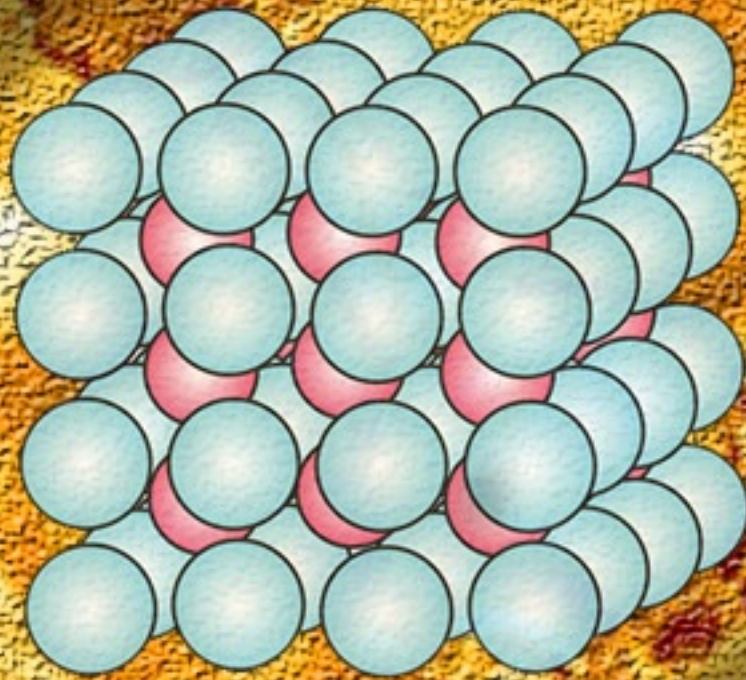


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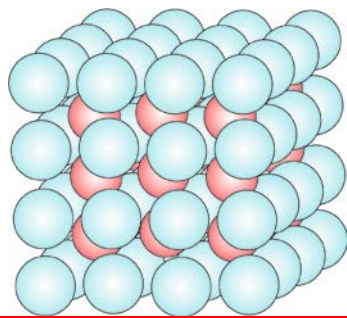
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Structure and properties of chromium carbide reinforced steel matrix composites produced from powder iron-ferrochrome mixtures

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Abstract: The influence of high-carbon ferrochrome on the features of structure formation and properties of chromium carbide steels based on the Fe-FKh800 system was investigated. It was shown that the optimal combination of hardness and tensile strength with sufficient crack resistance has a carbide base of 65% Fe - 35% (wt.) FKh800. A typical microstructure of sintered carbide is a metal matrix composite consisting of chromium steel of composition close to Kh17 and double carbide ($\text{Cr}_{0.799}\text{Fe}_{0.201}$) $\gamma\text{-C}_3$. The effect of TiB_2 additive on the structure, phase composition, mechanical and tribotechnical properties of materials based on the Fe- 35 (%wt.) FKh800 system was also investigated. Additions of titanium borides in the amount of 0.38-1.48 (% wt.) leads to some increase in hardness, noticeable increase in the flexural strength and leads to increase wear resistance of carbidosteels.

KEYWORDS: POWDER MATERIALS, COMPOSITE, SINTERING, FKH800, TiB_2 , MICROHARDNESS.

Iron-chromium-carbon alloys, chromium steels and cast irons, are widely used in modern mechanical engineering for the manufacture of machine parts, mechanisms and equipment operated under conditions of simultaneous action of friction forces, abrasive, corrosive and erosive wear [1]. Having a heterogeneous structure, they are characterized by a significant difference in the properties of the components - carbide and metal phases - in their hardness, strength, ability to plastic deformation, resistance to fracture, etc. by changing the ratio of the metal and carbide components, it is possible to obtain material with different contents of hard and soft inclusions. Accordingly, hard inclusions can significantly increase the abrasion resistance, and soft - antifriction properties of alloys. Along with traditional methods, powder metallurgy technology is widely used to create such heterogeneous structures. In this embodiment, the finished solid additives are artificially introduced into the powder mixture or use special sintering modes that do not lead to homogenization of the structure of the material [2]. The list of such materials includes the materials we study from iron powders and high-carbon ferrochrome FKh800 [3].

In the works [3-5] performed by us earlier, it was shown that the use of high-carbon ferrochrome (8% C by wt.) instead of chromium carbide allows to obtain by powder metallurgy composite material based on iron, which is equivalent in wear resistance and strength exceeds materials type chromium steel - Cr_3C_2 . However, the influence of high-carbon ferrochrome content on the sintering temperature, structure formation, mechanical and functional properties of iron - FKh800 composites remain unclear.

The aim of the study was to study the effect of high-carbon ferrochrome content on the phase composition, structure and physical and mechanical properties of powdered chromium carbide steels.

Objects and research methods

For experiments used iron powder and high-carbon ferrochrome powder FKh800 (72.2% Cr, 18.8% Fe, 8.4% C, 0.6% O (% by weight), fractions -200 +100 μm). Other properties of FKh800, obtained by mechanical dispersion of lump ferrochrome, are presented in [3]. Powder mixtures were obtained by wet grinding in a ball mill according to the modes described in [6], in 5% increments.

Powder mixtures of materials were prepared by wet milling-mixing in a ball mill in alcohol medium according to the regimes given in [6] article. The samples were pressed in a closed die at 800 MPa. Sintering was carried out in a vacuum electric furnace according to pre-established regimes that ensure the production of

materials with maximum density. The mechanical properties of the samples were determined by standard methods for powder materials and hard alloys [7, 8]. The microstructure of the materials was examined on a REM-106I electron microscope. The phase composition of the samples was investigated by X-ray diffraction analysis (XRD) on the diffractometer "UltimaIV, Rigaku" (Japan).

Results and discussion

The construction of the polythermal cross section was carried out by the analytical - graphical method using projections of the solidus and liquidus surfaces and isothermal cross sections of the state diagram of the Cr-Fe-C system, published in the review [9]. The high-temperature region is represented by a compilation of works [10,11] (liquidus surface) and by thermodynamic calculations [12] (solidus surface). Solid-phase transformations are accepted by the results of thermodynamic modeling in [13], for which the authors of [14] later calculated a number of isothermal cross sections. Features of this version of the state diagram of the system Cr-Fe-C - equilibrium stability ($\gamma\text{-Fe}$) + (Cr, Fe) $_{23}\text{C}_6$ from 855 °C to the solidus temperature, which is consistent with detailed experimental studies [15].

The polythermal cross section shows wide areas of biphasic equilibria ($\gamma\text{-Fe}$) + (Cr, Fe) $\gamma\text{-C}_3$ and ($\alpha\text{-Fe}$) + (Cr, Fe) $\gamma\text{-C}_3$ and a certain similarity with the eutectic type state diagram (Fig. 1). It should be noted that the data on the position of the three-phase regions have a large variance and therefore in Fig. 1 they are shown in dotted lines. The constructed polythermal cross section allowed to estimate the composition of the eutectic as 73.7Fe-26.3 FKh800 (% by weight), its formation temperature as 1285 °C, as well as to determine the approximate, most suitable, sintering interval of iron-based composites with different content of FKh800 as 1100- 1250 °C.

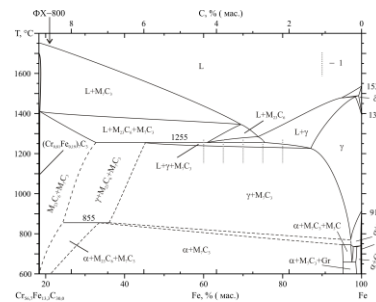


Fig. 1 - Polythermal cross section ($\text{Cr}_{0.81}\text{Fe}_{0.19}$) $\gamma\text{-C}_3$ - Fe of the state diagram of the Cr-Fe-C system

Typical microstructures of carbide steels with 25 and 35% (wt.) FKh800 are shown in Fig. 2. It is seen that their microstructure is heterogeneous and consists of metal and carbide phases and a number of pores. The microhardness of the carbide phase is 10-12 GPa, and the metal 2.5-2.8 GPa.

Micro-X-ray spectral analysis of the sample with 35% (wt.) FKh800 revealed that the metal phase contains 17.1% (wt.) Cr and the composition is close to chromium steel type X17: the average result of 23 measurements of 82.7% Fe - 17, 1% Cr - 0.2% C (% by weight). In the carbide phase received a carbon content of 7% (wt.) or 25% (at.), Which corresponds to the carbide (Cr, Fe) $\gamma\text{-C}_3$: 19.8% Fe - 73.1% Cr - 7.1% C (% by mass). But X-ray phase analysis clearly identifies the main phases as ($\alpha\text{-Fe}$) + (Cr, Fe) $\gamma\text{-C}_3$ (Fig. 3). Adjusting the carbon content to 30% (at.), we obtain the composition of the carbide as (Cr $_{0.799}\text{Fe}_{0.201}$) $\gamma\text{-C}_3$ or 71.7% Cr - 19.4% Fe - 8.9% C (% by weight).

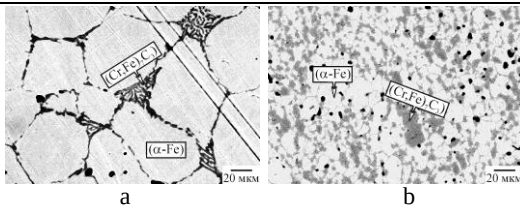


Fig. 2 - Influence of sintering temperature and TiB_2 additives on volume shrinkage (a), density (b) of samples from composite material Fe-35%FKh800

The results of X-ray indexing (Fig. 3) clearly indicate that the metal phase of carbide is a BCC phase based on $\alpha\text{-Fe}$ with a period $a = 0.2872$ nm. The lattice periods of the carbide phase also changed slightly compared to the binary compound: $a = 0.6988$, $b = 1.2076$ and $c = 0.4500$ nm. The texture is observed due to the fact that the diffraction pattern was taken from a section. Peaks that do not belong to the main phases were not detected.

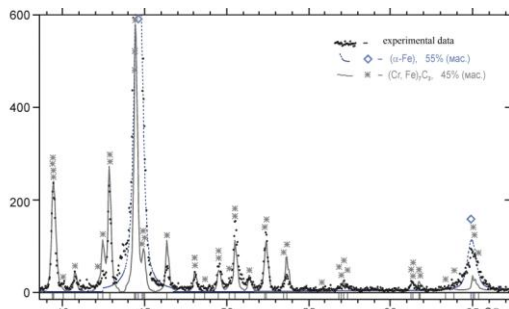


Fig. 3 - A fragment of a full-scale Rietveld analysis of Fe-35%FKh800 carbide steel obtained by sintering at 1250 °C

To establish the optimal composition, the effect of FKh800 content on the physical and mechanical properties of carbide steels was investigated. The obtained results showed that increasing the content of FKh800 from 25 to 35% (wt.) leads to an increase in hardness from 67 to 75.5 HRA and bending strength from 1100 to 1712 MPa (Fig. 4). The extreme nature of the concentration dependence of hardness and strength can be explained by the superposition of several factors: the simultaneous increase in hardness and brittleness with increasing content of FKh800 and significantly lower porosity of composites with 35 and 40% (wt.) FKh800 (2.6%) compared with composites with lower content solid component.

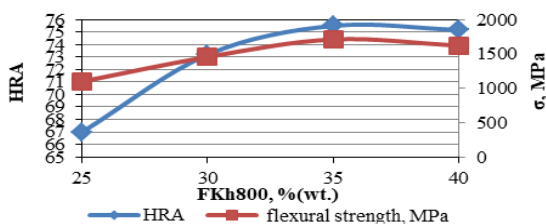


Fig. 4 - The effect of the content of FKh800 on the hardness and flexural strength of samples of composite materials

Along with flexural strength and hardness, an important characteristic is crack resistance, which determines the ability of a material to absorb the energy of cracks that develop in it during fracture. It is known that an increase in strength and hardness is often offset by a decrease in ductility, resulting in a decrease in fracture toughness. The study of the dependence of crack resistance on the content of FKh800 showed (Fig. 5) that, as expected, an increase in the content of the solid component leads to a decrease in the crack resistance of composites.

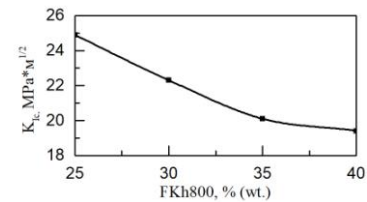


Fig. 5 - Crack resistance of composites with different content of FKh800, obtained at the optimal sintering mode: 30 min. at 1250 °C

Concentration dependences of hardness and flexural strength of Fe-FKh800 composites are characterized by maxima at 35% (wt.) FKh800: 75.5 HRA and 1712 MPa, respectively. Crack resistance is reduced from 25 $\text{MPa}\cdot\text{m}^{1/2}$ at 25% (wt.) FKh800 to 19.5 $\text{MPa}\cdot\text{m}^{1/2}$ at 40%. The optimal combination of hardness and tensile strength with sufficient crack resistance has a carbide base of 65% Fe - 35% (wt.) FKh800.

It is promising to additionally introduce strong carbide and boride forming elements into the composition of chromium steels and cast irons, which ensure the creation of special carboborides and the redistribution of chromium between the solid phase and the metal matrix. Since the basis of the composite material is iron or chromium steel, it is advisable to study the effect of boron additives on the structure and properties of the material iron - high carbon ferrochrome FKh800. TiB_2 additives were introduced in an amount of 0.38-2.2 (% wt.), which corresponds to the content of titanium 0.25-1.5 (% wt.) in the alloy Fe-35% FKh800.

The effect of titanium boride additives on the structure and properties of chromium carbide steel Fe-35 FKh800 (% wt.) was studied. The introduction of titanium borides in an amount up to 1.48 (wt. %) leads to a slight increase in the hardness of carbido steels, but a further increase in the content of the additive to 2.2 (wt. %) leads to a decrease in rigidity. This dependence can be explained by the fact that as a result of the interaction of titanium borides with the composite components, there is the formation of complex carboborides type Me_3CB , as well as complex iron-chromium carbides type Me_7C_3 , which contribute to increase their hardness. The flexural tensile strength of the Fe-35% FKh800 composite with an increase in TiB_2 content is maximum at 0.74 TiB_2 (wt.%), after which a further increase in the amount of titanium diboride leads to its significant fall (fig. 6). This can be explained by the optimal ratio of the amount of Me_7C_3 and $\text{Me}_3(\text{CB})$ at 0.74 TiB_2 (wt.%).

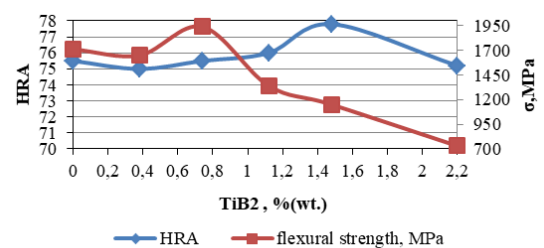


Fig. 6 - Influence of the amount of TiB_2 additives on the hardness and flexural strength of powder materials

Metallographic electron microscopic and local micro-X-ray spectral analysis of the Fe- FKh800 doped TiB_2 showed that their structure is microheterogeneous, multiphase and consists of light gray, gray, dark gray and black phases. The doping with TiB_2 affects the structure of the carbide phase of the composite, especially when the content of TiB_2 is 0.74-1.48 (wt. %) (fig.7). The size of the carbides decreases from 8-13 to 4-6 μm . Due to the simultaneous action of two factors, on the one hand, boron affects the decrease in sintering temperature, and, on the other hand, titanium additives contribute to the inhibition of grain growth. To increase the amount of titanium boride additives, dark gray phases appear in the structure of the material, their size being 3-5 μm . However, their number becomes significantly less when the content

of the additive is 2.2 (% wt.). According to the results of X-ray spectral analysis, the composition of the dark gray phases indicates that it is a complex chromium carbide of the Me_7C_3 , and the gray phases are the carboborides of the $\text{Me}_3(\text{CB})$.

