

# Effect of Hydrogen on the Interatomic Interactions of Elements in Metal Alloys and the Physicochemical Properties of the Related Articles

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**Abstract**—The hydrogenation of pure metals and the alloys based on them, which activate the interatomic interactions of alloy elements with absorbed hydrogen, and various types of fluctuations, polymorphic transitions, and the formation of phase-structural compositions changing the physicochemical properties of the products made from them are studied. Hydrogen is shown to be a fine instrument for adjusting the processes of cluster ordering and the formation of nanophase composites with various types of symmetry forms (crystalline, amorphous). The presence of hydrogen ensures the required structuring and the production of high-quality alloys with radically new physicochemical properties. The results obtained are analyzed with computer and experimental methods, the processes and mechanisms under study are explained, and optimum solutions are proposed to predict synthesis of functional materials.

**Keywords:** glass transition, melt, surfactant, Me (metal), M (metalloid), TCP (topologically close-packed) phases, interatomic interactions, types of bond, polymorphic and phase transitions, amorphous and quasicrystalline compositions (composites), phases in product matrices: ferrites ( $\alpha$ ,  $\delta$ ), austenite ( $\gamma$ ), graphite, carbides ( $\text{Me}_x\text{C}_{1-x}$ ), pearlite, martensite

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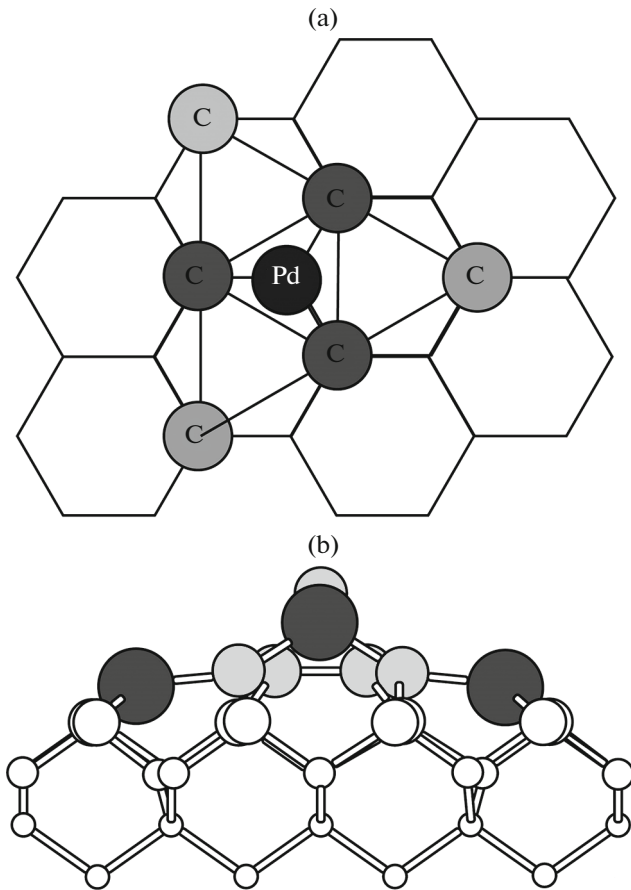
## 1. INTRODUCTION

The purpose of this work is to comprehensively study the influence of a surfactant, namely, hydrogen, absorbed by alloys on the interatomic interactions of the alloy elements, which ultimately determines the functional properties of the alloys. At the atomic level, we thoroughly analyze the mechanisms of the hydrogen-induced interatomic redistributions of elements and the structural transformations of the crystalline and dissipative quasicrystalline structural phase compositions that form in the alloy volume (clusters, macroclusters, Frank–Kasper intermetallic compounds, etc.). In heterogeneous multicomponent metal-based alloys, the intensification of multidirectional diffusions of elements in the cycle solid  $\leftrightarrow$  heating  $\leftrightarrow$  melting  $\leftrightarrow$  melt  $\leftrightarrow$  cooling under the influence of various external influences accelerates the formation and relaxation of the low-entropy dissipative phase compositions formed due to a high degree of element ordering [1–3]. To produce high-quality functional products from them without intergranular cracks, it is necessary to perform accurate diagnostics of all phase and structural transformations under changing external conditions and to search a specific engineering solution to eliminate undesirable consequences in

each case. For example, the authors of [2] showed that heat treatment can reconstruct the carbide phase of carbon in Fe–Cr–Ni alloys (0.45C–25Cr–35Ni). As was shown in [3], the lamellar  $\epsilon$ -phase crystals formed in the ferritic Fe–5.80% Ni–0.01% C alloy upon cooling, which worsen the properties of the  $\alpha$  phase, underwent the reverse transformation ( $\epsilon \rightarrow \alpha$ ) under a shock wave with  $P = 15$  GPa within a microsecond. When cooling high-carbon iron-based melts, the authors of [7] used treatment with magnesium and other surfactants to cause splitting of the interphase surfaces in graphite  $\leftrightarrow$  melt zones with the formation of spherical topologically close-packed (TCP) graphite crystals. Note that, when novel advanced technologies are developed, the requirements for testing metal products under extreme temperature, rate, and strain conditions must be met to avoid their premature failure during operation.

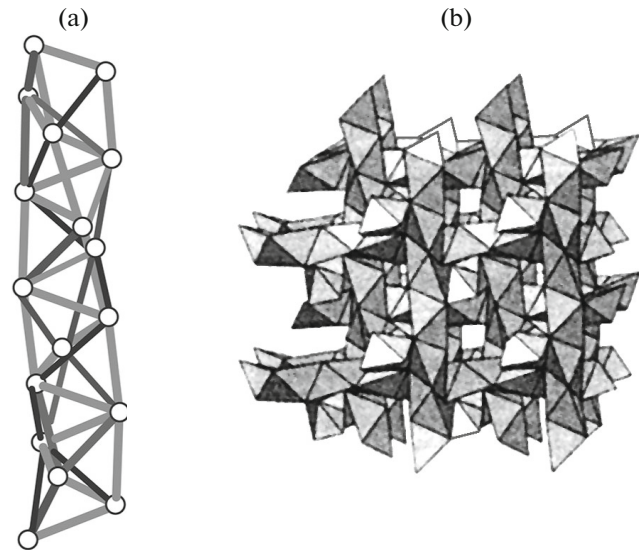
## 2. EXPERIMENTAL

Molecular dynamics (MD) simulations was used to analyze the cooperative dynamics of the interatomic interactions of elements in the temperature ranges from 300 K to  $T_m$  1/3 of cluster [4–7] and to  $T_m$  of bulk



**Fig. 1.** Formation of the heterostructure of the Pd<sub>561</sub>/G interface via the formation of Pd<sub>1</sub>C<sub>6</sub> ring clusters, an analog of isomerization near  $T_m$ : (a) top view and (b) side view.

