning structure appear in the specimens with the initial grain size about 0.5 μm and larger. As the initial grain size increases, the structure after SWI becomes predominantly lamellar and essentially inhomogeneous. It was determined that the presence of two phases: α - and ω -titanium is characteristic for both coarse-grained and nanostructured states. The fact of refinement of the grains larger than a certain size and the absence of further refinement of the nanostructure revealed after SWI [60] could be interpreted not only within the framework of the above-described hypothesis on the role of grain-boundary sliding and grain refinement due to fragmentation, in view of the fact that the degree of deformation under SWI (in accordance with the available theoretical models of fragmentation) is insufficient for the mature fragmented structure to be formed, let alone the formation of the nanostructured state. The effect dealt with here might be attributed to the concurrent development of considerable internal stresses of phase recrystallization during the $\alpha \rightarrow \omega$ transformation (both direct and reverse) in the course of shock-wave loading. Additional studies are required to test this hypothesis, including the use of computer simulation experiments.

1.3. Pulsed laser processing

It is well known that under the conditions of shock exposure or beam pulse (laser, electron, or ion pulses) irradiation of materials ultrapowerful megabar shock waves (SWs) could be excited on their surfaces [39]. During propagation of these waves in the materials as a result of shock-wave loading plastic deformation processes and polymorphic transformations take place.

One of the promising practical applications is surface modification of materials by irradiating them with ultrashort (nano- and femtosecond) laser pulses. Surface modification of metals and alloys using different non-contact methods of surface treatment allows improving their mechanical, physical-chemical and other properties of the surface and subsurface layers. Using multiple-pulse femtosecond laser radiation, a possibility of forming sub-wave quasi-periodic nanoscale structures (nanoarrays) was investigated [61, 62].

The results on the effect of local ultrahigh pressures (in the GPa–TPa-range) during laser ablation of material surfaces with ultrashort (femtosecond) laser pulses (USP) is of great interest for hardening shock-wave processing of metal-cutting tools in mechanical engineering and structural-phase modifications of alloys for biomedical applications. The use of ultrasonic measurements in a time-of-flight mode allows performing non-contact diagnostics of such superhigh local ablation pressures and shock waves accompanying them [63]. The authors of [64] report the results of comparative desk-top non-contact ultrasonic measurements of the parameters (initial pressure and shock-wave velocity) of megabar shock waves generated under conditions of high-intensity single-pulse femtosecond laser ablation of the surface of a thick plate and a thin foil from the VT1-0 titanium alloy. The non-contact diagnostics allowed monitoring the initial SW pressure, and the contact measurements characterized SW propagation and their interaction with the target. In [64], relying on the experimental data it was established that at low SW amplitudes ($10\text{--}10^2$ GPa) in the