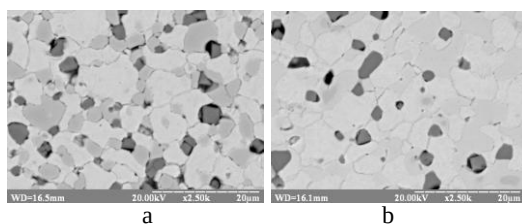


Fig 7 - Electron microscopic image of the microstructure of samples of materials Fe-35% FK800 with TiB_2 additives 0.74 (a), 1.48 (b) (% wt.)

We studied the effect of TiB_2 additives on the abrasion resistance of Fe-35 FK800 materials (wt. %) when they are treated with ASB 160/125 diamond wheel fixed particles according. The tests were carried out under such friction conditions: sliding speed - 1 m/s, load - 0.5 MPa, friction path - 1 km, friction at room temperature in air, without lubrication.

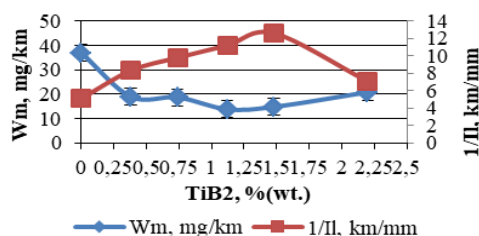


Fig. 8 - The effect of the amount of TiB_2 additives on the mass wear W_m (mg / km) and the wear resistance of the materials of the Fe- FK800- TiB_2 system

The results of the studies showed (Fig. 8) that an increase in the amount of TiB_2 supplement from 0.38 to 1.48 (% wt.) leads to a decrease in mass wear (W_m) from 36.94 to 14.8 mg / km and linear wear (I_L) from 0.197 to 0.079 mm / km. This can be explained by the formation of complex carbides type Me_7C_3 and carboborides type Me_3CB , which increase the microhardness of carbide phases, as well as increase the adhesive strength of solid grains by the metal matrix. However, a further increase in the amount of dopant to 2.2 (wt. %) leads to an increase in mass wear (from 14.8 to 20.8 mg / km) and linear wear of the samples (from 0.079 to 0.141 mm / km).

Conclusions

Studies of the effect of the amount of high-carbon ferrochrome FK800 25-40 % (wt.) on the mechanical properties of composites showed that the concentration dependences of hardness and flexural strength of Fe-FK800 composites are characterized by highs at 35% (wt.) FK800: 75.5 HRA and 1712 MPa in accordance. Crack resistance is reduced from 25 $\text{MPa}\cdot\text{m}^{1/2}$ at 25% (wt.) FK800 to 19.5 $\text{MPa}\cdot\text{m}^{1/2}$ at 40%. The optimal combination of hardness and tensile strength with sufficient crack resistance has a carbide base of 65% Fe - 35% (wt.) FK800. A typical microstructure of sintered carbide is a metal matrix composite consisting of chromium steel of composition close to Kh17 and double carbide 71.7% Cr - 19.4% Fe - 8.9% C (% by wt.) or $(\text{Cr}_{0.799}\text{Fe}_{0.201})_7\text{C}_3$.

The effect of TiB_2 additive on the structure, phase composition, mechanical and tribotechnical properties of materials based on the Fe- FK800 system was also investigated. Additions of titanium borides in the amount of 0.38-1.48 (% wt.) leads to some increase in hardness and noticeable increase in the flexural strength of carbidosteels. It has been shown that titanium boride supplements provide the formation of a multiphase, microheterogeneous matrix-filled structure. The doping of the

composite with TiB_2 additives in the amount of 0.74-1.48% (wt.) leads to the crushing of the structure of the matrix and carbide phases. Investigation of the effect of TiB_2 additive on abrasion resistance, showed that an increase in the amount of dopant from 0.38 to 1.48 (% wt.) leads to a decrease in mass (W_m) from 36.94 to 14.8 mg / km and linear (I_L) from 0.197 to 0.079 mm / km of carbidosteel wear.

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Phase transformations in non-metallic inclusions under laser action

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Abstract. *It was found that in the process of pulsed laser action, various phase and structural transformations occur in non-metallic inclusions, which take place under nonequilibrium conditions. It is shown that the melting of inclusions under laser action is corresponded with change of their structure and phase composition. Also it is shown that the nature of these transformations depends on the type of nonmetallic inclusion. It was found that nonequilibrium phase transformations contribute to a change in the structure, phase composition, properties and sizes of nonmetallic inclusions, as well as the inclusion-matrix interphase boundaries of steel. It is shown that changes in the structure and properties of non-metallic inclusions affect their behavior and the formation of defects in the laser-strengthened layer of steel products.*

KEYWORDS: NON-METALLIC INCLUSIONS, STEEL, PHASE TRANSFORMATIONS, LASER TREATMENT

1. Introduction.

Steels contain non-metallic inclusions which influence on the character of strengthening during laser quenching. In the process of laser treatment non-metallic inclusions are fully or partly melted down or are remained hard, in reference [1-13]. In spite of short-term treatment the energy of laser radiation turns out sufficient for melting of the high-melting and low-melting inclusions, and also for the development of mass transfer processes which lead to enrichment of steel matrix with the elements of inclusions and also transfer of matrix elements to the surface zone of inclusions. Areas of steel matrix near non-metallic inclusions are the strongly oversaturated solid solution with different types of gradient and composite structures: gradiental zones with cascade and "spot" distribution of elements and nanohardness, dispersal zones with different types of microphases and nanophases, "tunnel" zones, and also zones with combine structure [1,14-20].

It is known that laser action affects the behavior of nonmetallic inclusions and the formation of defects during subsequent

deformation [1, 21, 22], contributing to a change in the conditions for the formation of cracks. Therefore, it is of interest to study the nature of transformations occurring in nonmetallic inclusions under laser action. The goal of this investigation was to research phase and structural transformations in non-metallic inclusions under laser treatment of the steels.

2. Materials and Procedures

Specimens made of steels R7, 08Yu, 08T, 08Kp, 08Ch18N10T, ShCh15, NB-57, 12GS, E3, 60G were irradiated by laser in GOS-30M installation with an excitation voltage of 2,5kV and pulse energy of 10, 18, 25 and 30 J at heating rate of 10^5 °C/s and cooling rate of 10^6 °C/s with the action time of (1,0, 2,5, 3,6, 4,2 and 6,0) 10^{-3} s. Non-metallic inclusions were identified by metallographic, X-ray micro spectral and petrographic methods [1]. Distribution of elements, microhardness and nanohardness of steel matrix near non-metallic inclusions were determined.

3. Results and discussion.

Phase transitions in nonmetallic inclusions occurring at the moment of laser action are their dissociation and melting (Fig. 1, a, b). This process is considered in works [1-9], where the features of crushing of non-metallic inclusions in the process of their partial dissolution and melting under pulsed laser exposure are investigated, which are associated with the following processes:

- disordering of their crystal lattice as a result of the occurrence of stresses caused by an increased density of defects and the penetration of atoms from the molten steel matrix by anomalous mass transfer;
- the formation of a micrometallurgical bath at the time of laser action, in which hydrodynamic flows arise, creating conditions for convective mass transfer of elements and the formation of heterophase complexes;
- the appearance in the structure of a microheterogeneous melt of dynamic heterophase complexes at the moment of melting of the initial inclusions, which are the centers of rapid crystallization of new "satellite" particles.

In the moment of laser action process of dissolution or melting of non-metallic inclusion happens owing to disordered transitions of atoms of inclusion over boundary with molten steel matrix. Mechanism of super-speed dissolution and melting of inclusions connects with mutual mass transfer of atoms (inclusion ↔ matrix) across interface boundaries which are melted also. Abnormal mass transfer across inclusion-matrix boundaries are accompanied by means of electrons exchange between inclusions (donors) and steel matrix (acceptor) [1]. Electromagnetic field inducing in the time of laser radiation

influence on the conditions of mass transfer. Definite forces action on the components of alloy under this field and direction of these forces depends on magnetic properties of components of alloy. Action of forces causing with electromagnetic field promotes of mass transfer of components of inclusions and steel matrix which possess of different magnetic properties (magnetic moments). Thus electron interaction between inclusion and steel matrix is got complicated owing to electromagnetic interaction between atoms of contacting phases. Mass transfer of components from steel matrix to the surface layer of inclusion can to accelerate the process of dissolution or melting of inclusion if solubility of these elements in inclusion is sufficiently great. Variation of chemical composition on the surface of inclusion and advance of solubility limit of matrix elements realizes the conditions for transition of surface layer of inclusion into liquid state with minimum energy expense on the break of interatomic bonds. Evidently that perhaps connected with distortion of inclusion lattice with the atoms of steel matrix and also with appearing of high-density of crystalline defects and considerable stresses in surface layer of inclusion. Thus in hyper-nonequilibrium conditions of laser action the zone with high-density of vacancies and dislocations in surface layer of inclusion contacting with melted steel matrix is formed. According to dislocation theory of melting, for example [1-9], regions of this zone imagining heavy distortion areas with practically disordering lattice perhaps the nucleuses of liquid phase. Atoms with the most breaching electron configurations present in heavy distortion area on the surface of inclusion (nucleus of liquid phase).

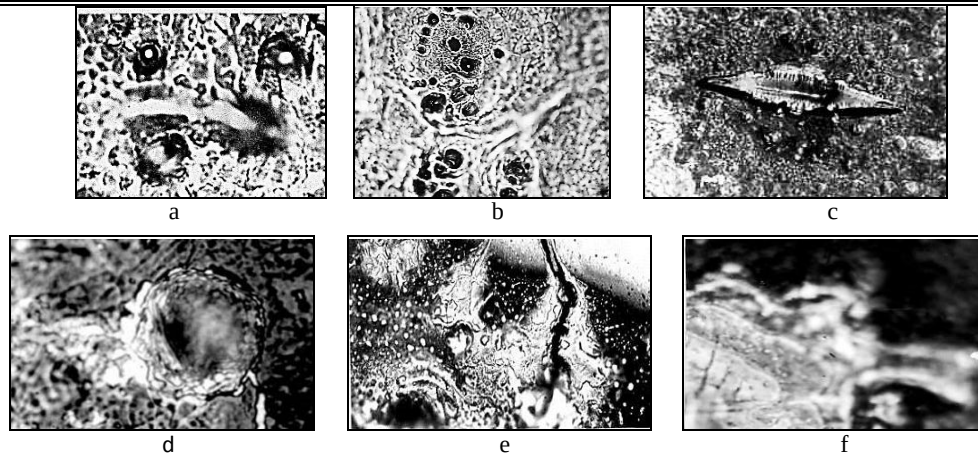


Figure 1. Dissolution and melting of non-metallic inclusions under laser action (a, b), bands of rapid crystallization in non-metallic inclusions (c, d) and Phase decay of non-metallic inclusions under laser crystallization (e, f); x500x6

After laser quenching from liquid state the areas of laser crystallization in surface layer or in all volume of inclusion are formed. Ultrasmall graininess, columnar shape of grains, zones of shear are characteristics of these areas (Fig. 1, c, d). In the time of laser melting the high degree of nonequilibrium of liquid phase, bifurcation of melt and also transition from laminar to turbulent flow of liquid are appeared that ensure gradient of oscillation pressure on the inclusion-matrix boundary (liquid if inclusion and steel matrix were melted, or semi-liquid if steel matrix was hard) controlling convective and abnormal flows of mass transfer. Considerable stresses appearing in thin surface layer of inclusion and steel matrix in the result of local heat flashes of laser radiation [1], together with action of reactive forces of recoil owing to ejection from zone of treatment of liquid allows to high-temperature deformation of liquid interlayers continuing under crystallization during cooling. In some non-metallic inclusions being homophase before laser action phase decay in process of nonequilibrium crystallization

was happened. That connects with mixing of liquid under action of hydrodynamics forces and temperature gradients. In inclusions disperse particles of second phase (Fig. 1, e) or interlayers of different chemical compositions (Fig. 1, f) were appeared. The size of these new phases do not depends on energy of impulse practically but it is increased with increase of the time of laser action.

Melting of inclusions under laser action is corresponded with change of their structure and phase composition. Mass transfer of components from steel matrix to the surface layer of inclusion can to cause various transformations.

The components of steel matrix penetrate into surface areas of non-metallic inclusions that promotes formation of solid solutions (Fig. 2, 3, a). For example surface area of inclusion Al_2O_3 in the steel 08Yu corresponds to $(Fe,Mn)O \cdot Al_2O_3$. The width of saturated zones in inclusions is about 5...10 mcm. Carbon has to penetrate into surface areas of inclusions too and carbide phases can to form.

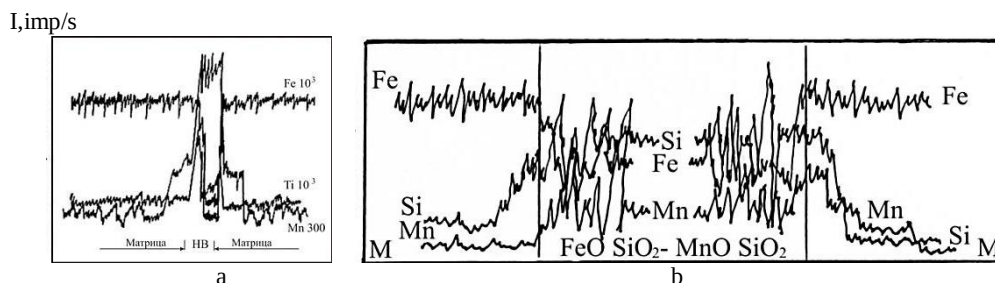


Figure 2. Distribution of elements in contact zones inclusion-matrix steel: $MnO \cdot TiO_2$ (a), $FeO \cdot SiO_2 - MnO \cdot SiO_2$ (b)

One of the results of interaction between non-metallic inclusions and steel matrix is the formation of new bounding phases around inclusions (Fig. 3, b). The width of these phases is about 5...7 mcm. They represent the two-dimensional interlayers hardly connecting with both inclusion and steel matrix. Formation of bounding phase at a little time of laser action bears witness about collective character of this process owing to activation of group of different atoms in the conditions of high temperature and pressure. In the results on the boundary inclusion-steel matrix the complicated system is realized owing to thickening of some quantity of components:

$$N_i = n_i^i \cdot V_i + n_i^m \cdot V_m + G_i \cdot F_{i-ph} \quad (1)$$

where N_i – quantity of redistributing atoms; n_i^i and n_i^m – atoms densities of Mn, S, Fe, Al etc;

V_i and V_m – atoms volumes of inclusion and steel matrix; G_i – adsorption on the interphase boundary having area F_{i-ph} .

Formation of bounding phases in the moment of laser action happens when non-metallic inclusion, steel matrix and interphase boundary inclusion-matrix are melted. Owing to interaction between inclusion and steel matrix the bounding phase having the chemical composition and structure differed from initial inclusion and steel matrix is formed.