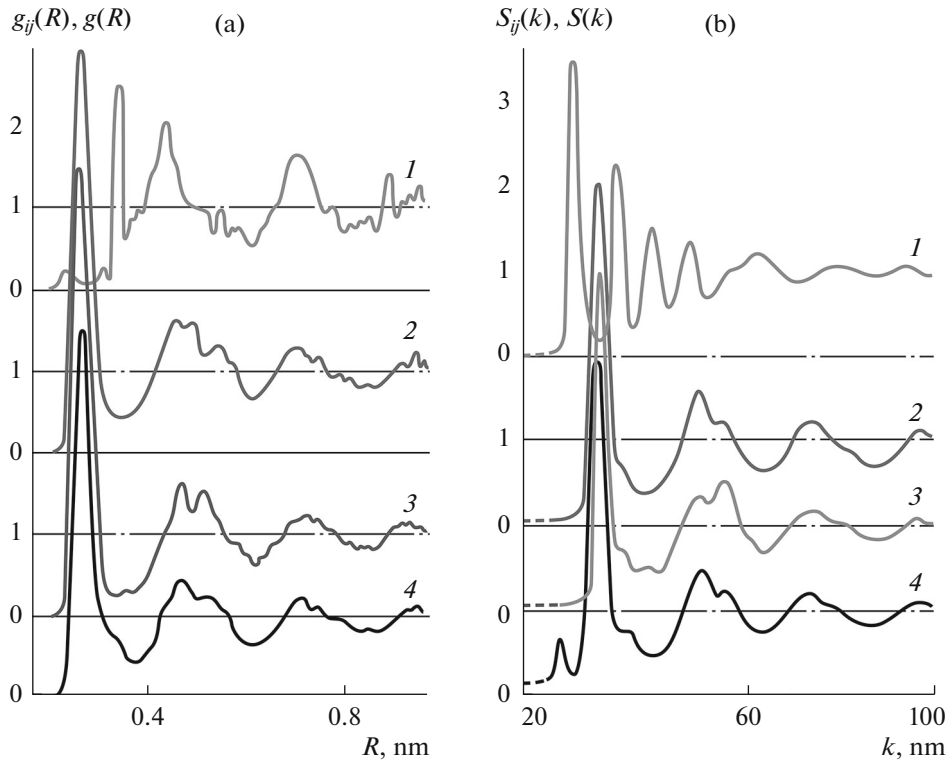
iron systems [6]. The self-diffusion coefficients of the elements are estimated and compared in various zones. When clusters (small objects) are heated, the beginning of melting is characterized by an increase in the number of density fluctuations, a redistribution of the kinetic and potential energies, and nanoscale effects initiated by the transitions of fcc cuboctahedra into icosahedra accompanied by isomeric transformations of aggregates breaking structural stability in the system volume. The classification of newly formed aggregates allowed us to identify the mechanism of the appearance and annihilation of mutually competing heterogeneous isomers in cluster composites and to estimate the average statistical scale of their coherent structural “bifurcations” (from regular coherently local to disordered ones [8]). Figure 1 illustrates the formation of an interface heterostructure upon heating to the beginning of melting of the Pd<sub>561</sub>/G cluster with the formation of Pd<sub>1</sub>C<sub>6</sub> ring clusters as an analog of structural isomerization [4, 5]. The triangles in the figure indicate the periodic structure made of assembled and thermally activated node clusters.



**Fig. 2.** Illustration of the intermetallic phases in microclusters: (a) fragment of 30/11 spiral ((heavy lines) helicoidally twisted 15/4 spiral) and (b) microcluster structured by a helicoidal screw axis [2].

### 3. INFLUENCE OF EXTERNAL ACTIONS ON THE ATOMIC STRUCTURING IN FORMING PHASE COMPOSITIONS

The alloy structures formed upon cooling remain stable and have positive Gibbs free energy ( $\Delta G$ ), which is related to enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) through temperature ( $T$ ) and pressure ( $P$ ) changes ( $\Delta G = \Delta H - T\Delta S$ ,  $\Delta H = \Delta U + P\Delta V$ ) [7]. According to the Arrhenius equation, the rate constant ( $k$ ) of the interatomic ordering in alloys in the cycle solid  $\leftrightarrow$  heating  $\leftrightarrow$  melting  $\leftrightarrow$  melt  $\leftrightarrow$  cooling is determined by activation energy  $E_a$  and positive values of  $\Delta S$  ( $k = k_0 e^{-E_a/RT}$ ). When  $T$  increases, the metastable structures of crystalline modification compositions turn out to be kinetically stable in alloys; when  $P$  increases, formed small phase compositions become more stable. The typical representatives of the materials structured by small compositions are glasses (“liquid” with a very high viscosity) [1, 8]. Transitions into new structural modifications are retarded in them because of the extremely low rate of formation of cross-link (interatomical) bonds. Small phase compositions were detected in product matrices, at grain boundaries. They are structured along the shear deformation axis by clusters of the same elemental composition ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ) with varying positions from weak changes to complete interatomic disordering in clusters. The clusters are composed of tetrahedra by strong covalent chemical bonds into TCP lattices of small phase compositions with unique physicochemical properties. It was also found that structuring by the axis of a helical spiral can be used to form bulk materials with enhanced physicochemical properties. Figure 2 illustrates a 15/4 helical



**Fig. 3.** Calculated RDF and structure factor  $S(k)$  of the  $\text{Pd}_{10.8}\text{Si}_{0.2}$  glass: (a) calculated RDF of the  $\text{Pd}_{10.8}\text{Si}_{0.2}$  alloy at  $T = 70$  K for atoms (1) Si, (2) Pd, (3) unlike, and (4) total; (b) corresponding  $S(k)$ .

twisted spiral and a microcluster assembled from such spirals.

Covalent bonds can be used to form bulk materials from both neutral atom elements and molecular microclusters with a covalent bond. One of the examples is a high-strength material, namely, filamentary graphite, which is structured by covalent-bond-twisted helical carbon basal layers. These layers have no wedging effects, which are characteristic of the intermolecular van der Waals bonds of the basal layers in graphite. The phase composites of Frank–Kasper and  $\beta$ -Mn polyhedra formed from substructures by a  $15/4$  helix have a high plasticity (compression  $\leftrightarrow$  tension). Crystal  $\leftrightarrow$  melt zones were found to exhibit polymorphic phase transitions, transformation of TCP structures into bcc modifications, and the formation of structural configurations (quasicrystals). Nevertheless, the formed quasicrystalline alloys without periodic translation symmetry have a long-range coordination order (LRCO) with icosahedral symmetry axes. Quasicrystalline structures are embedded in three-dimensional space predominantly with fivefold symmetry and, sometimes, 8-, 10-, or 12-fold symmetry, and can coherently scatter incident radiation. The research methods developed in [2, 8–16] make it possible to comprehensively study forming phases, phase compositions, and the morphology of their incorporation into the matrix of metal products.