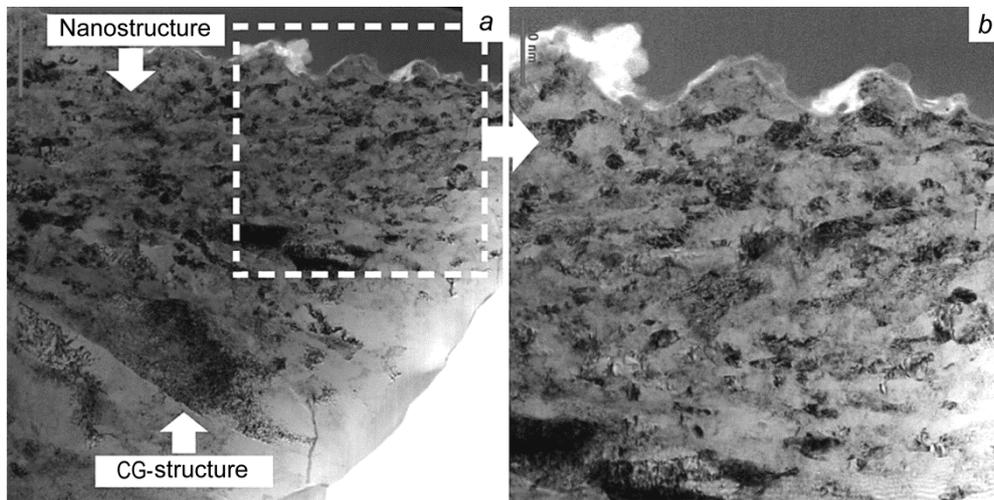


Fig. 2. Structure of the cross section of a thin foil from the subsurface layer of the VT6 alloy processes under the mode of strong ablation ($F \geq 350 \text{ mJ/cm}^2$, $N \approx 500$): subsurface layer (a), enlarged fragment of the selected region “a” (from the data reported in [68]).

course of plastic deformation of the target material and subsequent phase transformations the energy dissipates in thick targets only. An increase of the SW amplitude to 10^2 – 10^3 GPa results in the similar SW propagation character both in the relatively thick titanium target and in the thin foil. This peculiar feature suggests a superelastic mode of SW propagation due to the ultrashort durations of SWs preventing the formation of a plastic SW [65, 66]. The X-ray diffraction investigations after this impact did not reveal any signs of changes in the structure and phase composition in the subsurface layers of the material under study. This is thought to be due to the process of surface ablation during which the modified layer is removed and surface roughness is formed. Under these conditions the intensity is observed to decrease and the X-ray reflections are broadened, which impedes identification of new phases.

It is well known that surface microroughness is one of the key factors determining adhesion of the bone-forming cells and their dispersal during bone-tissue formation on the implant surfaces [67]. On the basis of different data, microroughness with asperities from 1 to 10 μm is thought to ensure the highest degree of cohesion between the implant and mineralized bone tissue. For medical titanium materials, in addition to bulk mechanical and chemical characteristics of great value are the topographic characteristics (relief texture), which strongly affect the surface wettability, corrosion properties, biocompatibility and bioactivity [1]. The action of femtosecond laser pulses on the surface of titanium results in the formation of quasi-periodic nanorelief with multi-scale roughness, which was shown by a team of workers, including the author, using the VT1-0 submicrocrystalline titanium alloy [61, 62]. The relief parameters can be changed, varying the treatment process parameters and its implementation in different media [51].

By the example of the alloys VT6 (Ti–6Al–4V) and VT16 (Ti–3Al–4.5V–5Mo) the changes of the subsurface layer microstructure were investigated and the level of residual microstresses was measured after texturing the surface of the specimens by the femtosecond laser in [68]. The VT6 alloy in the initial state had the laminar structure with the plates measuring 40–150 μm in length and 10–15 μm in thickness, and the VT16 alloy structure represented globular grains about 3 μm in size. After the laser treatment, on the surfaces of both alloy specimens quasiperiodic nanoarray formed, which consists of protrusions and recessions 0.3 and 0.15 μm in width and height, respectively with a period of 0.5 μm and the average roughness $R_a \sim 0.03$ – $0.04 \mu\text{m}$. During processing of the VT6 alloy under the mode of strong ablation ($F \geq 350 \text{ mJ/cm}^2$, $N \approx 500$), a 1 μm -thick subsurface nanostructured layer is formed where the grain size is $(80 \pm 9) \text{ nm}$. It should be noted that the structure in the bulk remains to be coarse-grained (Fig. 2). A schematic representation of this structure presented in Fig. 3 demonstrates that superfast cooling of the surface layer due to a fast sink of the heat in the case of a femtosecond laser pulse duration results in the formation of nanostructure, while the material microstructure in the bulk is sustained. The maximum microstresses are observed at the depth on the order of 0.2 μm both for the α - and β -phases.