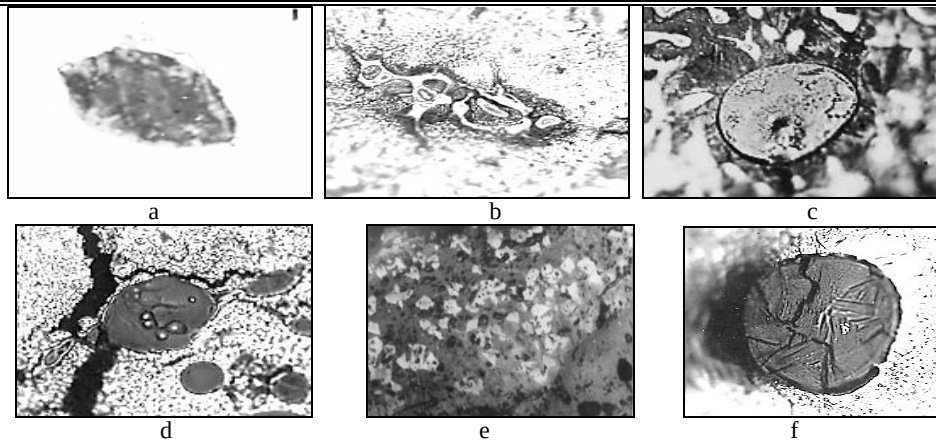


Figure 3. Non-metallic inclusions after laser action: x500

In the liquid state this layer perhaps close to the local state with coordination of atoms corresponding to the structure of metastable phases for temperatures and pressures in given region. If in the moment of laser melting the interaction of components on the interphase boundary is not carried out one can leads to formation of heterophase fluctuations close to the structure of any stable or metastable phases. Diffusion of any components in inclusion and steel matrix is described according to equations of Fick with different coefficients of diffusion so one can carries out the withdrawal of that component from the interphase boundary into inclusion or steel matrix. Also on the interphase boundary the layer with new chemical composition and structure one can to form. The chemical composition of bounding layer or bounding phase depends on temperature, pressure, concentration of elements in inclusion and steel matrix and also on the character of thickening of these parameters on interphase boundary in the moment of laser action. Bounding phase can to have transitional state from the inclusion to steel matrix or represents solid solution on the base of components of both inclusion and steel matrix or also represents the intermediate phases. State of the bounding phase perhaps is stable but more often it is metastable.

Formation of new phase owing to mass transfer across interphase boundary inclusion-steel matrix perhaps is accompanying with displacement of initial position of that boundary (Kirkendall effect). Energy of activation of bounding phase formation is:

$$W_{ph} = N_{at} \cdot \lambda_{ph} \quad (2)$$

where λ_{ph} – heat of the transition to new state; N_{at} – quantity of atoms in the bounding phase.

Change of free energy ΔW_{ph} determining probability of the formation of bounding phase under laser action is:

$$\Delta W_{ph} = \Delta W_{chem} + \Delta W_{sur} + \Delta W_{elas} + \Delta W_{def} \quad (3)$$

where ΔW_{chem} – change of the chemical energy; ΔW_{sur} – change of the surface energy in consequence of the formation of new interphase boundary; ΔW_{elas} – change of the elastic energy determining with difference of atom volumes of inclusion, steel matrix and bounding phase; ΔW_{def} – change of the energy connecting with interphase defects.

The research of bounding phases was shown that they may be different not only with chemical composition but also with structure. Bounding phases with crystalline, nanocrystalline and also amorphous structure were discovered.

In some non-metallic inclusions being on the surface of steel specimens which has homophase structure before laser action the new phases in thin surface layer were discovered. The analysis was shown that their nature is not the same. In the inclusions of some simple oxides (MeO , Me_2O_3 , MeO_2) and of the some complicated oxides ($MeO \cdot Me_2O_3$, $nMeO \cdot MeO_2$) the dispersed particles of more lower oxides (Fig. 3, c) or of the pure metal were discovered (Fig. 3, d). The products of dissociation of oxides are shown in Table 1.

Evidently in the simple oxides the reduction of metal happened partly or fully and some products of reduction, for example Al_2O_3 , CrO , SiO , are typical for the high-temperature state and at low temperatures they are not stable [1]. Reduction of the complicated oxides happened without decomposition on the simple oxides. Metal of the compound lower oxide was fully restored, metal of compound higher oxide was partly restored. Dissociation of oxide happens owing to laser action when ions of oxygen are removed from the lattice of initial oxide. These ions are moved to surface and removed to environment but in the places of oxide lattice the distortions are arisen. Growth of local distortions leads to reconstruction of lattice of the higher oxide to lattice of the lower oxide or metal which is strongly distorted owing to high concentration of oxygen vacancies.

Process of reduction of oxides is begun on a few reaction nucleous – the crystalline defects. It passes with high speed in the conditions of generation of the new crystalline defects. The depth of penetration of reduction process is about 10...15 mcm. On the surface of each inclusion the areas with different stage of reduction are been. That bears witness about inhomogeneity of laser radiation and of the defect structure of oxides and also about high speed of reduction process. This process happened more easy in the lower oxides MeO than in the higher oxides both independent and being in the composition of spinels and silicates.

Table 1. Products of dissociation of oxides

Initial inclusion	New phases	Initial inclusion	New phases
Simple oxides		Complicated oxides	
Al_2O_3	Al_2O_3 , Al	$FeO \cdot TiO_2$	Fe, TiO
Cr_2O_3	CrO , Cr	$MnO \cdot Al_2O_3$	Mn, Al_2O_3
FeO	Fe	$MgO \cdot Al_2O_3$	Mg
TiO_2	TiO, Ti	$MgO \cdot Cr_2O_3$	Mg, CrO
MnO	Mn	$FeO \cdot Cr_2O_3$	Fe, CrO
MoO_2	MoO	$FeO \cdot SiO_2$	Fe, SiO, Si
V_2O_5	VO_2	$MnO \cdot SiO_2$	Mn, SiO, Si

In the inclusions of endogenic or exogeneous complicated silicates having multicomponent composition and representing in initial state the oversaturated solid solutions the dispersed particles were observed after laser action. These inclusions are low-melting and they are melted under laser action forming liquid solutions. In the result of the new liquid phases are formed which are crystallized as the hard phases under following very rapid cooling (Fig. 3, e). Chemical composition of these phases depends on the composition of initial inclusion and character of liquation phenomenon.

Laser treatment allows to fix some high-temperature phases of inclusions and also the whole inclusions. For example, SiO, CrO, Al₂O, Cr₂O, Cr₂O₃, Mn₃O₄, Cr₃O₄. These inclusions were discovered in the areas of melting and intensive evaporation

of steel under laser action. The compared analysis of microhardness of inclusions showed that it is increased after laser action (Table 2).

The two groups of the non-metallic inclusions are shown. Microhardness of the inclusions of the first one is risen in 1,1...1,2 time. Microhardness of the inclusions of the second one is risen in 1,5...1,8 time. This is connects with presence or absence of polymorphic transformations in inclusions. In non-polymorphic inclusions microhardness rises in 1,1...1,2 time owing to increase of density of crystalline defects and also of the thermal stresses. In inclusions Al₂O₃, SiO₂ ets polymorphic transformations happen with high speed over to shear mechanism. That may to lead to the brittle fracture of inclusion (Fig. 3, f).

Table 2. Microhardness of non-metallic inclusions before (1) and after laser action (2)

steel	inclusion	H _μ , · 10, MPa	
NB-57, 08kp	MnO	275	360
08kp	FeO	428	548
08kp	Fe ₂ O ₃	1250	1900
08YU	Al ₂ O ₃	1984	3028
08H18N10T,	Cr ₂ O ₃	1568	2575
E3	SiO ₂	1581	2856
08T	TiO ₂	624	1083
08H18N10T	FeO-TiO ₂	556	912
SHH15	MgO	1262	1499
08kkp	FeO-Fe ₂ O ₃	605	955
IIIX15	MgO-Al ₂ O ₃	1724	1920
08GCYU TF	MgO-Fe ₂ O ₃	1518	1702
08XH	FeO-Cr ₂ O ₃	564	638
08YU	MnO-Al ₂ O ₃	1600	1730
08T	Ti ₂ O ₃	1525	2229
E3	2FeO·SiO ₂	860	980
NB-57, R6M5	2MnO·SiO ₂	916	1140

Phase stresses in the lattice arising under shear polymorphic transformations promote increase of microhardness of inclusions in 1,5...1,8 time. Microhardness of some complicated silicates increased in 2,0...2,7 time after laser action. Evidently this connects with amorphization of these inclusions.

4. Conclusions. Laser action causes various phase and structural transformations in non-metallic inclusions, which take place under nonequilibrium conditions. The nature of these

transformations depends on the type of non-metallic inclusion. Nonequilibrium phase transformations contribute to a change in the structure, phase composition, properties and sizes of nonmetallic inclusions, as well as the inclusion-matrix steel interphase boundaries. These changes affect the behavior of non-metallic inclusions and the formation of defects in the laser-strengthened layer during the subsequent operation of steel products.

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Structure transformation in graphite at high-energy ball milling treatment

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Abstract: The changes in the structure of the crystalline graphite are studied during high-energy ball milling (BM) treatment. It was found by XRD analysis the milling time increasing up to 3.5 h leads to the formation of an amorphous phase in the milling process. After 10 h of ball milling treatment, complete amorphization of graphite takes place. It has been shown by high-resolution electron microscopy the individual particles have complex morphology which depends on the BM time. After 1 h of BM carbon materials characterized by an onion-like structure: the individual particles have a spheroidal shape with a size of ~ 10 nm. However, unlike the previous ones after 10 h of ball milling carbon nanomaterials are characterized by a disordered structure, which is typical for amorphous carbon.

Keywords: GRAPHITE, ONION-LIKE, BALL-MILLING, XRD, MICROSTRUCTURE

1. Introduction

The attention to carbon has been focused for a long time due to a broad spectrum of allotropic modifications depended on the degree of sp -hybridization of valence electrons [1-4]. Under the classification scheme of Heimann and coworkers [5], the basic forms of carbon allotropes are diamond, graphite and carbin with integer degrees of bond hybridization sp^3 , sp^2 and sp , respectively. The new spatial forms of carbon (fullerenes and nanotubes) have non-integer degrees of bond hybridization sp^{2+x} ($x < 1$). A broad class of disordered carbon materials related to transitional carbon is in the center of the scheme. These substances (amorphous carbon, soot, vitreous carbon, diamond-like carbon, carbon spheres, cokes, coals, etc.) consist of randomly arranged carbon atoms at the different hybridization states [5]. Due to the unique physical, chemical, and mechanical properties carbon nanomaterials are extensively used in the industry and are very promising in the future, also.

The amorphous carbon can be easily produced by either high-energy ball-milling (BM) of graphite [6, 7] or high-voltage electric discharge treatment of hydrocarbon precursors [8, 9]. There are a large number of methods for the synthesis of onion-like carbon materials. The heat treatment and electron beam irradiation of nano-diamonds are most extensively used [10, 11]. The first method consists of the formation of onions due to the heating of pre-obtained ultrafine diamonds. The formation of ions takes place by graphitization of the nano-diamond. This process begins on the surface and spreads to the center of the particle. As a result of heat treatment, the graphite layers are curved and closed, forming nested fullerene-like shells. Since nano-diamonds tend to form agglomerates, a joint shell for several ions can be formed at the junctions of particles as a result of the diffuse mobility of carbon atoms under the action of temperature. In our previous work, the onion-like structure was synthesis by high-frequency electric discharge treatment of propane-butane [12].

In this work, we investigate the formation of different carbons allotropic forms during ball mill treatment of crystalline graphite.

2. Materials and methods

Crystalline spectrally pure graphite powder (99.99 % C) was used as the starting material. Graphite samples were milled on the Fritsch Pulverisette P-6 laboratory planetary mill in argon gas atmosphere at room temperature for 0.5, 1, 2, 3.5, and 10 hours, respectively. The sample weight, the rotational speed of the vial (400 rpm), the amount of the steel balls (20 mm; 15), and the ball-to-powder ratio (30:1) were kept in all experiments. Every 5 min of milling was followed by the 5 min of standby. Then milling process was continued with the reverse vial rotation. All samples were handled and stored in the small containers in the glove box filled with purified argon (99.998%) to prevent the powders from oxidation.

X-Ray data were collected using a standard powder diffractometer with monochromatic $Mo-K_{\alpha}$ radiation (primer pirographite monochromator). The experimental structure factors and the radial distribution functions are calculated by the procedure described in [13, 14]. Electron microscopy investigations were

performed on the high-resolution microscope JEOL JEM-2100F and scanning electron microscope JEOL JSEM IT-500. Raman spectroscopy was performed on Horiba Jobin-Yvon T64000 spectrometer ($\lambda = 514$ nm) at room temperature.

3. Results and discussion

The XRD patterns of the graphite samples after ball milling for different times are shown in Figure 1. The intensive peak at 12.2° on the XRD pattern is a reflex from the (002) plane of the pristine graphite.

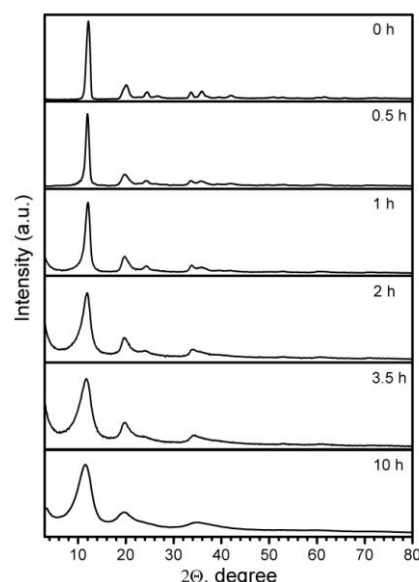


Fig. 1 The X-diffraction pattern of graphite before and after milling, $Mo K_{\alpha}$ radiation.

The decreases of intensity and broadening of the diffraction peaks with increasing milling time are observed. It can be due to gradual disorder of the graphite crystal structure and decrease of powders crystallite size. The increasing milling time to 3.5 hours leads to the appearance of a broad asymmetric halo of the (002) peak in the XRD pattern. It indicates the amorphous phase formed in the process of milling. After 10 hours of ball milling treatment, complete amorphization of graphite takes place. The amorphous carbon nanomaterials can be characterized by graphite- and diamond-like short-range order. However, the experimental XRD patterns do not reproduce complete data about the short-range type order that predominate in the structure of amorphous material. From XRD scattering intensities were calculated experimental total structure factors (SF) and radial distribution functions (RDF) (Fig 2).

The first intensive peak S_1 on SF corresponds to (002) interlayer graphite scattering. In the ball milling process of graphite, there is a shift relative to its position and broadening. For crystalline graphite, the first and second peaks in the RDF centers on 1.42 and 2.45 Å,

respectively, which is close to the literature value [14]. The increasing ball-milling time leads to a shift of the first and second peaks on the RDF in the direction of larger values. After 10 hours of milling, the positions of the first and second peaks on the RDF were 1.48 and 2.48 Å, respectively. This indicates a disorder of the crystal graphite structure with increasing grinding time and formation of amorphous carbon nanomaterial with the graphite-like type of the short-range order.

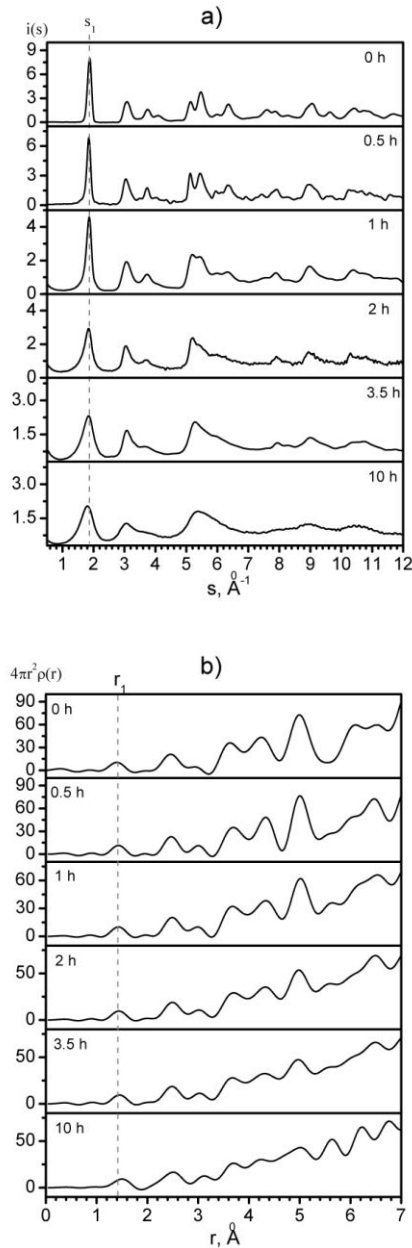


Fig. 2 Structure factor – (a) and radial distribution functions – (b) calculated from experimental XRD data for pristine and ball-milled graphite.