### 3.1. Effect of Surfactant on the Interatomic Interactions of Elements in Alloys

All surfactants present in multicomponent metal-based alloys stimulate the dynamics of interatomic interactions of alloy elements. The structuring of formed phases and their compositions is activated and the grain sizes and boundaries change, which ultimately influence the functional properties of the end products. Using computer simulations (MD simulations with quantum calculations of potential functions), the authors of [17–20] calculated radial distribution functions (RDFs) and corresponding structure factors  $S(k)$  for  $\text{Pd}_{10.8}\text{Si}_{0.2}$  and  $\text{Fe}_{1-x}\text{P}_x$  alloy clusters at 70 K and  $\text{Al}_{90}\text{Fe}_x\text{Ce}_{10-x}$  alloy clusters at  $T = 300$  K (see Fig. 3). Under the temperature–time conditions of transitions in the cycle solid  $\leftrightarrow$  heating  $\leftrightarrow$  melting  $\leftrightarrow$  melt  $\leftrightarrow$  cooling, clusters were found to change their state, acquire excess energy, and become thermally unstable. The changes caused by supercooling of a melt appear in the calculated and experimental RDF and  $S(k)$  curves for clusters in the glasses  $\text{Pd}_{10.8}\text{Si}_{0.2}$  and  $\text{Fe}_{1-x}\text{P}_x$  [15–17] and  $\text{Al}_{90}\text{Fe}_x\text{Ce}_{10-x}$  [9]. The parameters that meet the conditions necessary for stabilizing the state that retards the beginning of spontaneous homogeneous nucleation were determined. For example, prepeaks were detected in the structure factor  $S(k)$  curves in the liquid-phase short-wavelength

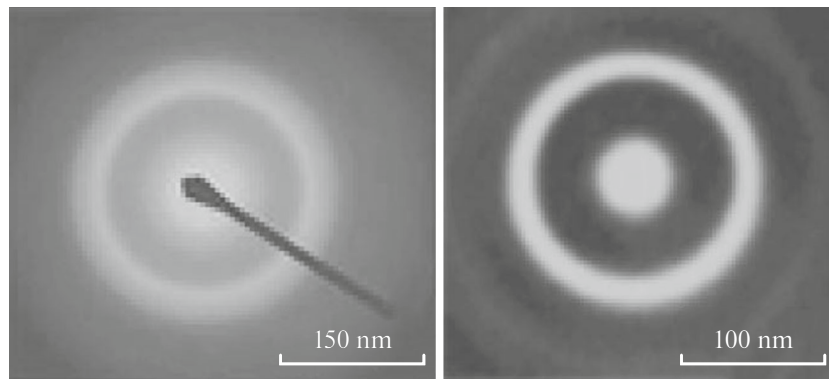


Fig. 4. Illustration of the diffuse halo of the  $\text{Pd}_{80}\text{Si}_{20}$  cluster and hydrogenated  $\text{H}:\text{Pd}_{80}\text{Si}_{20}$  with a clear appearing bright ring.

(low-angle) range during rapid melt solidification, and a hysteresis accompanying crystallization devitrification in the cycle given above was observed in the heating  $\leftrightarrow$  melting cycle in the same range. The main and subsequent RDF and  $S(k)$  peaks have subpeaks, which illustrate the aggregates formed by interstitial atoms with vacancy sink zones and with nucleation of dissipative structures in alloys. The of crystal  $\leftrightarrow$  melt transition zones have polymorphic TCP–BCC phase transformations and the formation of quasicrystal structural configurations [21–26]. The detection of all forming phases and phase compositions made it possible to explain the mechanism of their formation in a supercooled liquid during forced cooling of metal systems in terms of a general standpoint.

A detailed analysis of all forming phase-structural compositions at the boundary with a melt and the active nonstationary sources of nonequilibrium states for vacancy sinks, which create additional conditions for the appearance of new atomic configurations, made it possible to reveal the structural dimension of grains in the Fe cluster, which was about 100 nm, with hydrogen incorporated into its octahedral interstices (Fe–H) up to  $10^{-2}$  atomic fractions. There are studied by us the phase compositions formed upon forced cooling of melts with a small coordination ordering region (e.g., Ti–Ni–V and  $\text{Al}_6\text{Mn}$  compositions) were metastable. The structuring of their crystalline and glass-forming phases depends on both the mutual atomic sizes of the elements forming the basis of high-entropy alloys (Zr–Ni–Al–Cu, Zr–Ti–Cu–Ni–Be, Mg–Cu–Y) and the cooling rate of the melt [1, 27–32]. Under chosen conditions, any formed metastable structure can be kinetically stabilized in a metal product upon cooling an alloy. Stable phases with a large coordination ordering region form upon cooling melts (Al–Cu–Fe, Al–Zn–Mg) at the rates below the critical glass-transition rate.

### 3.2. Role of Hydrogen in the Energy of Force Fields during the Interatomic Interactions of Elements in Metal Alloys

The comprehensive studies [10–17] of the effect of hydrogen as a surfactant on metal alloys found that the total energy of the force fields during the  $\text{Me} \leftrightarrow \text{H}$  interatomic interaction includes the energies of the effective direct Coulomb (+) and indirect atomic interaction of H atoms with Me ions ( $\text{H} \leftrightarrow e^- \leftrightarrow \text{Me}^{+}$ ), up to 30% of the phonon fluctuations of exciton pairs in an electron gas in the  $e^-e^+$  zones ( $m_{\text{H}} \ll m_{\text{Me}}$ ), and the effects of quantum interactions at  $T < T_{\text{cr}}$ . Hydrogen has a very high thermal conductivity, solubility (up to 850  $\text{H}_2$  volumes in the Pd volume), and diffusion through almost all metals and alloys; as a result, it activates the interatomic interactions of all elements in open-type metal systems. The formation of a variety of intermetallic compounds and complex phases of carbides, small phase compositions, and polymorphic rearrangements in the  $\alpha \leftrightarrow \gamma \leftrightarrow \delta$  modifications are stimulated. In the materials made of molecular compositions, the weak van der Waals bond between molecules can be strengthened by hydrogen by 2–3 orders of magnitude. Upon the solid  $\leftrightarrow$  liquid transitions in alloys, the highest diffusion drag of electron-screened protons ( $\text{H}^+$ ) and the formation of a hydrogen-containing phase were detected. Similar effects were also experimentally revealed in Pd–Cu–P clusters [7, 17, 28] and hydrogenated  $\text{H}:\text{Pd}_{80}\text{Si}_{20}$  clusters, which generated a strong bright diffraction circle (Fig. 4, to the right) [15, 20].

In this case, the electron density in interatomic interactions shifts to a high-electronegativity element and increases there. As a result, hydrogen between elements is not fixed due to the extremely small size of its ion (stripped atom effect in physics). In hydrogen compounds with a hexavalent chalcogen (tellurium), hydrogen neutralizes a significant amount of its dangling bonds and facilitates the  $p_+ \leftrightarrow \text{H}^0$  valence transitions, increasing the susceptibility of alloys to amor-

phization. The technology of melt processing by surfactants ( $\text{Te} + \text{H}_2$ ) was applied for pouring cast iron rolls used in industry. As a result of increasing the chilled zone in a roll and its cleaning from graphite phase inclusions, the hardness and the wear resistance of rolls during operation were increased and the quality of the paper products was improved [7].