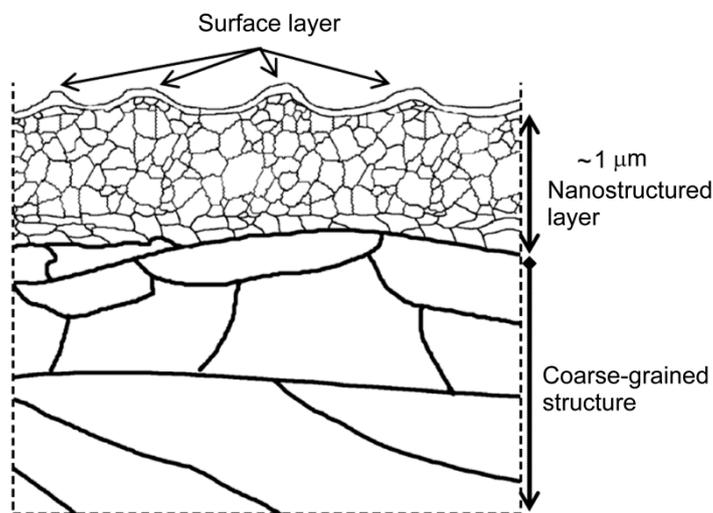


Fig. 3. Schematic representation of the surface layer of the VT6 titanium alloy processed under the mode of strong ablation ($F \geq 350 \text{ mJ/cm}^2$, $N \approx 500$) showing the $1 \mu\text{m}$ nanostructured surface layer and the coarse-grained material in the bulk [68].

SUMMARY

A review of the results of investigations has been made on modification of the structural-phase states, mechanical and other properties of metallic materials by high-intensity external loading, including the case of pressure treatment with large (severe) and megaplastic deformations, as well as explosion loading and irradiation with ultrashort laser pulses.

The data have been presented on the earlier unknown effect revealed (using the experimental cylindrical specimens of submicrocrystalline technically pure titanium (VT1-0 alloy) cut from long commercial rolled metal workpieces), which consists in propagation of the bands of localized large plastic deformation in torsion (under conditions of quasi-static loading) with the strain rates in the subsurface layers of the cylindrical specimens as high as $10^2\text{--}10^3 \text{ s}^{-1}$, which corresponds to dynamic loading.

An anomalous behavior of the strength characteristics of submicrocrystalline metals has been considered (using submicrocrystalline nickel as an example) in the region of high loading velocities, consisting in essentially lower resistance to plastic deformation compared to that of coarse-grained materials. It has been shown that shock-wave loading (peak shock pressure up to 40 GPa) gives rise to considerable grain refinement in coarse-grained materials (on the order of $70 \mu\text{m}$) but practically does not change the grain size in the initial submicrocrystalline structure. It has been supposed that that this is due to an intensive development of grain-boundary sliding in NC- and SMC-materials or to the phase recrystallization in the conditions under study.

Special focus has been made on unique capability of the femtosecond laser irradiation ensuring processing of the external surface without a considerable heating of the processed materials or articles, which is quite critical for nanostructured and submicrocrystalline metals and alloys possessing low thermal stability.

The results of a series of studies on surface modification of nanostructured and submicrocrystalline materials by ultrashort laser pulses, which were performed in a collaboration with the research teams of the Institute of Problems of Chemical Physics of the RAS, M.V. Lomonosov Moscow State University, P.N. Lebedev Physical Institute of the RAS, A. M. Prokhorov General Physics Institute of the RAS, and Belgorod State National Research University, have been reported. By the example of titanium, the formation of a multiscale relief (and nanorelief) or (under special conditions) a sequence of thin oxide layers in the subsurface layers of the materials has been demonstrated. It has been

reported that the exposure to shock waves under femtosecond laser irradiation results in the formation of the grain structure with the grain size less than 0.1 μm and the development of compressive stresses preventing crack formation in the subsurface layers of metals and alloys. In addition, a characteristic change in the phase composition in the subsurface layers has been noted, which is associated with the processes of ablation and superfast cooling after the laser irradiation.

The possibility of nanostructure formation in the thin subsurface layers of metals and alloys by irradiating them with femtosecond laser pulse makes the simulation of laser action and selection of its optimal regimes, resulting in the grain refinement up to nanostructuring and hence in the formation of improved mechanical and other properties of the subsurface material layers, an interesting and urgent field of research. This study has been performed in accordance with the action plan of the IPCP RAS within the terms of reference of the Federal agency for science and education and the RAS Presidium Program.