To clarify the structure of carbon materials individual particles produced by ball-milling of the graphite, high-resolution electron microscopy (HRTEM) was employed. Typical micrographs of carbon nano-materials obtained for 1 and 10 hours of milling are shown in Fig. 3. Carbon nanomaterials obtained after 1 hour of mechanical activation have a complex hierarchical texture and are characterized by an onion-like structure (Fig. 3, b): an individual particle consists of multilayer partially closed defective graphene shells of irregular shape. In the middle of the particle is a disordered nucleus. It is clearly seen that individual particles are collected in agglomerates (Fig. 3, a) and have a spheroidal shape with a size of ~10 nm. However, the graphite powder after 10 hours of MA is

described by the disordered crystal structure, specific for amorphous carbon (Fig. 3, c) in contrast to the samples milled during shorter times. There are diffuse rings visible only and no reflexes on the electronic diffraction pattern (Fig. 3, d). It confirms the amorphous structure was synthesized in the graphite powder after 10 hours of MA. The HRTEM results are in good agreement with the results of the method of radial distribution of atoms.

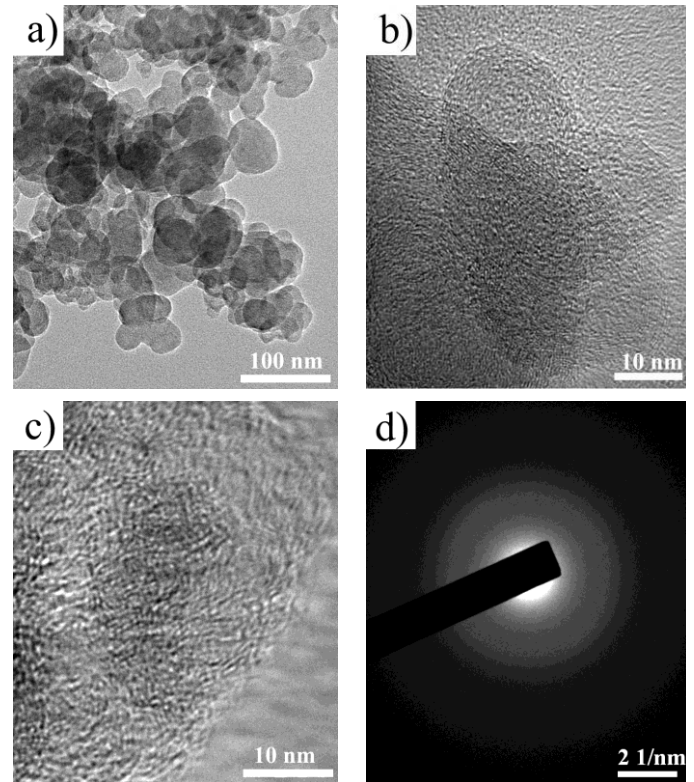


Fig. 3 Typical microphotographs of carbon nanomaterials obtained after ball mill treatment of graphite: a, b - 1 h, c - 10 h and d - electron microdiffraction for 10 h.

Raman spectroscopy has been applied to analyze carbon materials obtained for the different ball-milling times of crystalline graphite (fig. 4). Raman spectra are characterized by the presence of a G-band, which is shifted towards higher values in the wave vector relative to the tabular one (~1570 cm⁻¹) and corresponds to stretching vibrations of atoms with sp²-hybridized valence bonds, which are caused by antiphase vibrations of pairs of carbon atoms in various elements structures (rings, chains). Besides the G band, there is an equally intense D-band (the tabular value is ~1350 cm⁻¹) in the Raman spectrum. The origin of the D-band is caused by the selection rule due to small ordering regions, various types of defects, and structural disorder. The grinding time increase results in the redistribution in the D- and G- bands intensities. It indicates about the structural disorder in the milled powders. The (I_D/I_G)⁻¹ ratio becomes less due to the decrease in the size of the blocks in the graphene plane. After 1 hour of ball mill processing, the Raman spectrum takes the form typical for carbon nanomaterials. For a detailed analysis of the Raman spectra, the profile of the D and G bands was described by the Pseudo-Voigt function taking into account the background. It is clear the D- and G-bands have different half-widths FWHM (full width at half maximum). The longer the milling time, the more FWHM of the D- and G-bands. The FWHM half-widths of the D- and G-bands are shown in Table 1.

The sizes of the ordered domains L_a along the basal plane were calculated from the integrated intensities ratio of the I_D/I_G bands accordingly to the following equation.

$$L_{(HM)} = \frac{540}{E_1^4} \left(\frac{I_D}{I_G} \right)^{-1},$$

where E_1 is the laser radiation energy.

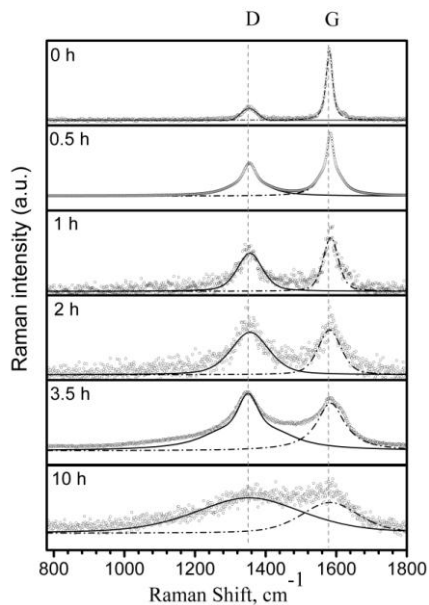


Fig. 4 The Raman spectra for pristine and ball-milled graphite.

Since a laser with a wavelength of $\lambda = 514$ nm was used as an excitation source, the energy of laser radiation E_1 in formula (1) is 2.41 eV. The size of the ordered domain decreases for the longer grinding time (see Table 1). So, the studies carried out using Raman spectroscopy showed that the synthesis products are typical amorphous materials, which confirms the results of X-ray structural analysis.

Table 1: Value of L_a ordering regions in the structure of ball-milled graphite.

№	G - band			D - band			$\left(\frac{I_D}{I_G}\right)^{-1}$	L_a , nm
	Centre, cm ⁻¹	FWHM, cm ⁻¹	I_G	Centre, cm ⁻¹	FWHM, cm ⁻¹	I_D		
0h	1580	11	8.42	1353	27	2.13	4	64
0.5h	1583	16	5.42	1354	29	5.05	1.07	17.1
1h	1584	25	8.68	1355	42	1.01	0.86	13.7
2h	1581	38	8.31	1355	63	1.29	0.64	10.2
3.5h	1584	48	5.11	1350	52	8.43	0.6	9.6
10h	1582	96	2.22	1353	180	4.79	0.46	7.4

4. Conclusion

It was shown, graphite crystal structure transforms into an amorphous state during the high-energy ball milling. The carbon powder synthesized by BM has a graphite-like type of the atomic short-range order. As it follows from the HRTEM results, carbon nanomaterials after 1 h of graphite ball-milling of powder has onion-like structure. Carbon powder obtained after 10 hours of BM is characterized by the globular morphology of individual particles with a structure typical to amorphous carbon.

5. Acknowledgement

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Martensitic transformation and magnetic ordering in as-cast Fe-Mn-Si-Ge and Fe-Mn-Si-Sn alloys

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Abstract: Crystal structure, morphology, peculiarities of martensitic transformation and shape memory effect were investigated in Fe-Mn-(Si,Ge) and Fe-Mn-(Si,Sn) as-cast alloys. It was found that regularly substitution of atoms Si with the Ge or Sn in Fe-Mn-Si alloys dramatically change the martensitic transformation behavior that displayed in calorimetry, resistometry and dilatometry curves during the cooling and heating the alloys. Crystal structure changed as well. As a result of alloying by Ge and Sn the substructure of samples became more inhomogeneous, well developed dendritic structure appeared, finally $(\text{Mn}_{0.5}\text{Fe}_{0.5})_3\text{Sn}_2$ phase and hexagonal phase with the structure $P6_3/mmc$ have precipitated in Fe-Mn-(Si,Sn) and Fe-Mn-(Si,Ge) respectively. The effect of alloying with Si or Ge on $\gamma \rightarrow \varepsilon$ temperatures of martensitic transformation, volume effect of transformation, Neel point caused by the influences of alloying components as well as the ferromagnetic phases appearing during as-cast process.

KEYWORDS: MARTENSITIC TRANSFORMATION, SHAPE MEMORY EFFECT, AS-CAST ALLOYS, CRYSTAL STRUCTURE, VOLUME EFFECT, NEEL POINT, CALORIMETRY, RESISTOMETRY, DILATOMETRY

1. Introduction

Despite the perfect shape memory effect (SME) in Fe-Mn-Si-based alloys [1, 2, 3, 4], the effect of the magnetic ordering on the SME, as well as on the $\gamma \rightarrow \varepsilon$ martensitic transformation (MT) remains a debatable issue [3, 5, 6, 4, 7]. Alloying Fe-Mn with Si enhances the localization of magnetic moments on Fe atoms [8] and increases the driving force $\gamma \rightarrow \varepsilon$ transformation, because reduces the Neel temperature T_N [9, 10, 8]. We assumed that Ge and Sn are elements that can affect the localization of magnetic moments like Si. These elements have similar chemical and physical properties (Table 1). The electronic configuration of the outer electronic shell of the elements atoms is the same – s^2p^2 , so alloying in the sequence Si $\rightarrow$ Ge $\rightarrow$ Sn should not significantly affect the position of T_N , but enhances the "metallization" of properties, which can increase the degree of occupancy of the d -band of Fe-Mn. Increasing the radius of the atom in this sequence can affect the position of the martensitic start point M_s as well as solubility of these elements in Fe-Mn. The goal of current study was to investigate the effect of the replacement Si in alloy with the Ge or Sn on MT, SME and magnetic ordering.

Table 1 Some properties of alloying elements of Fe-Mn alloys

	Si	Ge	Sn	Fe	Mn
Atomic radius, Å	1.46	1.52	1.72	1.72	1.79
Ionic radius (4^+), Å	0.42	0.53	0.71		
Electronegativity, eV	1.90	2.01	1.96	1.83	1.85
Crystal structure and electrical conductivity	diam(s/c)	diam(s/c)	β -Sn(s/c)		
(m – metallic, s/c – semiconductor)	$\downarrow 120\text{kBar}$	$\downarrow 90\text{kBar}$	$\downarrow -14^\circ\text{C}$		
	β -Sn(m)	β -Sn(m)	β -Sn(m)		
	$\downarrow 160\text{kBar}$	$\downarrow 130\text{kBar}$	$\downarrow 90\text{kBar}$		
	BCC(m)	BCC(m)	BCT(m)		

2. Experimental

The nominal composition of the studied alloys can be represented by the formulas $\text{Fe-22Mn-6}(\text{Si}_{1-x}\text{Ge}_x)$ at.% and $\text{Fe-22Mn-6}(\text{Si}_{1-x}\text{Sn}_x)$ at.% ($x = 0, 1.5, 3.0, 4.5, 6.0$). The composition and their label are shown in Table 2. The alloys were melted in an arc furnace in an argon gas atmosphere. As-cast samples cut, quenched into water from 950°C and investigated.

Crystal structure was investigated at room temperature using the X-ray Debye-Scherrer method on diffractometer Rigaku Ultima IV with $\text{Cu K}\alpha_{1,2}$ radiation. The temperature dependence of electrical resistance was measured by four-point method in a temperature interval between -196°C and 350°C . SME measurements were made by bending test using three-points bending described in details elsewhere [11].

Dilatometry measurements were made by Du Point TMA 934 dilatometer using liquid nitrogen to achieve temperatures below RT. Calorimetric measurements were made using modulated differential scanning calorimeter of TA instruments. Martensite morphology

and microstructure was investigated by optical microscopy (OM) and scanning microscopy (SEM) with PSEM501 instrument equipped by Link System analyzer to determine the local chemical composition.

Table 2 The composition of Fe-Mn-Si-Ge and Fe-Mn-Si-Sn alloys

Alloys	Fe at. %	Mn at. %	Si at. %	Ge at. %	Sn at. %
R	71.31	22.36	6.33		
GDr	71.21	22.47	4.67	1.66	
GDK	71.05	22.36	3.15	3.43	
GL	71.13	22.61	1.63	4.63	
GP	70.61	22.61	0.14	6.64	
BDr	71.39	22.24	4.55		1.82
BDK	72.57	20.78	3.05		3.61
BL	72.77	20.29	1.50		5.44
BP	73.70	19.57	0.19		6.54

3. Results and discussion

3.1. Microstructure of Fe-Mn-Si-Ge and Fe-Mn-Si-Sn alloys

The reference alloy R had a well-developed dendritic structure (Fig. 1a). Weak chemical inhomogeneities (~ 1 at.% Si) in dendritic branches are sized $\sim 50 \mu\text{m}$. Martensite crystals in the form of flat plates, which formed a self-accommodating triangular structure of ε -martensite, cross the dendritic branches maintaining their orientation (Fig. 1b).

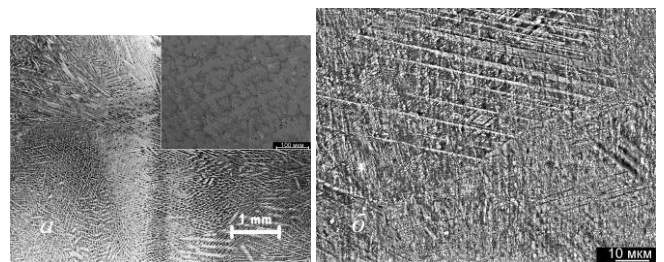


Fig. 1 Microstructure of alloy R: a) - dendrites (OM); composition stratification in dendrites (SEM) on insert; b) - plates of ε -martensite.

Replacement of Si with Ge caused stratification of alloys in composition, which increased with increasing Ge content (Table 3). The content of Ge + Si in the matrix was slightly $< 5\text{at.}\%$, in the inclusions increased up to $\sim 11\text{at.}\%$ with increasing content of Ge in the alloys.

Within one grain, one to three orientations of martensite crystals were observed. For all Fe-Mn-Si-Ge samples with a dendritic structure, the images of martensite crystals were not interrupted by dendrites or etching defects, but continued from one edge of the grain to another, as if the latter were "transparent" for martensite plates (Fig. 2). In most cases, the plates did not pass through the inclusions, but only wedged into them. A similar pattern of filling

the whole grain with the martensitic phase and the cross section of dendrites was observed in Fe-Mn-Si alloys [12]. Such interaction of martensitic crystals with these inhomogenities implies at least exact orientation relationship between the matrix and inclusions.

"The collision" of the plates of ε -martensite in some inclusions caused a weak striped contrast, while the direction of strips was $6\div8^\circ$ with the direction of ε -martensite plates (Fig. 2). According to XRD data strips in the inclusion could be crystals α -martensite. Because the plane of martensite crystals form self-assembling schemes with angles with each other close to 60° (Fig. 2a) the plane of the sample in Fig. 2a is close to $\{111\}_\gamma$. Because in most Fe-based alloys the gabitus plane of crystals α -martensite is $\{3,10,15\}_\gamma$ one can calculate the angles between the traces of ε - and α -martensite. Thus, a calculated angle between the traces of the plane $(\bar{1}11)_\gamma$ and $(3,10,15)_\gamma$, formed on the sample surface with normal $(111)_\gamma$ is 6.6° , confirming the hypothesis of the presence of crystals α -martensite in some inclusions.