In the Me–H interactions with low force field energies, partly ionized hydrogen passes into the excited state of an increased atomic radius and is incorporated into the interstices of the Me expanding lattice by a bridging bond with Me. Hydrogen in the form of protons can interact with the deepest electron shells in a metal or can be with it in hydride compounds due to the force field energies high enough for ionizing hydrogen and to a metallic bond during endothermic (Fe, Ni, etc.) and exothermic (Ti, Zr, Pd) Me  $\leftrightarrow$  H interactions. It should be noted that all metals connected with hydrogen by a metallic bond retain an increased strength and plasticity during operation of products under deformation conditions, since this bond is not broken when atoms are displaced under load conditions. Alkaline earth Me (Ba, Ca, Mg, Be) with high force field energies form hydrides ( $\text{H}^-\text{Me}^+$ ) with a lost metallic bond. Transition Me and alloys based on them, which have both metallic and ion-covalent bonds, are structured upon cooling, with one of them being predominant. In the compositions formed by free *s* electrons, a metallic bond is predominant, and the compositions formed by uncompensated *d* or *f* electrons are structured by an ion-covalent bond. In the structures of compositions with metallic bonds, the lower the energy required to remove electrons distributed over energy levels from Me, the higher their plasticity. The phase compositions of metalloids (M) in alloys with an ion-covalent bond carried out by a pair of electrons simultaneously belonging to two neighboring elements (Te, C, Si) are characterized by a high brittleness, and the geometry of the crystal lattice can be violated during the shifts in band structure levels caused by a change in the bond direction. Hydrogen interacts most effectively with the elements (chalcogen group nonmetals and semiconductors) that have high force field energies. For example, hydrogen interacts with nitrogen to form ammonia ( $\text{NH}_3$ ), interacts with carbon to form numerous hydrocarbons ( $\text{C} \leftrightarrow \text{H}$ ), and interacts with chalcogens to form chalcogenides (moving  $\text{O}_2$  to a separate group with  $\text{H}_2\text{O}$ ). At an oxidation level of  $2^-$ , chalcogens, like hydrogen ( $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$ ), can also take oxygen from oxides.

The diffusion processes during the interatomic interactions of elements in phase compositions with a metallic bond occur at the rates that are much higher than those in the processes occurring in metalloids with ion-covalent interactions of their elements. The diffusion of hydrogen from hydride molecular cluster compositions with a short-range interatomic interac-

tion of elements with a strong covalent atom  $\leftrightarrow$  atom bond, which is localized inside such “quasi-molecular clusters”, is retarded, which increases the hydrogen content in a cooled product by 30% and increases the tendency to destruction.

### 3.3. Polymorphism and Phase Transitions in Metal-Based Alloys

The products structured by the inclusions of polymorphic compositions of defect-free microclusters from unit cells (“building blocks”) with the properties of “easy” deformation of hexagonal close-packed (HCP) lattices with covalent bonds (as in Laves phases) have significantly improved physicochemical and operational properties. The variation of the size and composition of polymorphic compositions with various fractal ratios in formed dissipative structures under forced melt solidification allows one to form materials with fundamentally new physicochemical properties without additional actions on alloys (alloying, modification, etc.). Aperiodic compositions with main subgroup elements (mainly Mg, Al, Si, Te) are fixed in transition-metal-based alloys. Small-atom elements (C, H, N, B) are easily incorporated into the “loose” bcc lattice with connecting pores and high self-diffusion rates of atoms (ions) in ferrite phases ( $\alpha$ - and  $\delta$ -Fe) without changing the lattice parameters. Cu, Mn, Al, Si, Mn, Ni, or Cr atoms substitute for Fe atoms to be incorporated into the “dense” fcc lattice of austenite ( $\gamma$ -Fe) with isolated pores; they are also located in its interstices, dislocations, defect and vacant zones, and grain boundaries.

The valence electrons of the incorporated elements are fully or partially collectivized with the formation of interatomic metallic bonds. In the iron alloys under study, the dense fcc lattice with the retarded diffusion of incorporated elements transforms into the bcc tetragonal lattice during rapid cooling. The properties of this lattice are determined by its tetragonality, which depends on the electrons of ionized atoms that are in changed energy states crystals and the shape of interatomic pores for their incorporation. For example, with the lattice changes, a martensite phase with introduced 2.03% carbon forms. As a result, the tendency of the resulting product to brittle fracture increases in contrast to ferrite crystals (bcc Fe–C alloy structure) with introduced ionized carbon atoms ( $\alpha$  up to 0.025% C,  $\delta$  up to 0.08% C). This phase is characterized by a high plasticity, heat resistance, and diffusion motion rate.

A distinctive feature of high-speed solidification technologies for the formation of the necessary functional and operational properties of the end product is an extremely high sensitivity to the elements introduced into melts. For example, when up to 1% Cu is introduced into a melt, nucleation is activated, the number of structured phase composites is increased, and their sizes are limited. As a consequence of the positive enthalpy of mixing Cu with Fe, the Cu clus-



ters forming along  $\alpha$ -Fe boundaries serve as the centers of spontaneous nucleation of fragmented phases with the transfer of the stage of homogeneous (first) crystallization to the heterogeneous (second) one. The polymorphic modifications of the structures of iron alloys are the nuclei of isomers (“quasi-molecular clusters”) with the same quantitative composition and different atomic arrangement of elements in the phase compositions (polytope) space. The polymorphic modifications of phase compositions with the minimum atom surface energy for isomer formation are the first to be structured in a melt. Relative to the axis of group symmetry, their frequency spectra are characterized by three types of oscillations ( $\omega$ ), two of which are associated with longitudinal (parallel) oscillations ( $\omega_{\parallel}$ ) and one, with transverse (perpendicular) oscillations ( $\omega_{\perp}$ ). The longitudinal frequencies in metallic bonds are twice as high as the transverse frequencies, and the difference between the longitudinal and transverse mode frequencies for covalent bonds is even larger, namely, three times for  $\text{Pd}_n\text{H}$ . In the case of the  $\alpha \leftrightarrow \beta \leftrightarrow \gamma \leftrightarrow \delta$  polymorphic transformations, hydrogen increase and decrease jumps during hydrogen diffusion are detected in newly formed Fe phases.