REFERENCES

1. Yu. R. Kolobov, *Russ. Nanotekhn. Nanoobzory*, **4**, Nos. 11–12, 19–31 (2009).
2. V. V. Rybin, *Large Plastic Deformation* [in Russian], Metallurgiya, Moscow (1986).
3. Yu. R. Kolobov, R. Z. Valiev, G. P. Grabovetskaya, *et al.*, *Grain-Boundary Diffusion and Properties of Nanostructured Materials* [in Russian], Nauka, Novosibirsk (2001).
4. N. I. Noskova and R. R. Mulyukov, *Submicrocrystalline and Nanocrystalline Metals and Alloys* [in Russian], UrB RAS, Ekaterinburg (2003).
5. R. Z. Valiev and I. V. Aleksandrov, *Nanostructured Materials Produced by Severe Plastic Deformation* [in Russian], Logos, Moscow (2000).
6. E. V. Kozlov, A. M. Glezer, N. A. Koneva, *et al.*, *Fundamentals of Plastic Deformation of Nanostructured Materials* [in Russian], Fizmatlit, Moscow (2016).
7. *Ultrafine-Grain Metals*, in: *Proceedings of 6-th Sagamore Army Materials Research Conference*, **16**. (Eds. J. J. Burke and V. Weis) Syracuse University Press (1971).
8. V. A. Moskalenko, V. I. Betekhin, B. K. Kardashev, *et al.*, *Phys. Solid State*, No. 8, 1590–1596 (2014).
9. Yu. S. Nechaev, in: *Proc. VI All-Russian Conf. Nanomaterials with Elements of Scientific School for Young Researchers, NANO-2016*. Moscow, 22–25 November, 2016, IMET RAS (2016).
10. M. L. Bernshtein, *Thermomechanical Treatment of Metals and Alloys*, in 2 Vol. [in Russian], Metallurgiya, Moscow (1968).
11. M. B. Ivanov, Yu. R. Kolobov, E. V. Golosov, *et al.*, *Russ. Nanotekhn.*, **6**, Nos. 5–6, 108–114 (2011).
12. E. F. Dudarev, O. A. Kashin, Yu. R. Kolobov, *et al.*, *Russ. Phys. J.*, **42**, No. 12, 1188–1192 (1998).
13. R. Z. Valiev and I. V. Aleksandrov, *Bulk Nanostructured Materials: Manufacture, Structure and Properties* [in Russian], IKZ Akademkniga, Moscow (2007).
14. R. Z. Valiev, A. P. Zhilyaev, and T. G. Langdon, *Bulk Nanostructured Materials: Fundamentals and Application*. The Minerals, Metals and Materials Society, John Wiley and Sons. Inc. (2014).
15. V. F. Terentiev, *Metalloved. Termobr. Metallov*, No. 10, 21–28 (2007).
16. V. G. Pushin, D. V. Gunderov, N. I. Kourov, *et al.*, *Ultrafine Grained Materials III*, TMS, Charlotte (2004).
17. A. M. Glezer, *Izvest. RAS. Ser. Fiz.*, **71**, No. 12, 1764–1772 (2007).
18. V. I. Trefilov, Yu. V. Milman, and S. A. Firstov, *Physical Fundamentals of Strength of Refractive Metals* [in Russian], Naukova Dumka, Kiev (1975).
19. V. I. Vladimirov and A. E. Romanov, *Disclinations in Crystals* [in Russian], Nauka, Moscow (1985).
20. V. E. Panin, V. A. Likhachev, and Yu. V. Grinyaev, *Structural Level of Deformation of Solids* [in Russian], Nauka, Novosibirsk (1985).