Table 3 Chemical compositions of matrix and inclusions in Fe-Mn-Si-Ge and Fe-Mn-Si-Sn as-cast alloys

Alloy	Phase	Fe	Mn	Si	Ge	Sn
GL	Matrix	72.2 $\pm$ 1.4	23.1 $\pm$ 1.1	1.4 $\pm$ 0.1	3.4 $\pm$ 0.3	
	Inclusion	59.7 $\pm$ 1.7	30.7 $\pm$ 0.9	2.2 $\pm$ 0.1	7.4 $\pm$ 0.8	
GP	Matrix	73.5 $\pm$ 1.2	21.8 $\pm$ 0.9		4.7 $\pm$ 0.3	
	Inclusion	57.6 $\pm$ 1.6	31.4 $\pm$ 1.0		11.0 $\pm$ 0.7	
BDk	Matrix	75.3 $\pm$ 0.7	20.7 $\pm$ 0.5	3.0 $\pm$ 0.2		1.0 $\pm$ 0.2
	Inclusion	35.3 $\pm$ 2.7	34.9 $\pm$ 1.0			29.8 $\pm$ 1.7
BL	Matrix	74.1 $\pm$ 2.6	22.0 $\pm$ 1.2	1.9 $\pm$ 0.2		2.0 $\pm$ 1.4
	Inclusion	34.6 $\pm$ 1.0	34.5 $\pm$ 0.2			30.9 $\pm$ 0.8

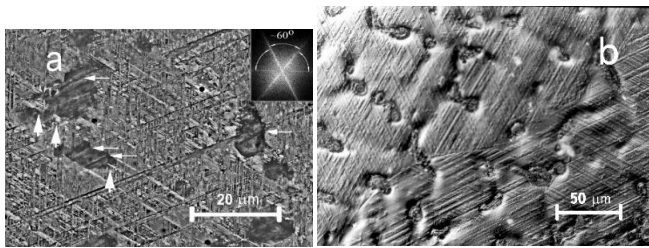


Fig. 2 As cast Fe-Mn-Si-Ge alloys: a) - SEM image of ε -martensite and inclusions in the GL alloy; vertical arrows indicate the plates of ε -martensite, which is wedged in the inclusion, horizontal - the plates of the α -phase inside them; Fourier image on the insert; b) - OM images of relief ε -phases that intersect the inclusion in the GDK alloy; deep grooves - etched dendrite structure formed by inclusions.

The replacement of Si with Sn caused the appearance of inclusions, recorded as deep etching on OM images in the BDr alloy (Fig. 3a) and irregular phases in BDk, BL, BP alloys (Fig. 3b,c,d). These inclusions formed a dendrite structure that became clearer with an increase Sn content. It was found that the inclusion in alloys is a ternary phase with a chemical composition close to $\text{Fe}_{0.35}\text{Mn}_{0.35}\text{Sn}_{0.3}$, which can be interpreted as $\text{Fe}_{0.33}\text{Mn}_{0.33}\text{Sn}_{0.33}$ as well as $(\text{Mn}_{0.5}\text{Fe}_{0.5})_3\text{Sn}_2$ (Table 3). Consequently, the stimulus to the concentration stratification in as-cast alloys increases in the Si $\rightarrow$ Ge $\rightarrow$ Sn sequence.

Only in BDr and BDk alloys plates of ε -martensite "flowed around" the inclusions (Fig. 3a,c). Penetration in the inclusions is not observed. Instead, martensite crystals as if "stopped" nearby it, and "continued its movement" after obstacle at a certain distance (Fig. 3c). With an increase Sn content part of areas free from martensite became more (Fig. 3c,d). Certain areas in the alloy BL can be interpreted as free from martensite, in which wide plates of ε -martensite (marked with oblique arrow in Fig. 3d) penetrate. Morphology of martensite plates in alloys with high content of Sn is characterized by the presence of narrow and short plates, sometimes zigzag form (Fig. 3d). In the contact area with martensite plates, there was observed occasional fine plates. Their orientation was the

same as in ε -martensite. These formations are not α -phase; twin plates or shear bands are not excluded.

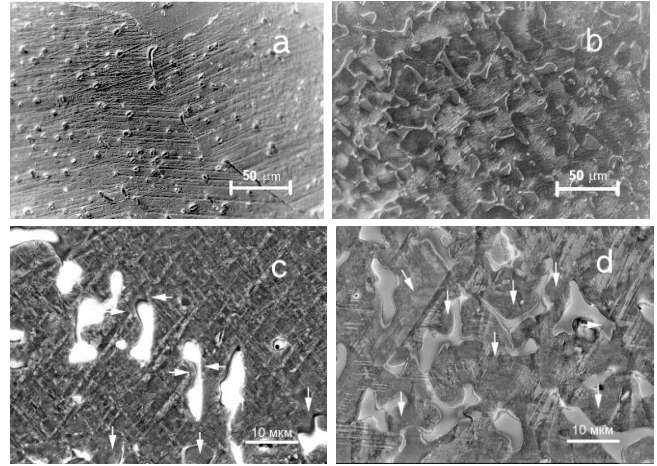


Fig. 3 a) - the relief on BDr alloy surface; b) - OM of BL alloy; c) - SEM of BDk alloy; d) - SEM of BL alloy; vertical arrows indicate areas free of crystals of martensite, horizontal - the places of "collisions" of ε -martensite with inclusions.

3.2. Crystal structure and phase composition

XRD studies have shown that the reference alloy R contained mainly ε and α phases with a small amount of residual γ phase (Fig. 4), which is a typical structure of martensite for thermally activated $\gamma\rightarrow\varepsilon$ MT in Fe-Mn alloys, where the α -phase is formed in the intersection of the plates of the ε -phase [13].

Replacement of Si with Sn causes a decrease in the intensity of reflexes from the ε -phase, the appearance and subsequent intensification of reflexes from the orthorhombic phase with the space group Pnma (Fig. 4, alloys BDr, BDk, BL). Most reflexes from the orthorhombic phase overlap with reflexes from the hexagonal phase with the space group $P6_3/mmc$. The presence of a hexagonal phase with the structure $P6_3/mmc$ isostructural either to $(\text{Mn}, \text{Fe})_{2-x}\text{Sn}$ ($x = 0\div0.35$) with $c/a > 1$ or to $(\text{Mn}_{1-x}\text{Fe}_x)_3\text{Sn}_{1-\delta}$ ($x \leq 0.5$, $\delta = 0\div0.35$) with $c/a < 1$ cannot be excluded (Fig. 4, BL alloy). Depending on the annealing temperatures and composition, both the hexagonal phase with the composition Mn_{2-x}Sn and the stoichiometric orthorhombic phase Mn_3Sn_2 can coexist in Mn-Sn alloys [14]. In addition, there are several orthorhombic phases in the vicinity of the Mn_{2-x}Sn composition [15]. All of them, including the hexagonal one, can be considered as intermediates between hexagonal structures of the NiAs and Ni_2In type. Therefore, some of the reflexes are well interpreted as belonging to both types of structures. Part of the reflexes can be interpreted as belonging to the hexagonal phase with $c/a < 1$ and lattice parameters close to that in phase $(\text{Mn}_{1-x}\text{Fe}_x)_3\text{Sn}_{1-\delta}$ [16] and Sn content 25 $\div$ 28at.%. Taking into account the composition of inclusion they are rather isostructural Mn_3Sn_2 with Pnma spatial group. The lattice parameters of the orthogonal phase are close to those found in [17, 15] in magnetocaloric alloys $\text{Mn}_{3-x}\text{Fe}_x\text{Sn}_2$.

Reflexes from ε , α , and γ phases were observed in the spectra of Ge doped alloys with exception of GL and GP alloys (Fig. 4). After immersion sample in liquid nitrogen, ε phase lines appeared in the GL alloy. The lines of both ε and γ phases in the GL alloy were widened, while in the GP alloy the peaks are narrow and clearly separated. In alloys with a lower Ge content, the volume of the unit cell of the ε phase is smaller than in the γ phase, while in the alloy GP the volume of the unit cell of a hexagonal phase is $\sim 4\%$ larger than in the γ phase. The lattice parameters of this phase are close to those in alloys $(\text{Mn}_{1-x}\text{Fe}_x)_3\text{Ge}_{1+\delta}$ ($0 < x < 0.34$, $-0.2 < \delta < 0.25$) [18]. It is natural to assume that the phase is enriched in Mn and Ge (Si) and is the one that has a $P6_3/mmc$ structure. The inclusions are isostructural to $(\text{Mn}_{1-x}\text{Fe}_x)_3\text{Ge}$ and have lattice parameters close to the ε -phase parameters ($a \approx 2 \cdot a_\varepsilon$, $c \approx c_\varepsilon$). This makes it "transparent" to martensite plates, in the sense that the stresses caused by the

collision of the plates on one side of the inclusion are transmitted through them to the other side. The matrix phase, on the other hand, undergoes a $\gamma \rightarrow \varepsilon$ transformation, and the α -phase can be formed at the intersections of the ε -phase plates [13] and at some points of collision of the ε -phase plates with inclusions (Fig. 3). It also contributes to the "transparency" of inclusions for martensite, and the role of the stress transducer is played by α -phase plates.

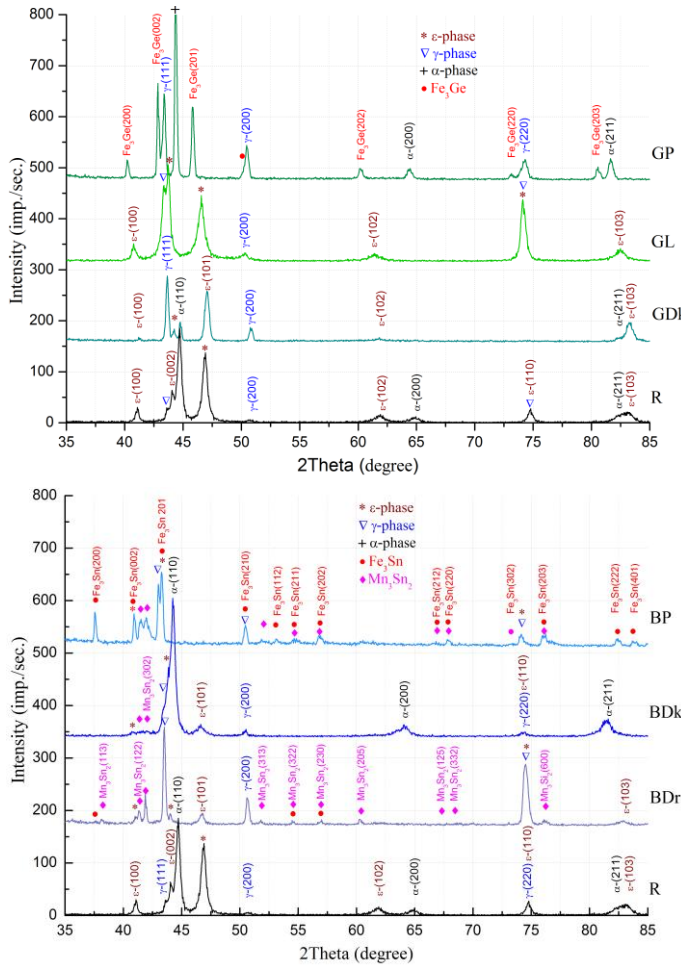


Fig. 4 XRD spectra of alloys Fe-22Mn-6(Si_{1-x}Ge_x) (top) and Fe-22Mn-6(Si_{1-x}Sn_x) (bottom)

3.3. Some physical properties and characteristic points of $\gamma \rightarrow \varepsilon$ martensitic transformation and magnetic transformation

A comparative analysis of the temperature dependences of electrical resistance and sample elongation (dilatometry) (Fig. 5), the sample bending by four-point scheme (SME) and calorimetry (DSC) (Fig. 6) showed that there are two types of transformations in Fe-Mn-(Si, Ge, Sn) alloys. One of them is $\gamma \rightarrow \varepsilon$ martensitic transformation with a temperature hysteresis of 130-170 K, a significant heat effect, a negative volume effect, and which is responsible for the SME. The second transformation is revealed in alloys with a predominant content of Ge or Sn, characterized by a narrow hysteresis, negligibly small thermal effect and small positive volume effect. MDSC studies of the temperature dependence of heat capacity C_p clearly revealed another transformation localized in the range from 30 to 60°C (Fig. 7). The peculiarities of the temperature dependence of the BP alloy, where the $\gamma \rightarrow \varepsilon$ transformation was suppressed (step, hysteresis is negligibly small), correspond rather to second order phase transition. At the same time, for alloy R and alloys with lower content of Si (BDk) and especially Ge (GP, GDk) the temperature dependence of heat capacity corresponds to the first order phase transition (peak heat flux, available hysteresis). Thus, the heat capacity jump is associated with the Neele temperature,

which in alloys with a significant content of Ge and especially Sn is within the interval of direct $\gamma \rightarrow \varepsilon$ MT. By the nature of the temperature dependence of C_p , the features on the resistometric, calorimetric and dilatometric curves, it rather corresponds to the transformation of paramagnetic (PM) $\rightarrow$ antiferromagnetic (AFM) in the γ phase.

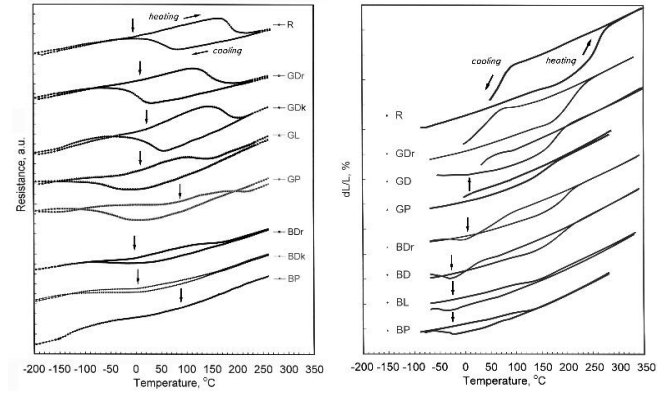


Fig. 5 Temperature dependence of electrical resistance (on a left); elongation of the sample (on a right). Arrows indicate non martensitic transformation.

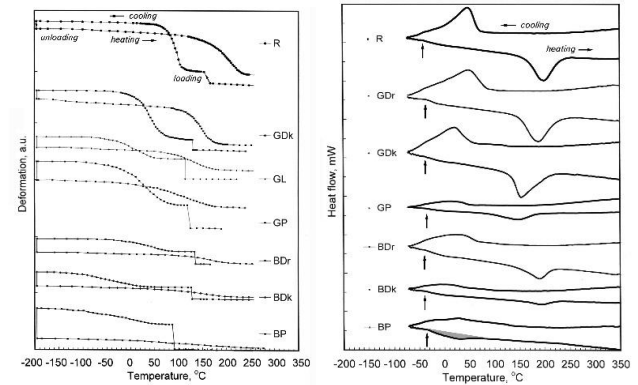


Fig. 6 Temperature dependence of the sample bending by four-point scheme (SME) (on a left); DSC analysis (on a right). Arrows indicate start of reverse martensitic transformation.