Constructing simplicial channels in  $\text{Me}_n\text{-H}$  clusters by the Delaunay method, we were able to find that, as a surfactant, hydrogen causes a substantial modification of short-range ordering and distortion of the interatomic distances, transforming pentagonal–pyramidal  $\text{Me}_7\text{H}$  structural aggregates into octahedral ones with the motion of one of the metal atoms into the second coordination ( $\text{Me}_6\text{H} + \text{Me}$ ). The hydrogen desorption to the surface from the volume of cluster fragments with a metallic bond proceeds at the rates that are much higher than those of the desorption from nonmetal hydride clusters with ion–covalent bonds. Nuclei of a new phase hydride composition can appear only after desorption of the next portion of hydrogen, and they are characterized by the appearance of a small number of phase-forming compositions. The presence of hydrogen absorbed by commercial iron alloys activates multidirectional diffusion interatomic interactions of alloy elements in structured phases (austenite, ferrite, martensite, carbides, etc.), determines their dimension and the character of structuring in various directions, and (hence) forms the morphology of matrix and the properties of metal products. Intermetallic carbon macroclusters actively absorb hydrogen to form linear shapes of a graphite phase, which increase the brittleness and the susceptibility to cracking in products. To understand the processes occurring during the spatial organization of formed phase composites, we [8, 11–17] used MD simulations and statistical-geometric analysis of Voronoi–Delaunay polyhedra to study the formation and structural growth of phase composites in Fe–C clusters with their coherent and incoherent joining upon long-range ordering. At the stages of heating, melting, and

forced cooling, we investigated the dependences of physicochemical parameters, the morphology of boundaries, and the heterogeneity of the internal structure of disordered systems. Depending on the rate of temperature changes in a cluster in the heating–melting and cooling–solidification ranges, the role of atomic dynamics in the surface zones was found and the statistical temperatures of structural transformations of atomic configurations were determined [6, 7, 25].

The liquid phase was shown to undergo labile rearrangements of nanosized aggregates via continuous reconstruction of the polyhedra of periodic crystalline packing into an aperiodic spiral packing of icosahedra ( $I_\lambda$ ; the reverse process is observed upon cooling and solidification of a liquid cluster). In the temperature regime heating–melting, regular coordinations “as clusters-around-cluster” of a quasi-equilibrium structure form, the structure decomposes, the regular coordinations undergo isomerization, and short-lived phase-structural compositions of close-packed dynamic icosahedral coordinations form. Under high-speed cluster solidification, the organization of large atomic groups of close-packed icosahedral coordinations ensures an increase in the thermal stability and strength characteristics of the alloys.

According to [20, 25, 28], two types of ordering ( $\alpha$  and  $\beta$ ) with specific correlation functions of rates and shear stresses with non-Arrhenius temperature dependences of the corresponding diffusion and shear viscosity coefficients manifest themselves in the character of relaxation processes in cooling during the formation of the most stable nucleation centers. It was this region that corresponded to the temperature range of crossovers, namely, the dynamic crossover ( $T_D$ ) with a change in the atomic dynamics characterized by a sharp increase in viscosity and the structural crossover ( $T_A$ ,  $T_D > T_A$ ), with the subsequent formation of coherent cluster aggregates on the scale of medium ordering [28] and vitrification  $T_g$  ( $T_g$  is the glass transition temperature),  $T_D > T_A > T_g$ .

Thus, medium-scale ordering and the symmetry of short-range clusters depended not only on the quenching rate, but also on the choice and parameterization of a potential function. At certain interatomic distances  $R$ , the polynomial shape of a potential function with wavevector  $k$  and phase shift  $\varphi$  parameters specifies the frequency (period) and the phase shift of attraction branch oscillations and the position of the main potential well. The variation of the parameters, which are dependent on the shape of the oscillation attraction branch of interaction potentials, determines the specific features of short-range coordination, the nature of packing, and the angular distribution over atomic bonds. For example, an icosahedral structure with fivefold orientational-order symmetry forms at  $k = 6.25$  and  $\varphi = 0.62$  and a phase composite with a periodic twofold symmetry structure is modeled at  $k =$

7.50 and  $\varphi = 0.53$  [20]. The parameterization of a pair interaction potential under the same kinetic conditions at different parameterization parameters affects the supercooling at the beginning of the characteristic stages of structuring, nucleation, and phase formation [11, 14]. In the framework of computer simulation using specific parameterized potential functions, the authors of [20, 25, 29] proposed fitting constants  $k$  and  $\varphi$  to enhance the interatomic correlations as an alternative to disclination networks on the short-range scale  $R < 2^{1/2}R_0$  ( $R_0$  corresponds to the first minimum of  $V(R)$  and the average statistical interatomic distance in the system under study). As a result of studies on this scale, they separated regular polytetrahedral configurations, described their symmetry, and performed statistical–geometrical analysis of their coherent joining in a global structure.

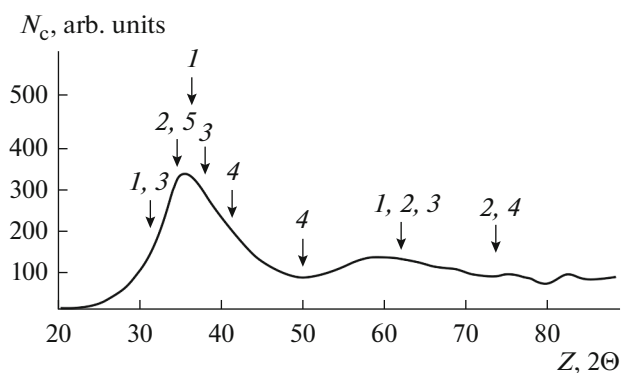
Using parametric constants  $k$  and  $\varphi$ , which determine the dependences of polynomial potential function oscillations, we [25, 29] comprehensively studied the structural properties, the energetics, and the interatomic bonds of highly symmetric small and medium clusters with at most 100 atoms. As primary building blocks, such clusters with an optimized structure were shown to substantially determine the stability of larger functional clusters 5–10 nm in size. The initial stage of nanostructuring was controlled by the rate of decrease of temperature and the melt supercooling via the formation of a spatial (volume) distribution of cluster nodes (their network) with different types of atomic coordination and different orders of axes of orientational symmetry [22–28]. When the rate of cooling from a liquid state is increased, the fraction of structural composites of predominantly icosahedral symmetries in the volume after cooling a cluster increased. The longitudinal and transverse mode frequencies for covalent bonds turned out to be three or more times higher than for metallic bonds (e.g.,  $\omega_{\parallel} \sim 2400 \text{ cm}^{-1}$  for longitudinal frequencies  $\omega_{\perp} \sim 1200 \text{ cm}^{-1}$  for transverse frequencies for  $\text{Pd}_n\text{H}$  and  $\omega_{\perp} \sim 600 \text{ cm}^{-1}$  and  $\omega_{\parallel} \sim 2000 \text{ cm}^{-1}$  for Si). For hydrogen isotopes, the dynamics of adsorbed atoms on isolated clusters with a metallic bond ( $\text{Me}_{4-10}\text{-H}$ ) and Me elements Ni and Pd was characterized by an ion–electron dispersion character of interparticle interaction, and its was characterized by a dipole–dipole interparticle interaction in clusters with a covalent bond ( $\text{Si}_n\text{-H}$ ). The activation energy is caused by deformation of a local structure for ( $\text{Me-H}$ ) and by breaking chemical bonds for ( $\text{Si-H}$ ). First-order (monotropic) phase transitions proceed relatively slowly, and their unstable polymorphic modifications before transitioning to an irreversible form can be studied. Second-order (reversible) phase transitions occur under thermodynamic equilibrium ( $\Delta G = 0$ ) at the rate of transformations of the composites structured in a melt such that it is impossible to fix intermediate (metastable) phases, which directly depend on the spatial location of the entire set of element atoms