21. R. Z. Valiev, Diffusion-Controlled Processes at Grain Boundaries and Plasticity of Metallic Polycrystals [in Russian], Nauka, Novosibirsk (1998).
22. V. M. Segal, V. I. Reznikov, V. I. Kopylov, *et al.*, Processes of Plastic Structure Formation in Metals [in Russian], Nauka i Tekhnika, Minsk (1994).
23. Matthias Epple, Biomaterials and biomineralisation, Teubner (2003).
24. M. J. Yaszemski, D. J. Trantolo, K. Lewandrowski, *et al.*, Biomaterials in Orthopedics, Marcel Dekker (2004).
25. S. M. Barinov and V. S. Komlev, Bioceramics based on Calcium Phosphates [in Russian], Nauka, Moscow (2005).
26. V. I. Kalita, Fiz. Khim Obr. Mater., No. 5, 28–45 (2000).
27. Yu. R. Kolobov, A. G. Lipnitskii, M. B. Ivanov, *et al.*, Russ. Phys. J., **54**, No. 8, 918–936 (2011).
28. Yu. R. Kolobov, E. F. Dudarev, O. A. Kashin, *et al.*, A Method for Production of Ultrafine-Grained Titanium Workpieces [in Russian], RF Patent No. 2251588, 03.06.2003.
29. O. A. Kashin, E. F. Dudarev, Yu. R. Kolobov, *et al.*, Materialoved., No. 3, 25–30 (2003).
30. Yu. R. Kolobov, G. P. Grabovetskaya, E. F. Dudarev, K. V. Ivanov, Vopr. Materialoved., No. 1(37), 56–63 (2004).
31. Yu. R. Kolobov, G. P. Grabovetskaya, N. V. Girsova, *et al.*, A Method for Production of High-Strength Foils from Titanium [in Russian], RF Patent No. 2243835, 17.07.2003.
32. A. N. Shapoval, S. M. Gorbatyuk, and A. A. Shapoval, High-Intensity Processes for Tungsten and Molybdenum Treatment under Pressure [in Russian], Ruda i Metally, Moscow (2006).
33. S. P. Galkin, E. A. Kharitonov, and V. K. Mikhailov, Titan, No. 1(12), 39–45 (2003).
34. S. Yu. Belaev, Yu. M. Bagazeev, and V. S. Dushin, Titan, No. 1(22), 61–64 (2008).
35. E. A. Kharitonov, P. L. Alekseev, and V. P. Romanenko, Titan, No. 1(18), 43–46 (2006).
36. M. B. Ivanov, A. V. Penkin, Yu. R. Kolobov, *et al.*, Deform. Razrush. Mater., No. 9, 13–18 (2010).
37. V. I. Betekhtin, Yu. R. Kolobov, M. V. Narykova, *et al.*, Zh. Eksp. Tekh. Fiz., **81**, No. 11, 58–63 (2011).
38. M. B. Ivanov, Yu. R. Kolobov, E. V. Golosov, *et al.*, Ross. Nanotekhn. **5–6**, Nos. 72–78, (2011).
39. V. E. Fortov, Experimental State of Matter [in Russian], Fizmatlit, Moscow (2009).
40. G. N. Epshtein, Structure of Metals Deformed by Explosion [in Russian], Metallurgiya, Moscow (1980).
41. M. B. Ivanov, A. V. Penkin, and Yu. R. Kolobov, Pis'ma ZhTEF, **40**, Iss. 23, 97–103 (2014).
42. S. V. Razorenov, A. S. Savinykh, E. B. Zaretskii, *et al.*, Phys. Solid State **47**, Iss. 4, 663–669 (2005).
43. Yu. Ivanisenko, L. Kurmanaeva, J. Weissmueller, *et al.*, Acta Mater., No. 57, 3391–3401 (2009).
44. Yu. R. Kolobov, A. G. Lipnitskii, M. B. Ivanov, *et al.*, Kompos. Nanostr., No. 2, 5–32 (2009).
45. Yu. R. Kolobov, G. P. Grabovetskaya, M. B. Ivanov, *et al.*, Scripta Mater., **44**, No. 6, 873–878 (2001).
46. Yu. R. Kolobov, G. P. Grabovetskaya, K. V. Ivanov, *et al.*, Interface Sci., **10**, No. 1, 31–36 (2002).
47. Yu. R. Kolobov, G. P. Grabovetskaya, K. V. Ivanov, *et al.*, Solid State Phenom., **94**, 35–40 (2003).
48. R. Z. Valiev, I. V. Alexandrov, Y. T. Zhu, *et al.*, J. Mater. Res., No. 11, 5 (2002).
49. S. X. McFadden, R. S. Mishra, R. Z. Valiev, *et al.*, Nature, No. 398, 684 (1999).
50. Yu. R. Kolobov, V. N. Perevezentsev, A. Yu. Kolobova, *et al.*, Kompos. Nanostr., 8, No. 1, 16–29 (2016).
51. Shock Waves and Extreme States of Matter [in Russian] (Eds. V. E. Fortov, L. V. Altshuler, and R. F. Trunin, Nauka, Moscow (2000).
52. A. R. Kutsar and V. N. German, in: Proc. III Int. Conf. On Titanium, VILS, Moscow (1978).
53. V. A. Zilbershtein, N. P. Chistotina, A. A. Zharova, *et al.*, Fiz. Met. Metall., **39**, No. 2, 445–447 (1975).
54. F. P. Bandi, New Materials and Methods of Investigation of Metals and Alloys [in Russian], Metallurgiya, Moscow (1966).
55. A. Dewaele, V. Stutzmann, J. Bouchet, *et al.*, Phys. Rev. B., No. 91, 134108 (2015).
56. N. Velisavljevic, M. K. Jacobsen, and Y. K. Vohra, Mater. Res. Express. No. 1, 035044 (2014).
57. A. P. Zhilyaev, V. Popov, A. R. Zharafutdinov, *et al.*, Pis'ma o Mater., **1**, 203–207 (2011).