Another feature on the temperature curves was observed between -50 and -100°C. It can be associated with a paramagnetic $\rightarrow$ ferromagnetic (FM) transformation in the phase (Mn,Fe)₃+_γSn₂-_γ in alloys Fe-22Mn-6(Si_{1-x}Sn_x) (or in the phase enriched in germanium in alloys Fe-22Mn-6 (Si_{1-x}Ge_x)), so with the magnetic transition from the antiferromagnetic to the paramagnetic state of the ε -phase. The nature of the change of volume effect sign is different in alloys with Ge and Sn. It is due to the formation of the α -phase and with competing contributions to the dilatation effect of $\gamma \rightarrow \varepsilon$ and $\gamma \rightarrow \alpha$ transformation in the former. In the latter it is suddenly appears due to the deformation of the sample by the martensitic mechanism, stimulated by magnetostriction due to PM $\rightarrow$ FM transition [17] in Mn_{3-x}Fe_xSn₂.

The start temperatures of direct MT (M_s) and the finish of the inverse MT (A_f) decrease monotonically with increasing Ge and Sn until their values became equal to the Neele point T_N , determined from the resistance curves (R) and dilatometric curves (TMA), and then practically do not change (Fig. 8). This is due to the formation of (Mn_{0.5}Fe_{0.5})₃Sn₂ or inclusions with high content of Mn and Ge. The result is a stable matrix composition in alloys with a high content of Ge and Sn and at the same time a decrease in the volume available for the development of MT. Taking into account the composition of the matrix (Table 3) and comparing the predicted values of martensitic points with those in homogenized alloys with the same content of Mn and Si [19], we find that Ge and Sn reduce M_s on ~26 and 51°C/at.%, respectively. First is close to the value of 21°C/at.% in a homogenized alloy of Fe-24Mn-6Ge [20, 21, 22]. There was also found complete suppression of MT, because the

temperature $\gamma \rightarrow \varepsilon$ MT was significantly lower than T_N . Therefore, antiferromagnetic ordering suppresses $\gamma \rightarrow \varepsilon$ MT.

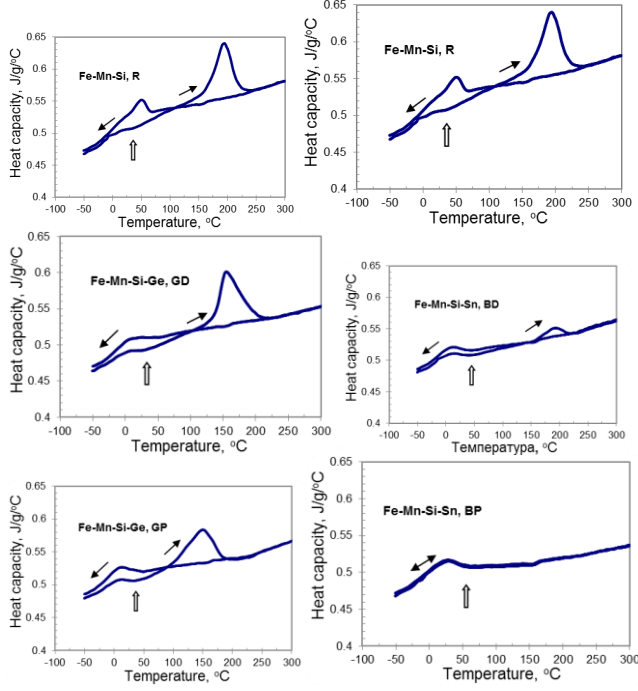


Fig. 7 Temperature dependences of C_p for Fe-Mn-Si-Ge and Fe-Mn-Si-Sn alloys. Contour arrows indicate the AFM ordering

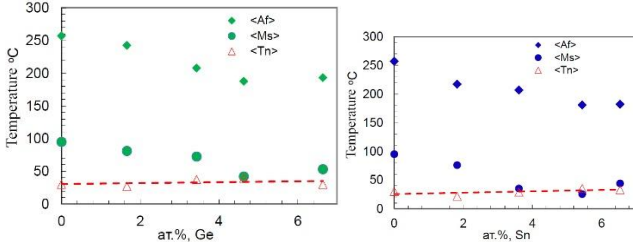


Fig. 8 Dependence of MT points and Neele point on Ge content in Fe-Mn-Si-Ge alloys (on a left) and Sn in Fe-Mn-Si-Sn alloys (on a right)

The decrease in MT temperatures is due to the increase in the atoms size of the alloying components in the Si $\rightarrow$ Ge $\rightarrow$ Sn sequence. For Fe-24Mn-(2 $\div$ 4)Geat.% alloys [21] the lattice parameter of the γ -phase increases with increasing Ge content. This is equivalent to anisotropic stretching of the lattice. Since during $\gamma \rightarrow \varepsilon$ MT specific volume decreases, the replacement of Si atoms by Ge and Sn atoms causes a decrease in M_s .

3.4. Effect of magnetic ordering and magnetic inclusions in Fe-Mn-Si-Ge and Fe-Mn-Si-Sn alloys on MT

Addition Ge to Fe-30Mn alloys reduces T_N on $\sim 15^\circ\text{C/at.\%}$ [23], while addition Si reduces T_N on $\sim 15^\circ\text{C/at.\%}$ for alloys with a Mn content of 28–32 at.% and up to $27^\circ\text{C/at.\%}$ for alloys with 22–25 at.% Mn [24]. Comparison of the values of T_N in the matrix, calculated by the empirical formula in [25], with the experimentally found ones confirms the assumption of a weak effect on T_N when replacing Si with Ge.

The depressing $\gamma \rightarrow \varepsilon$ MT due to the AFM ordering can be explained from the considerations illustrated in Fig. 9. Consider the orientation of the spins of 12 atoms from the vicinity of atom 4 in the FCC structure (Fig. 9b). The spin of each of those atoms $\vec{S}_i$ interacts with 12 others (four triplets), each of which has different direction: in the basal plane two triplets (in the corners of two triangles) and one triple in the upper and lower basal planes. The components of the spins of each of the triplets lying in the basal planes mutually compensate each other, and the sum of the components perpendicular to the basal planes is equal to $-\vec{S}_i$. Thus,

the magnetic interaction of the spin of each atom with the spins of the 12 nearest neighbors in the FCC lattice is:

$$(1) \quad E_{antiferr}^{FCC} = -4J\vec{S}_i\vec{S}_i = -4JS^2$$

The orientation of the spins in the HCP structure, which is formed due to the shift of every second basal plane in one of the directions $\langle 112 \rangle$ (Fig. 2c), differs in that in one of the basal planes the sum of spins is equal to $-\vec{S}_j \neq \vec{S}_i$. That is, the magnetic interaction is:

$$(2) \quad E_{antiferr}^{HCP} = -3J\vec{S}_i\vec{S}_i - J\vec{S}_i\vec{S}_j$$

The difference between the energies of the magnetic interaction of the HCP and FCC structures

$$(3) \quad \Delta E = J\vec{S}_i\vec{S}_i - J\vec{S}_i\vec{S}_j = JS^2(1 - \cos \widehat{\vec{S}_i\vec{S}_j}) = JS^2(1 - \cos 109.47^\circ) = \frac{4}{3} \cdot JS^2$$

always greater than zero. Here, as in (1) and (2), J is the exchange integral, the value of which is positive for AFM interaction.

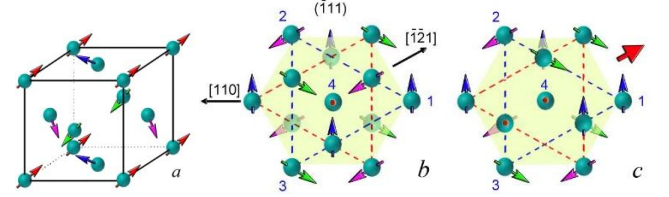


Fig. 9 a) AFM ordering of spins Fe-Mn alloys (anticollinear structure, 3Q state) in the FCC lattice [26, 27]; b) the orientation of the spins of the 12 nearest neighbors of the central atom in three consecutive basal planes $\{111\}_\gamma$ (the middle plane is highlighted in color); c) orientation of the spins after the shift in the direction $[1\bar{1}2]$ of the upper plane with the formation of packing ABAB... (HCP lattice). Spins 1, 2, 3, the projections of which on the basal plane mutually compensate each other, have the sum of normal projections equal in modulus and opposite in sign to spin 4 (directed perpendicular to the plane $(\bar{1}11)$).

This is equivalent to an increase in the stacking fault energy, and hence a decrease in the driving force $\Delta G_{\gamma \rightarrow \varepsilon}$ $\gamma \rightarrow \varepsilon$ transformation. If the M_s is slightly above the T_N , the MT is further suppressed by AFM ordering in the residues of the γ -phase [5]. The decrease in $\Delta G_{\gamma \rightarrow \varepsilon}$ is not very sharp, because AFM ordering is a second order transition. The different path of the heating and cooling curves for alloys with a high content of Ge and Si also indicates $\gamma \rightarrow \varepsilon$ transformation at temperatures below T_N . Indeed, in [19] it was shown that martensite can be formed even after the γ -phase has undergone AFM ordering, i.e. in the case of $T_N > M_s$.

4. Conclusion

In Fe-20 $\div$ 22Mn-(Si, Ge, Sn) alloys with a content of Si+Ge and Si+Sn ~ 6 at.% $\gamma \rightarrow \varepsilon$ transformation with a temperature hysteresis of 130 $\div$ 170K, a significant heat and negative volume effects is responsible for SME. Increasing the Ge or Sn content also manifests the PM $\rightarrow$ AFM transformation in the γ phase with a narrow hysteresis, negligibly small heat and positive volume effects. Increasing the Ge or Sn content reduces M_s to T_N on ~ 26 and $51^\circ\text{C/at.\%}$ respectively, due to increasing the size of the atoms in the Si $\rightarrow$ Ge $\rightarrow$ Sn sequence, which is equivalent to the negative hydrostatic pressure experienced by the alloy.

When Si is replaced by Sn, the phase $(\text{Mn}_{0.5}\text{Fe}_{0.5})_3\text{Sn}_2$ (Pnma) and the hexagonal phase isostructural to $(\text{Mn},\text{Fe})_{2-x}\text{Sn}$ are formed. When Si is replaced by Ge, the alloy stratifies into regions depleted with Si, Ge and with Mn content close to nominal and regions enriched in Mn and Ge (Si) isostructural to $(\text{Mn}_{1-x}\text{Fe}_x)_3\text{Ge}$ with lattice parameter values commensurate with such in ε -phases $a \approx 2 \cdot a_\varepsilon$, $c \approx c_\varepsilon$.

Due to the invariance of the Fe and Mn content in the matrix, the Neele point changes weakly, and the magnetic ordering in the γ -phase stabilizes $\gamma \rightarrow \varepsilon$ MT, because the magnetic interaction energy in HCP is higher than in FCC structure. In Fe-Mn-Si-Ge, the contributions to the dilatation effect of $\gamma \rightarrow \varepsilon$ MT in the matrix and $\gamma \rightarrow \alpha$ MT in inclusions enriched with Mn and Ge (Si) determine the

course of dilatation and SME curves. In Fe-Mn-Si-Sn, as the Sn content increases, the deformation of the sample by the martensitic mechanism stimulated by the magnetostrictive effect of the magnetic transformation into $\text{Mn}_{3-x}\text{Fe}_x\text{Sn}_2$ changes the sign of the volume effect.

In Fe-Mn-(Si,Sn) alloys ϵ -martensite plates do not stop with inclusions with a thickness of less than $1\div 2\mu\text{m}$, sometime shear bands are formed in places of "collision" in the inclusions. In Fe-Mn-(Si,Ge) the α -phase is formed at the points of collision of the ϵ -phase plates with inclusions. Areas comparable in the thickness with martensite crystals enriched in Mn and Ge(Si) are "transparent" for martensite due to either elastic stress transfer or stress transfer by α -phase plates.

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Features of electromechanical properties of carbon nanostructures

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Abstract: *Non-standart properties of carbon nanomaterials and nanostructures open wide possibilities of their application. The electrical resistance of bulk arrays of carbon nanotubes in cyclic loading-unloading processes was studied. It is shown that when the volume of the powder sample decreases, the resistance first decreases sharply, and at a certain degree of compression the process of its change begins to occur more smoothly, which is associated with increased contacts between neighboring nanostructures and van der Waals bond between them.*

KEY WORDS: CARBON NANOTUBES, NANOMATERIALS, ELECROMECHANICAL PROPERTIES, RESISTANCE

Introduction

The study of carbon nanotubes properties is due to their unusual properties: they combine high strength and elasticity, thermal and electrical conductivity. Mechanical deformation and defects affect the electronic structure, concentration of charge carriers, electrical, emission and other properties. Defects occur both in the process of synthesis (growth and gas impurities) of CNTs, and under external influences, especially during radiation exposure.

The geometry of CNTs changes under the action of elastic deformation, which can significantly deform the profile of the entire nanotube, or locally at the intersection of contact nanotubes, which affects the electronic structure at the point of deformation, which controls the electrical properties of not only one nanotube but the entire CNT array. The electrophysical properties of isolated CNTs are being studied in many laboratories around the world for their use in nanoelectronics. The properties of an individual nanotube are to some extent known – along the axis it is a good conductor of current and heat, but in the radial direction the movement of charge carriers and phonons is limited by the outer cylindrical carbon layer. To expand the scope of CNT, it is necessary to increase the flow of heat and current, for which it is necessary to investigate their properties in bulk or consolidated state. In bulk CNTs usually do not conduct electricity, but with little compression the situation changes.

In this work is shown that the restrictions for current carriers are removed during the deformation of the CNT array by compression, as a result of which such an array passes into an electrically conductive state. It should be noted that multilayer CNTs have a very low concentration of charge carriers, which limits the scope of their possible application, but the mobility of charge carriers is three orders of magnitude higher than in copper. Therefore, it is important to find ways to increase the concentration of charge carriers and electrical conductivity in the CNT array and increase the flow of heat and current. The influence of CNT orientation, degree of packing (ordering) of CNTs in the array, number of contacts, their total area, nature of connection between CNTs, type and number of defects in CNTs on electrical and thermoelectric properties was also investigated. In this regard, the CNT array can have a wide range of properties, which opens up perspectives for further research and expansion of applications.

Experiment

The electrical resistance of the CNT array was measured on a fairly accurate installation, which allowed to record voltage up to 10^{-5} mV [1]. Resistance was measured using a dielectric cylinder, the bottom and piston of which served as electrodes. The density of the material was changed by means of a movable piston. After reaching the maximum compression, the piston was gradually lifted and at the same time the electrical conductivity of the elastically relaxing material was measured. Due to the elastic relaxation, the electrical contact of the test material with the electrodes was maintained, which allowed to measure the electrical conductivity during unloading. The cessation of the relaxation expansion of the material led to the breaking of the electric circuit and a sharp

increase in the electrical resistance between the electrodes (relaxation transition).

Thus, the inverse measurement is that when reaching the maximum density during the direct measurement, the material elastically relaxed and, starting from this value, went in the opposite direction of decreasing density, i.e. gradually raised the micrometer rod, as long as the test material retained electrical contact with electrodes.

Results

The electronic properties of carbon nanotubes are determined by their unique anisotropic structure and high electronic conductivity. A distinction should be made between the electrical resistivity of individual nanotubes (single-layer and multilayer) and the resistivity of a material or composite consisting of such tubes. The resistivity values of individual nanotubes, which are measured by different groups, can differ from each other within several orders of magnitude. This is due to differences in the structures of nanotubes, chirality, the presence of defects in the hexagonal layer, attached radicals (-OH, -CO, etc.), which change the position of the valence band and the conduction band.

Multiwall carbon nanotubes (MCNTs) differ from single-layer ones by a wider variety of shapes and configurations. Most often, these are coaxially nested single-layer nanotubes. The situation for an array of individual nanotubes or a material consisting of them may be different due to the presence of contacts between adjacent nanotubes, electrodes, contact pressure and other factors. When the volume in which the array of electrically conductive CNTs is placed at a certain critical value, the nanotubes can be closed with the manifestation of characteristic signs of percolation transition. The latter is known to be a geometric analogue of the metal-insulator transition [2].