and electrons in certain energy states with ion–covalent chemical bonds. The electrons of atoms in metals with a large coordination number ( $Z$ ) in crystal lattices fill the gaps between ions, penetrate into the inner zones, and make metallic bonds more plastic. Semi-metal compositions are characterized by a brittle lattice and a relatively small  $Z = 8 - p$ , where  $p$  is the number of valence electrons. Thus, the short-range order in them was ensured by the short-range effect, which depends on the density of interatomic bonds, the mutual repulsion of valence electrons and the spatial restrictions between atoms, and the electron pairs of two nearest ions bound by covalent bonds.

### 3.4. Technology of Producing Nanoscale Compositions and Finemet Materials

The investigations of the states of deep supercooling of melts during rapid cooling from 5000 to 1250–1400 K in MD models of  $\text{Fe}_{1-x}\text{P}_x$  cluster compositions under long-term temperature conditions of high structural dynamics detected the temperature range of metastable crossover states, namely, initial dynamic crossover ( $T_D$ ) with the formation of phonon precursors according to the Regel excitons of transverse modes (as in semiconductors [28]) and structural crossover ( $T_A$ ) with the formation of coherent cluster groups up to medium-scale ordering and the beginning of glass transition ( $T_g$ ). The energy of local Debye frequency excitations in the initial stage of cooling melts is on average 450 meV, and the energy of phonon precursors (Regel excitons) turned out to be less than 5% and too low to deviate the kinetic characteristics from the Arrhenius dependences. In the short crossover range from  $T_D$  to  $T_A$  of the metastable state during ultrafast cooling of the MD Fe model melt (from 5000 to 1500 K), these ranges were estimated at 2300 K with approximation to  $T_A$  and at 1950 K with approximation to  $T_g$ , and the exciton frequency energy corresponded  $\sim 250 \text{ meV}$  (which is almost 20% of a Debye frequency energy of 750 meV). In the course of cooling in the crossover temperature range from  $T_D$  to  $T_A$  ( $T_D > T_A$ ) and glass transition temperature  $T_g$ , the viscosity exhibited an anomalously high increase, which coincided with the onset of the relaxation of growing cluster configurations up to the formation of a medium-range order and the decay of the local longitudinal mode excitations of the diffusion component of the Van Hove function [13].

To choose compositions for the formation of nanoscale crystalline and amorphous alloys, it is necessary to select elements with a significant difference in their atomic radii ( $R_{pd} - 4R_{Si}$ ) and to form the compositions corresponding to complex phases according to the Frank–Kasper type [20, 28]. This ensures the formation of the following noncrystalline structures in compositions: structures with predominant fivefold symmetry, icosahedral and helicoidal (fractional sym-



**Fig. 5.** X-ray diffraction pattern ( $N_c$  is the intensity, arb. units;  $Z$  is the angle of reflection ( $2\theta^\circ$ )) of a hydrogenated amorphous  $Zr_{55}Cu_{35}Ti_{10}$  membrane alloy after hydrogen permeability tests. Arrows and numerals indicate the phases that appear upon heating of the alloy from 450 to 530 K: (1) Zr, (2)  $Zr_{2.26}Cu_{1.74}$ , (3)  $ZrH_{1.82}$ , (4) CuTi, and (5) ZrTi [28].

metry) structures, and coherent packings with directional hybridized bonds. In the temperature profile of the melt cooling rate, it is necessary to fix the temperature ranges of metastable states, namely, crossovers  $T_D$  and  $T_A$ , down to glass transition temperature  $T_g$  ( $T_D > T_A > T_g$ ) to achieve a deeply supercooled state [28]. In the studies based on the results of simulation of fragmentary compositions, their structures, and atomic dynamics, we controlled a change in free energy by fixing the most dissipative structures (mesophases). This fixation was achieved by a directional change in the conditions of their self-organization with optimization of the functional characteristics of the formed phase compositions, which are characterized by a significant energy reserve in comparison with their crystalline analogs. For binary amorphous and nanocrystalline  $Me^I-Me^II$  alloys, we determined the size criterion  $1/25 < R_A/R_B < 0.88$ , and the fraction of the formed and developed grain boundary should not be more than 50% of the total grain volume. To select metal (Me)–metalloid (M) alloy compositions, the difference in the valences in the proportions (5, 6) and (3–5), respectively, is essential for glass transition processes. The formed states of amorphous phase compositions are effectively stabilized by hydrogenation, which decreases the eutectic minima during the supercooling of metal system melts and determines the stoichiometry of the formed compositions with their valence, electronegativity, and the atomic radii of the elements interacting in them [29–31]. The MD studies [1, 2, 14–17, 28] showed the feasibility of producing FINEMET composite materials with amorphous and crystalline structures of iron-based two-component alloys, namely,  $Me^I-Me^{II}$  and Me–M (metal–metalloid). These investigations also revealed the effective influence of the anomalously high hydrogen mobility

on the formation of phase composites. Upon ultrafast cooling, the characteristic redistribution of elements was found to change and to be accompanied by deformation of the interatomic distances with a decrease in the cross sections in saddle configurations (Me atom triangles) in a supercooled hydrogenated melt when an electron-shielded  $H^+$  proton passes through the Me–Me diffusion channels in  $H:Fe_{80}B_{20}$  and  $H:Fe_{80}P_{20}$  alloys. When phase composites form in the narrow zone separating their boundaries, the number and density of dangling bonds (charge carriers) decrease significantly and horizontal diffusion  $p^+ \leftrightarrow H^0$  appears. The proper geometry of the boundary surface at the grain junctions of crystalline and noncrystalline symmetries provides optimization of the properties. When all of these requirements for the formation of nanosized phase composites are met, FINEMET alloys acquire their unique properties in the products made of them. Hydrogen desorption from the alloy volume during cooling proceeds with the formation and degradation of numerous structural phase composites at the rates controlled by the interatomic bonds of alloy elements. The desorption of  $H_2$  from the structures of phase composites with metallic interatomic bonds of elements proceeds without obstacles. The desorption of H from phase composites with covalent-ionic interatomic chemical bonds with the strongest covalent bond of elements (atom  $\leftrightarrow$  atom) localized inside the “quasi-molecular cluster” is only possible after removal of the existing portions of H [7–15].