58. Feng Xu, Xiyan Zhang, Haitao Ni, *et al.*, *Mater. Sci. Eng. A*, No. 564, 22–33 (2013).
59. O. L. Pervukhina, *Izvest. VolgSTU*, No. 6, 86–88 (2004).
60. Yu. R. Kolobov, S. S. Manokhin, A. Yu. Kolobova, *et al.*, *Pis'ma Zh. Tekh. Fiz.*, **42**, Iss. 18, 63–71 (2016).
61. E. V. Golosov, V. I. Emel'yanov, A. A. Ionin, *et al.*, *Inorgan. Mater.: Appl. Res.*, **2**, No. 3, 206–209 (2011).
62. A. A. Ionin, S. I. Kudryashov, S. V. Makarov, *et al.*, *Quant. Electr.*, No. 41 (9), 829–834 (2011).
63. A. A. Ionin, S. I. Kudryashov, S. V. Makarov, *et al.*, *Pis'ma Zh. Tekh. Fiz.*, **94**, Iss. 1, 35–39 (2011).
64. Агеев Е. И. Ageev, , Вейко В. П. Beiko, S. I. Kudryashov, *et al.*, *Pis'ma Zh. Tekh. Fiz.*, **102**, Iss. 9–10, 785–789 (2015).
65. V. V. Zhakhovskii and N. A. Inogamov, *Pis'ma Zh. Tekh. Fiz.*, **92**, Iss. 8, 574–580 (2010).
66. N. A. Inogamov, V. V. Zhakhovskii, V. A. Khokhlov, *et al.*, *Pis'ma Zh. Tekh. Fiz.*, **93**, Iss. 4, 245–251 (2011).
67. D. E. T. Braber, J. E. Ruijter, L. A. Ginsel, *et al.*, *Biomaterials*, **17**, No. 21, 245–252 (1996).
68. Yu. R. Kolobov, E. V. Golosov, T. N. Vershinina, *et al.*, *Appl. Phys. A: Mater. Sci. Proc.*, **119**, 241–247 (2015).