The electrical conductivity of a material consisting of nanotubes largely depends on the degree of contact between adjacent nanotubes, as well as on the presence and composition of impurities. Due to its physicochemical properties and significant potential for applied use, CNTs are the subject of research in many laboratories around the world.

The electrical characteristics of the CNT bulk array obtained by the gas phase deposition method on catalysts Al_2O_3 - Fe_2O_3 - MoO_3 were studied. TEM- image is presented in fig. 1. In accordance with the basic assumption of transmission microscopy that the intensity of the image contrast directly depends on the amount of scattered matter, it follows that the darker areas in the positive images correspond to denser areas of the sample or heavier atoms present in the sample, narrow dark bands that observed, attributed to the walls of nanotubes. This indicates an extremely high elasticity of the array of undirected CNTs.

The statistical distribution of nanotubes by outer diameter showed that the diameter of nanotubes is in the range of 10-20 nm. When the volume in which the interacting nanotubes are placed decreases, the electrical circuit closes and the system (nanotube-air) goes into a conductive state. (fig. 2)

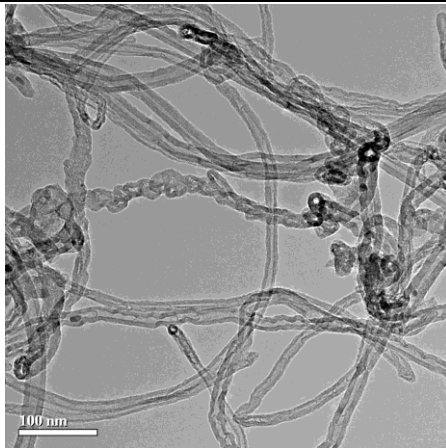


Fig. 1. TEM-image of CNT on the catalyst $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-MoO}_3$

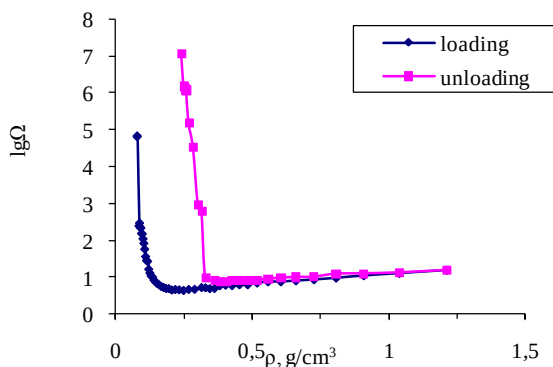


Fig. 2. Dependence of the logarithm of the electrical resistivity Ω of an array of multilayer carbon nanotubes on the change in its density ρ during compression and subsequent unloading

When compressed under the piston, the resistivity drops abruptly by 4 orders of magnitude, reaches a minimum value of 4,37 (Ohmcm), at a density of 0,25 g/cm³. Subsequent compression to a density of 1,2 g/cm³ leads to a slight increase in resistivity to 15 (Ohmcm). Deformation leads to the appearance of mechanical stresses, which contribute to the emergence of additional potentials at which the conduction electrons are dissipated during the passage of current. This causes an increase in electrical resistance.

The observed effects (Fig. 2) are explained by the action of two competing mechanisms: 1) an increase in the total area of contacts between neighboring CNTs, which contributes to the growth of electrical conductivity; 2) elastic deformation, which contributes to the reduction of electrical conductivity.

After compressing the sample to $\rho \approx 1.2$ g/cm³, the piston was lifted and at the same time the electrical resistivity of the elastically relaxing material was measured, which is restored to the maximum value and provides contact with the electrodes. The reverse course of the curve $\Omega(\rho)$ in the process of elastic relaxation of the CNT repeats the course of the curve when compressed over a large section of the piston path. Completion of the relaxation process was recorded by a sharp increase in electrical resistivity $\Omega(\rho)$ and breaking of the electric circuit. This process was fixed by the density of the relaxation transition. The appearance of hysteresis between the transition to the conductive state and the relaxation transition is caused by inelastic processes associated with the displacement of nanotubes during deformation.

The array of carbon nanotubes was subjected to loading-unloading processes cyclically.

After four cycles of load-unloading deformation of the CNT array, the density of the transition to the conductive state increases from 0.08 to 0.22 g/cm³ (Fig. 3), which almost coincides with the relaxation transition $\rho_{\text{rel}} = 0.23$ g/cm³, and the curve $\Omega(\rho)$ practically repeats a course of a curve of loading-unloading for the

subsequent cycles. This indicates the ordering of CNTs in the process of cyclic deformation.

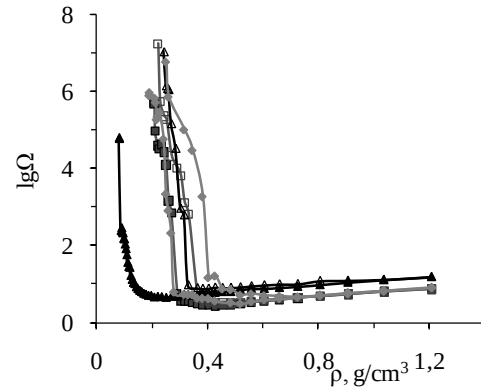


Fig. 3. Influence of cyclic deformations on the electrical resistance $\Omega(\rho)$ of multilayer CNTs: for 1, 2 and 4 measurement cycles: 1 - $\diamond$, 2 - $\square$, 4 - $\bullet$ - loading, 1 - $\triangle$, 2 - $\circ$, 4 - $\square$ - unloading

The thermo-EMF method provides important information about the state of the electronic subsystem of the nanocomposite with nanotubes. In [3] it was found that the highest value of thermo-EMF is observed for the most purified CNTs and is $\alpha = 23,7$ $\mu\text{V/K}$, and the calculated electron concentration at 0 K is $n_e = 1,3 \cdot 10^{19}$ cm⁻³. Less purified nanotubes, ie more defective, have a smaller value of α and a larger n_e , so an increase in the concentration of electrons reduces the coefficient of thermo-EMF, which has a plus sign.

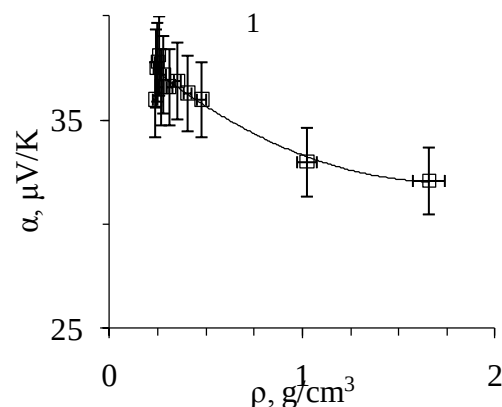


Fig. 4. Dependence of the Seebeck coefficient (α) on the density (ρ) of the CNT array obtained on the catalyst $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-MoO}_3$

Deformation of the CNT array leads to a slight decrease in the Seebeck coefficient, which may be due to the suppression of the effect of phonon hole capture when the CNT is reoriented to a predominantly perpendicular direction of phonon flux. The maximum value of α for CNTs is 36 $\mu\text{V/K}$ (Fig. 4) at array densities of 0,2-0,5 g/cm³, and with increasing density, the coefficient α gradually decreases and reaches values of 32 $\mu\text{V/K}$ at $\rho = 1,7$ g/cm³.

Conclusions

In the process of cyclic deformation of the CNT array, there is an increase in electrical resistance by 4-5 times at a density $\rho = 0,86$ g/cm³, which indicates the ordering of nanotubes and the appearance of the predominant orientation of the axis perpendicular to the current lines.

The Seebeck coefficient of the CNT array significantly depends on its density, orientation, the presence of defects and is in the range of $\alpha = + (26-34)$ $\mu\text{V/K}$. A positive sign indicates a predominantly hole contribution to the electrical conductivity in the radial direction.

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Development of new composite electrotechnical materials with advanced characteristics for application in novel equipments

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Abstract: An urgent task for the electrical industry is to develop new soft magnetic materials, in particular composites. The greatest interest present composites in which filling components have metal-dielectric-metal (MDM) interaction. Recent few years many research centres are carry out intensive developments of soft magnetic composites (SMC) based on use of soft magnetic particles, usually based on iron, with an electrically insulating coating on each particle. The carried out preliminary researches of a composite magnetic material based on iron ASC 100.29 and Atomet 1001HP powders, surface of which is capsulated by ferrite, have shown perspectives of their application in engineering. Unique specific parameters of a softmagnetic composite material - a magnetic induction of saturation 2.1 Tesla, work in a frequency range up to 100 kHz at Curie temperature from above 800°C allow to use it in high speed valve and valve-jet electromachines and as chokes and high-frequency transformers.

Keywords: SOFT-MAGNETIC COMPOSITE MATERIAL, IRON POWDERS, INSULATING COVER, HIGH-FREQUENCY TRANSFORMERS, STATORS AND ROTORS OF ELECTROMACHINES

1. Introduction

Currently, known soft magnetic alloys are mainly used in the production of electrical machines. 90% of them are various types of electrical steel. Also Fe-Si and Mn-Zn-ferrites alloys are used [1-3]. Such materials have practically reached the limit of their physical, mechanical and operational properties. To create a new generation of products it is necessary to develop a completely new class of soft magnetic materials with improved characteristics. The advantages of a composite magnetic material over electrical steel and other soft magnetic alloys make it possible to ensure their wider application in electrical machines in order to increase the specific power at a high rotation speed with lower losses. Manufacturability and ease of cores production by the compacting method is much superior to the method of sheet assembly from electrical steel. There is not practically waste in the manufacture of magnetic cores [4-6].

One of the new directions in the soft magnetic material fabrication is using of encapsulated powders, the initial grain of which is covered with a layer of alloying components, which can be organic and inorganic materials [7-8]. The process of encapsulation of each particle makes it possible to create a thin and uniformly distributed electrical insulating shell on the surface of an iron powder or its alloys at a high concentration of ferromagnet per unit volume. This allows a significant increase in electrical resistivity, which limits eddy currents and reduces magnetic losses. The magnetic properties of materials made from such powders are the same in all directions, that is, they are isotropic, which distinguishes them from electrical steels.

Similar materials have already been developed and released by various companies. For example, composite materials based on metal powders with encapsulated particles developed by Micrometals (USA), Atomet (Canada), etc. have one of the highest saturation inductions, and in this parameter they surpass all other traditional alloys. But the cost of such materials reaches 100 USD per 1 kg, which complicates the mass using of such materials. Therefore, an important task is to find cheaper materials that allow to achieve high efficiency of magnetic components for using in the electronics industry.

2. Results of development

In Scientific-Practical Materials Research Centre NASB are actively developed composite magnetic materials (SMC) based on various types of pure iron powder, for example, ASC 100.29 (Sweden), Atomet 1001HP (Canada), etc. Fig. 1 shows the relationship between permeability and saturation induction for a number of known soft magnetic alloys. It can be seen that composites based on iron powders with encapsulated particles (ferritized Fe powders) have one of the highest saturation inductions, and in this parameter they are superior to all other alloys.

For comparison, Table 1 shows the main parameters of Fe-Si alloys, Mn-Zn ferrites and the investigated magnetic composite material based on ASC100.29. Developed material is superior to iron-silicon alloys and ferrites by almost all characteristics. In addition, the cost of the composite is much less than the cost of ferrite materials.

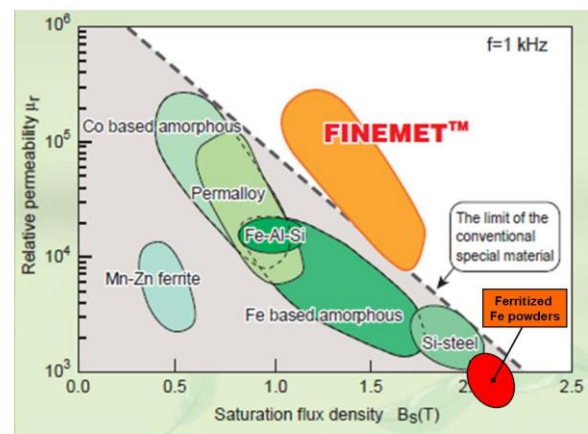


Fig. 1 Relationship between permeability and saturation flux density in several soft magnetic alloys

Table 1: Properties of Fe-Si alloys, Mn-Zn-ferrites and magnetic composite material

Parameters	Fe-Si alloy	Mn-Zn-ferrite	Composite based on ASC100.29
Saturation induction, T	1,8	0,45	2,1
Working induction, T	above 1,5	above 0,2 - 0,3	above 1,8
Maximum magnetic permeability	4000 – 7000	500 – 4000	500 – 1000
Field dependence of inductance	Non-linear	Non-linear	Close to linear
Environmental factor	Potential harmful effects	Environmentally friendly	Environmentally friendly
Core manufacturing	Complex	Simply	Simply
Electrical resistance	10^{-6} Ohm m	10^6 - 10^9 Ohm m	10^4 - 10^6 Ohm m
Price, USD/kg	2	~20	2

In order to successfully compete in the electric vehicle segment, it is currently necessary to develop an electric vehicle that will not only be innovative in its technical and driving characteristics, but also have an accessible price within the price of a classic car. The cost of a car consists of two main factors: the price of the energy storage unit and the price of the electric drive. It is very difficult to influence on the cost of batteries due to the monopoly on the materials contained in them. And in order to reduce the cost of an electric drive, it is necessary to propose new scientific and technical solutions, which are primarily based on the using of new materials. One of such solutions is the creation of an axial flow electric motor-generator with magnetocomposite cores.

It is quite difficult for car manufacturers to regulate the cost of batteries, and hence the final cost of an electric vehicle. Accordingly, in order to remain competitive in the electric vehicle market, it is necessary to reduce their price, which is possible only with the constant development and modernization of existing technologies for the manufacture of an electric drive and an increase in its efficiency.

A synchronous axial flow electric motor-generator based on new composite materials will significantly improve the characteristics of the product itself and significantly reduce its price. Due to the design features and high electromagnetic characteristics of the material, according to calculations, it is possible to create an electric motor with a higher power density, smaller weight and size parameters and low manufacturing costs in comparison with other types of electric motors. Indicators of specific power density range from 11 kW/kg, depending on the tasks and design.

The design of the stator of such a motor assumes a change in the direction of the magnetic flux, which is possible only with the use of a composite soft magnetic material, in contrast to electrical steel (Fig.2). The high efficiency of the proposed electric motor is due to the presence of two stators or two rotors. Stators or rotors can be made from separate parts of the magnetic cores, as shown in Fig. 3. Such parts are manufactured by pressing in special molds under a pressure of 10 t/cm², followed by annealing in air at a temperature of 400°C. The main advantages of the developed electric motor are compact size and light weight combined with a high degree of protection, high operating temperature and long service life, energy saving by 15% compared to existing ones, no "sliding" current collectors and elements, low maintenance costs and long service life. The multi-pole design will allow for the most smooth running and stable operation over a wide power range. A stator made of soft magnetic composite materials with high electrical properties will allow:

- refuse to use electrical steel,
- to reduce the requirements for additional cooling of the coil windings due to the material's insensitivity to induction heating,
- achieve high efficiency - 98% and specific power 12-18 kW/kg.

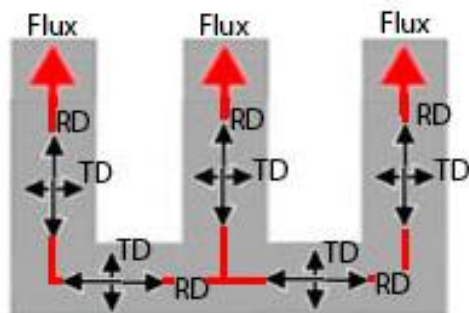


Fig. 2 Magnetic field distribution in a composite core



Fig. 3 The stator of a prototype two-stator electric motor using a composite soft magnetic material based on ASC100.29

The described technologies are also suitable for another following applications, which are used in microelectronics:

- manufacture of microforms using micro-pressing technology;
- manufacture of mechanical parts for micro-positioning - gears, stands, etc.;
- manufacture of magnetic cores;
- stators and rotors for brushless and stepper motors (including linear ones);
- production of arrays of microlenses, filters.