We analyzed both binary and ternary (Zr–Cu–Ti) amorphized alloys formed by quenching at optimized cooling rates  $\Delta T/\Delta t \sim 10^4-10^7$  K/s. During vitrification at these rates, we were able to bypass the processes of nanocrystalline phase formation using a  $T-T-t$  kinetic diagram. For example, for the ternary  $Zr_{55}Cu_{35}Ti_{10}$  membrane composition, amorphous states were stabilized at reduced crystallization and glass transition temperatures due to the presence of Ti, as follows from the diffraction data in Fig. 5 [28]. The theoretical estimates [7] demonstrate that this result should promote a higher hydrogen solubility and permeability in membrane materials with this composition.

In the selected zirconium content range in the  $Zr_{55}Cu_{35}Ti_{10}$  melt, dehydrogenation occurs, so that most hydrogen atoms do not leave the melt. The effect of the presence of Ti as an alloying component in the composition can result in a significant increase in the service characteristics of membranes, namely, their thermal stability, the time of reliable functioning, and the resistance to deformation loads (e.g., in bending and tension).

Thus, the crystallization of alloys with several polymorphic modifications is characterized by the fact that the sequence of their formation significantly depends on the adsorption energy of surfactant atoms on the surface of a phase composition nucleus. The surfactants in iron alloys play the role of initiators of diffu-



sion processes when these processes are inhibited under forced cooling conditions. Under the conditions of spatial limitations of the mutual repulsions of elements as a result of close packing with a localized atom  $\leftrightarrow$  atom effect, clusters, macroclusters “as clusters-around-cluster”, bulk materials, and nanoscale composites are formed of “as clusters-around-cluster” with a localized covalent bond of elements inside macrocluster. By redistributing the atoms of alloy elements and stimulating the formation of fragments for new phases and polymorphic compositions, surfactants directly affect the morphology of their structuring in matrices and the properties of the related product. In this case, phase composites are formed on the basis of polymorphic structures from nanocluster “building blocks”, which consist of “quasi-molecular clusters” with elements of neutral (atom  $\leftrightarrow$  atom) and hybridized (atom  $\leftrightarrow$  ion) atoms, and structure the composites by covalent, covalent–ionic, or hydrogen inter- and intra-clusters chemical interatomic bonds. With inter- and intra-“quasi-molecular cluster” hydrogen bonds, hydride phase composites are structured, and they are characterized by a shift of molecules to an element with a high electronegativity. Hydrogen is not fixed in close-packed hydride “quasi-molecular clusters” because of the minimum sizes of the  $H^+$  and  $H^-$  ions. Therefore, the specific features of the stochastic structural transformations in polymorphic systems are due to the existence of regions with different surfactant contents in them. The condition for the conservation of metastable states in iron alloys is limited dynamics of component atoms with the predominance of cooperative diffusion mechanisms, which determine low rates of relaxation processes. All these factors are interconnected due to the nature of their action. The results obtained showed that a control analysis is necessary to determine the contents of hydrogen and other surfactants in alloy compositions to develop technologies related to forced cooling of melts to produce articles from iron alloys with predictable functional and service properties [31, 32].

The structured fraction of a certain phase can be optimized by varying the additive concentration in a melt to ensure the formation of the most dissipative mesophase structure in the entire volume of the alloy with the determination of its concentration corresponding to the bifurcation point of the process. On a local level, the process of formation and structuring of mutually agreed coordination symmetry forms of short- and long-range order takes place in a melt. At bifurcation points, the formation of intermediate structures between octahedral, cuboctahedral, amorphous, icosahedral, quasicrystalline, and other dynamic hybrid forms of ordering is possible [20, 28].

By optimizing the kinetics of phase transitions in the direction of self-organization of dissipative structures, hydrogen effectively increases their metastability, preventing the nucleation of crystalline phases, and also promotes atomic redistribution and coherent

joining of noncrystalline cluster structural blocks. Thus, hydrogen is fine tool for tuning the processes of cluster ordering and formation of nanophase composites with various types of symmetry forms (crystalline, noncrystalline). High-quality metal products and as products with fundamentally new physicochemical properties can be manufactured under forced cooling of hydrogenated alloys and controlling the atomic dynamics of elements in order to form structural blocks for nanophase composites with various types of symmetry form of ordering and structuring in an alloy matrix.

#### 4. CONCLUSIONS

(1) In the forming phase compositions of binary TMe–M alloys, the “clusters-around-cluster” that structure them, specifically, their relative size, shape, mass, and the polarity of the interatomic bonds of the elements inside them, are of particular importance. The energy of their lattices is determined by the density when space is filled with ions (environment of cations with anions and anions with heavy cations, high degree of bond polarity of “quasi-molecular cluster” elements).

(2) Changes in the thermodynamic and aggregative states (allotropic, phase, structural) of metallic alloys under the spatial limitations of the mutual repulsion of elements as a result of close packing with a localized atom  $\leftrightarrow$  atom effect and nanoclusters of “quasi-molecular clusters” (atom  $\leftrightarrow$  ion) with covalent bond localization inside them determine conditions for forming and degrading localized composite phases with the possibility of controlling them by changing the amount of hydrogen dissolved in the alloys.

(3) To produce Fe-based binary alloys with nanoscale (crystalline, amorphous) FINEMET structures, the following requirements must be met in choosing elements for compositions: the presence of deep eutectic minima and valences in combined elements, stoichiometric compounds of intermetallic cluster fragments, electronegativity, and proper atomic radii of the elements. The structuring of phase composites requires the corresponding geometry of junctions in grain-boundary surfaces, the same volumes with a developed boundary between composite grains (up to 50% of the total material volume), and the absence of defects in grains and grain boundaries.

(4) A necessary condition for the production of amorphous compositions is the fact that temperature and rate cooling conditions are satisfied to form a narrow zone between a supercooled melt and the forming phase compositions that form the boundary separating them. During hydrogenation and in the presence of elements with an active hydrogen absorption surface, a significant number of dangling bonds decrease at boundaries. As a result of interatomic interactions with hydrogen, the density of states of charge carriers

decreases, horizontal  $p^+ \leftrightarrow H^0$  diffusion appears with an increase in the susceptibility to amorphization of the forming compositions, and the formed states are stabilized.

(5) The interatomic chemical bonds of alloy elements determine the rate of hydrogen desorption from the volume and the surface of the alloy. The desorption processes in phase compositions with covalent-ionic bonds are retarded, since new-phase nuclei in them can form only after the removal of the corresponding portions of hydrogen from the existing compositions. The hydrogen desorption from phases and their compositions with a metallic bond is much higher.

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#### REFERENCES

1. C. Suryanarayana and A. Inoue, *Bulk Metallic Glasses. Technology and Engineering*, 2nd ed. (Taylor & Francis, 2017).
2. V. S. Kraposhin and A. L. Talis, "Symmetry foundations of a polymer model for close-packed metallic liquids and glasses," *Russ. Metall. (Metally)*, No. 2, 101–108 (2016).
3. V. I. Zel'dovich, I. V. Khomskaya, E. F. Gryaznov, K. M. Demchuk, D. N. Martem'yanov, T. M. Sobolenko, and T. S. Teslenko, "Martensitic transformations caused by high static and dynamic pressures," *Fiz. Met. Metalloved.*, No. 1, 151–158 (1990).
4. V. A. Polukhin and E. D. Kurbanova, "Dependence of the thermal stability of the interface states of d metals (Cu, Pd, Ti, Ni) and Al with graphene on the character of sorption and diffusion mobility in a contact zone," *Rus. J. Phys. Chem. A* **89** (3), 531–546 (2015).
5. V. A. Polukhin and N. A. Vatolin, "Stability and thermal evolution of transition metal and silicon clusters," *Russ. Chem. Rev.* **84** (5), 498–539 (2015).
6. V. A. Polukhin, E. D. Kurbanova, and A. E. Galashev, "Classification of d-metal/graphene interfaces according to a sorption mechanism and the resistance to thermoactivated and melting. MD simulation," *Russ. Metall. (Metally)*, No. 8, 633–646 (2014).
7. R. M. Belyakova, V. A. Polukhin, and V. A. Kurbanova, "Effect of admixtures of surfactants in Fe–C–Si alloys under rapid solidification of melt on the quality of structural," *Metal Sci. Heat Treat.* **58** (3–4), 187–191 (2016).
8. U. Muller, *Inorganic Structural Chemistry* (Philipps-Universität Marburg, 2008).
9. H. Y. Hsieh, "Short-range ordering in amorphous  $Al_{90}Fe_{1-x}Ce_{10x}$ ," *J. Non-Cryst Solids* **135** (2–3), 248–254 (1991).
10. I. E. Gabis and I. A. Chernov, *Kinetics of Decomposition of Metal Hydrides* (Izd.-Poligr. Tsentr Kazakh.-Ross. Univ., Karaganda, 2014).
11. N. A. Vatolin, V. A. Polukhin, R. M. Belyakova, and E. A. Pastukhov, "Simulation of the influence of Hydrogen on the structural properties of amorphous iron," *Mater. Sci. Eng.*, No. 2, 551–554 (1988).
12. V. A. Polukhin, N. A. Vatolin, R. M. Belyakova, and E. A. Pastukhov, "Effect of hydrogen on the distribution functions of amorphous iron according to molecular dynamics simulation," *Dokl. Akad. Nauk SSSR* **287** (6), 1391–1394 (1987).
13. V. A. Polukhin and N. A. Vatolin, *Simulation of Amorphous Metals* (Nauka, Moscow, 1985).
14. V. A. Polukhin and N. A. Vatolin, *Simulation of Disordered and Nanostructured Phases* (Izd. UrO RAN, Yekaterinburg, 2011).
15. V. A. Polukhin, E. A. Pastukhov, and N. I. Sidorov, "Structure of alloys  $Pd_{1-x}Si_x$ ,  $Fe_{1-x}P_x$  in liquid and amorphous states," *Phys. Met. Metallogr.* **57** (3), 176–179 (1984).
16. V. A. Polukhin and N. A. Vatolin, "Simulation of partial distribution-functions for  $Pd_{1-x}Si_x$  glass," *Dokl. Akad. Nauk SSSR* **274** (4), 851–854 (1984).
17. E. A. Pastukhov, N. I. Sidorov, V. A. Polukhin, and V. P. Chentsov, "Short order and transport in amorphous palladium materials," *Defect Diffus. Forum* **283–286** (1), 149–154 (2009).
18. V. A. Polukhin, E. D. Kurbanova, and N. S. Mitrofanova, "Stability, atomic dynamics, and thermal destruction of the d-metal/graphene interface structure," *Russ. Metall. (Metally)*, No. 2, 116–126 (2017).
19. A. E. Galashev and V. A. Polukhin, "Computer analysis of the stability of copper films on graphene," *Rus. J. Phys. Chem. A* **88** (6), 995–999 (2014).
20. V. A. Polukhin, E. D. Kurbanova, and N. A. Vatolin, "Formation of an intermediate order in metallic glasses and a long order in nanocrystalline alloys with allowance for the character of binding and the transformation of the short order in a melt," *Russ. Metall. (Metally)*, No. 2, 95–109 (2018).
21. L. N. Kolotova, G. E. Norman, and V. V. Pisarev, "Glass transition of aluminum melt. Molecular dynamics study," *J. Non-Cryst. Solids*, No. 429, 98–103 (2015).
22. V. A. Polukhin and N. A. Vatolin, "Composite motifs, short- and long-range disorders in the structure of metallic melts, glasses and quasicrystals," *Melts.* **1** (5), 413–444 (1989).
23. A. E. Galashev and V. A. Polukhin, "Computer-assisted study of silver absorption by porous silicon dioxide nanoparticles," *Colloid J.*, No. 6, 761–767 (2011).
24. V. A. Polukhin and M. M. Dzugutov, "Statistic-geometry structure-analysis of molecular-dynamical model of amorphous and liquid aluminum," *Metal. Metallogr.* **51** (1), 50–55 (1981).
25. V. A. Polukhin, R. M. Belyakova, and L. K. Rigmant, "Spatial arrangement of the fragmented phases in nanostructured 3d metal alloys during a change in the melt

- composition and cooling conditions," *Russ. Metall. (Metally)*, No. 8, 681–698 (2010).
26. V. A. Polukhin, M. M. Dzugutov, A. M. Evseev, et al., "Short-range order and character of atom motion in liquid-metals," *Dokl. Akad. Nauk SSSR* **73** (6), 761–767 (1975).
27. R. Z. Valiev, A. P. Zhilyaev, and T. G. Langdon, *Bulk Nanostructured Materials: Fundamentals and Applications* (Wiley, 2013).
28. V. A. Polukhin, N. I. Sidorov, and N. A. Vatolin, "Pre-solidification changes in the structural–dynamic characteristics of glass-forming metallic melts during deep cooling, vitrification, and hydrogenation," *Russ. Metall. (Metally)*, No. 8, 758–780 (2018).
29. R. M. Belyakova, V. A. Polukhin, and R. I. Sidorov, "Formation of the structure and properties of multi-component iron-based alloys as a function of the melt solidification and hydrogenation conditions," *Rasplavy*, No. 5, 594–606 (2018).
30. V. A. Polukhin and N. A. Vatolin, "Thermal stability and deformation mechanisms in graphene- or silicene-reinforced layered and matrix metallic composites," *Russ. Metall. (Metally)*, No. 8, 685–699 (2018).
31. Y. Q. Cheng, "Atomic-level structure and structure-property relationship in metallic glasses," *Progr. Mater. Sci.*, No. 56, 379–473 (2011).
32. N. A. Vatolin, R. M. Belyakova, V. A. Polukhin, et al., "Method for the formation of an amorphous ribbon ( $H_2$  bubbling of a melt before casting; embrittlement hydrogenation of amorphous ribbons before milling)," RF Patent 1551, 1993.

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