3. Summary

An experimental technology for producing composite materials has been developed. For production, commercially available pure iron powders (ASC100.29 Hoganas AG, Sweden) are used. The surface of individual iron particles is covered with a special oxide layer. The results obtained can find further application in the development of new soft magnetic materials with specified characteristics and in the creation of new types of highly efficient technological electrical devices.

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Phase transformations in high-entropy FeNiCoCrAl alloys during oxidation

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Abstract: The evolution of phase composition and mechanical properties and the formation of oxide layers on Fe_{40-x}NiCoCrAl_x ($x = 5$ and 10 at.%) alloys in long-term oxidation at 900 and 1000 °C were studied. In the initial cast state, depending on the aluminum content and valence electron concentration, the alloys contain only an fcc solid solution ($VEC = 8$ e/a) or a mixture of fcc and bcc phases ($VEC = 7.75$ e/a). Thin continuous oxide scales containing Cr₂O₃ and NiCr₂O₄ spinel formed on the surface of both alloys oxidized at 900 °C for 50 h. A further increase in the annealing time to 100 h leads to the formation of aluminum oxide Al₂O₃ in the scale on the Fe₃₀Ni₂₅Co₁₅Cr₂₀Al₁₀ alloy, having high protective properties. An increase in the oxidation temperature to 1000 °C results in partial failure of the protective layer on the alloy with 10 at.% Al. Long-term holding at 900 °C (100 h) + 1000 °C (50 h) does not change the phase composition of the Fe₃₅Ni₂₅Co₁₅Cr₂₀Al₅ alloy matrix, being indicative of its high thermal stability. In the two-phase Fe₃₀Ni₂₅Co₁₅Cr₂₀Al₁₀ alloy, the quantitative ratio of solid solutions sharply changes: the amount of the bcc phase increases from 4 to 54 wt.% and its B2-type ordering is observed. The mechanical characteristics of the starting alloys and those after long-term high-temperature annealing were determined by automated indentation. It is shown how the hardness (H_{IT}) and the elastic modulus (E) of alloys change after oxidation, depending on the Al content.

KEYWORDS: HIGH-ENTROPY ALLOY, VALENCE ELECTRON CONCENTRATION, OXIDATION, HIGH-TEMPERATURE OXIDATION RESISTANCE, SCALE, OXIDE, SOLID SOLUTION, ORDERING, AUTOMATED INDENTATION, HARDNESS, MICROSTRUCTURE.

1. Introduction

A new class of alloys, called high-entropy alloys (HEAs), possessing low free energy and high mixing entropy has been of research focus recently. They contain more than four elements in an equiatomic or close ratio [1]. The HEAs are peculiar in that they form simple substitutional solid fcc or bcc solutions or a mixture of bcc + fcc solid solutions [2, 3]. Differently doped alloys in which simple bcc and fcc solid solutions form are among HEAs that have been studied most extensively. Numerous papers focus on the optimization of alloy structures and mechanical properties [4–8]. There are currently very limited data on the high-temperature oxidation resistance of these materials and the stability of their phase composition and mechanical properties in long-term high-temperature holding [9–14].

Our objective is to examine the effect of aluminum on the stability of phase composition, structure, and mechanical properties and on the formation of oxide layers in long-term temperature oxidation of the Fe_{40-x}NiCoCrAl_x alloys ($x = 5$ and 10 at.% Al) at 900 and 1000 °C.

2. Experimental procedure

The Fe_{40-x}NiCoCrAl_x alloys ($x = 5$ and 10 at.% Al) were produced by arc melting in a high-purity argon atmosphere. The ingots were melted six to seven times to homogenize their composition. The starting components were high-purity materials (at least 99.98% purity).

The oxidation resistance of the alloys was examined in an electric arc furnace at 900 and 1000 °C in air. The samples were periodically weighed in 5 , 10 , 25 , 50 , and 100 h. To measure the weight change of the samples, we used a Radwag precision balance (± 0.0001 g). The oxidation resistance was assessed from the specific change in weight of the samples q (mg/cm²·h).

The phase composition of the starting alloys and those after high-temperature oxidation was analyzed with an Ultima IV diffractometer in monochromatic Cu-K α radiation. The X-ray diffraction data were processed using the PowderCell 2.4 software for full-profile analysis of X-ray spectra for a mixture of polycrystalline phase components. The morphology and microstructure of scales on the starting and annealing alloys were examined with a Jeol Superprobe 733 scanning electron microscope and with a MIM-8 optical microscope. The mechanical properties were determined by automated indentation with a Berkovich pyramid under $3N$ load employing a Micron Gamma unit.

3. Results and discussion

The fcc solid-solution phase is known [15, 16] to form at elevated valence electron concentrations, $VEC \geq 8$ e/a, in high-entropy alloys in most cases, while the bcc solid-solution phases are stable at $VEC \leq 6.87$ e/a. If the valence electron concentration is $7.2 \leq VEC \leq 8$ e/a, a mixture of two, bcc and fcc, solid solutions forms. According to our calculations, $VEC = 8$ e/a for the Fe₃₅Ni₂₅Co₁₅Cr₂₀Al₅ alloy and 7.75 e/a for the Fe₃₀Ni₂₅Co₁₅Cr₂₀Al₁₀ alloy (Table 1). Hence, the cast Fe₃₅Ni₂₅Co₁₅Cr₂₀Al₅ alloy should contain only an fcc solid solution and the Fe₃₀Ni₂₅Co₁₅Cr₂₀Al₁₀ alloy the bcc and fcc phases. X-ray diffraction data confirm the predicted phase composition of the alloys (Fig. 1 a, c). The Fe₃₅Ni₂₅Co₁₅Cr₂₀Al₅ alloy is a single-phase solid solution with an fcc lattice with parameter $a = 0.3571$ nm and the Fe₃₀Ni₂₅Co₁₅Cr₂₀Al₁₀ alloy is two-phase and contains bcc and fcc solid solutions. The fcc phase is predominant; its amount reaches 96 wt.% and that of the bcc phase is thus 4 wt.%. The lattice parameter a of the bcc solid solution is 0.2862 nm and that of the fcc solid solution is 0.3603 nm (Table 1).

TABLE 1. Phase Constituents of the Cast Alloys, Lattice Parameters of the Phases, and Valence Electron Concentrations

Alloy	Phase constituents, wt. %	Lattice parameter a , nm	VEC , e/a
Fe ₃₅ Ni ₂₅ Co ₁₅ Cr ₂₀ Al ₅	100 FCC	0,3571	8
Fe ₃₀ Ni ₂₅ Co ₁₅ Cr ₂₀ Al ₁₀	96 FCC	0,3603	7,75
	4 BCC	0,2862	

Metallographic analysis of the high-entropy alloys in starting (cast) state showed that the Fe₃₅Ni₂₅Co₁₅Cr₂₀Al₅ microstructure

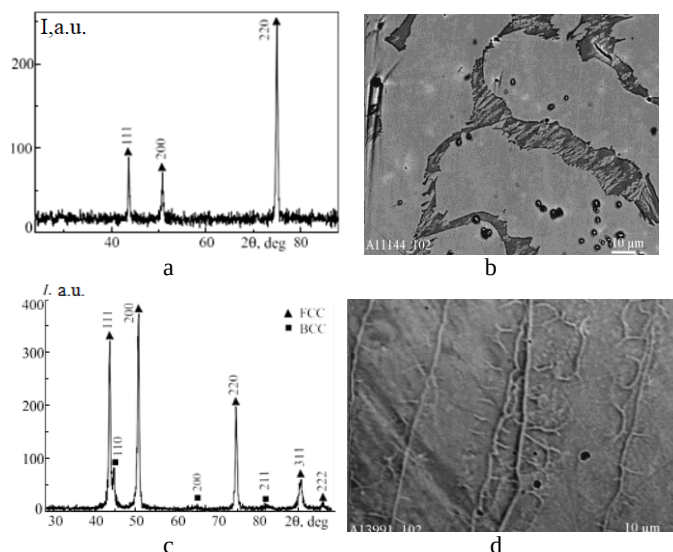


Fig. 1. X-ray diffraction patterns (a, c) and microstructures (b, d) for the $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ (a, b) and $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ (c, d) high-entropy alloys in starting state (SEM)

(Fig. 1b) included grains elongated in the crystallization direction and subgrains at grain boundaries and partially inside them. With higher aluminum content of the $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ alloy, dendritic crystallization leading to light dendrites and a darker phase in the space between the dendrites was observed (Fig. 1d). A greater aluminum content of the alloy reduces VEC, in turn indicating that stability of the fcc solid solution reduces and the bcc phase forms through solid-phase decomposition mechanism.

Figure 2 shows variation in the specific weight of the samples q (mg/cm^2) after oxidation of the $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ and $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ high-entropy alloys at 900°C for 100 h and then at 1000°C for 50 h.

After short holding for 5 h at 900°C , the specific weight of the alloy samples increased differently. The alloy with 10 at.% Al oxidized much more slowly for the first 5 h than the alloy containing only 5 at.% Al.

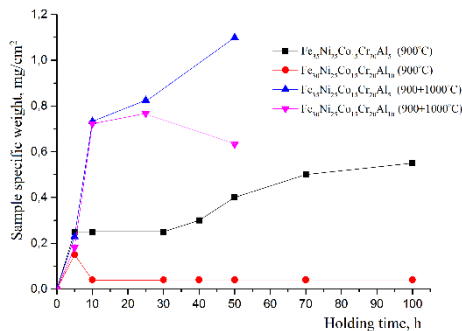


Fig. 2. Variation in the specific weight of alloy samples after oxidation at 900°C (100 h) and further at 1000°C (50 h)

The specific weight of the $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ alloy showed a stable gain for 30 h at 900°C and naturally increased further with longer holding as oxide film began to develop and grow. The $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ alloy behaved differently. The sample significantly gained weight after the first 5 h and then partially lost its weight, which was accompanied by the formation of a thin brittle scale that spalled in some places. A dense scale formed further and oxidation proceeded not only without weight losses but also without weight gain, being indicative of high protective properties of the oxide film. However, a further increase of the

oxidation temperature to 1000°C led to a sharp gain in the specific weight of the samples and growth of the scale thickness (Fig. 2).

The $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ alloy showed a continuous increase in the specific weight within entire holding at 1000°C ; q was minimum for the first 5 h and the oxidation rate sharply increased in a period between 5 to 10 h. During the next exposure in the interval from 10 to 25 hours, a significant slowdown in the oxidation process is observed, and then there is a significant increase in the increase in the mass of the samples, this may indicate that the scale formed on the surface of the alloy does not have high protective properties at a given temperature. The situation was different for the $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ alloy that contained more aluminum and less iron. After the first 5 h, the sample weight gain was much lower than that of the $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ alloy. In a period between 5 and 10 h, q substantially increased and then (10–25 h) the process sharply slowed down. In a period between 25 and 50 h, the curve showing variation in the specific weight changed its direction. When the sample cooled down, the scale partially spalled since the protective film failed under a cyclic change in temperatures because of different thermal expansion coefficients (TECs) of the scale and alloy matrix.

A two-phase oxide film containing Cr_2O_3 and NiCr_2O_4 spinel formed on both alloys at 900°C for 50 h. The scales were very thin (3–5 μm thick on the $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ alloy and 7–8 μm thick on the $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ alloy) and the X-ray diffraction patterns of both alloys had also reflections from the matrix phase of the fcc solid solution (Fig. 3).

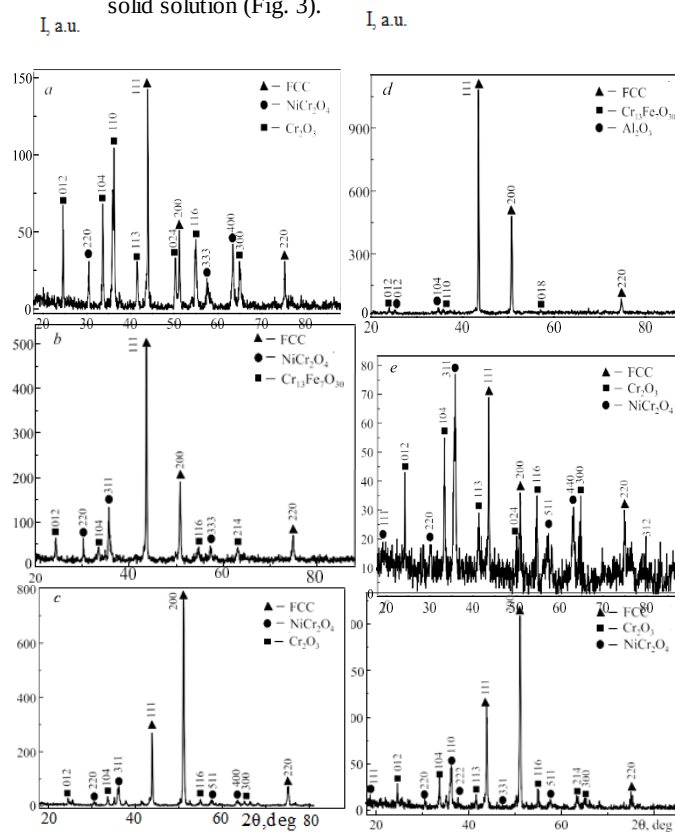


Fig. 3. X-ray diffraction patterns for the $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ (a, b, e) and $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ (c, d, f) alloys after oxidation at 900°C for 50 (a, c) and 100 h (b, d) and after oxidation at 1000°C for 50 h (e, f)

The lattice parameter of the fcc solid solutions in the $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ alloy increased compared to the starting state and became $a = 0.3577$ nm (since the near-surface metal layer was saturated with oxygen) and that in the $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ alloy substantially decreased and became $a = 0.3585$ nm, indicating that

metal ions diffused toward the oxidation front. Some diffusion processes occurred under the scale. For example, the aluminum diffusion rate increased with temperature. Hence, the aluminum concentration toward the metal surface became higher to promote the formation of Al_2O_3 . In turn, this indicates that the fcc phase became depleted of aluminum and its lattice parameter decreased. The amount of the fcc phase in the 5 at.% Al alloy was 7 wt.% and that in the 10 at.% Al alloy was 41 wt.%. This substantial difference can be attributed to varying thickness of the scales; as a result, X-rays penetrate to different depths of the sample. The main phase of the scales is presented by oxides of Cr_2O_3 structure: their amount reaches 83 wt.% for $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ and 42 wt.% for $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$. The amount of NiCr_2O_4 spinel in the scale of the $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ alloy was 10 wt.% and that in the $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ alloy was 17 wt.%. Further holding changed the scale phase composition. The alloy with lower aluminum content had a scale after 100 h at 900°C containing two phases: $\text{Cr}_{13}\text{Fe}_7\text{O}_{30}$ and NiCr_2O_4 (Fig. 3b). The presence of $\text{Cr}_{13}\text{Fe}_7\text{O}_{30}$ can be explained by the fact that iron oxidized in long-term holding to form FeO that dissolved in Cr_2O_3 to create the $\text{Cr}_{13}\text{Fe}_7\text{O}_{30}$ phase with lattice parameters $a = 0.4986$ nm and $c = 1.3646$ nm, which is isostructural to Cr_2O_3 . The NiCr_2O_4 lattice parameter increased after oxidation at 900°C and became 0.8350 nm. In oxidation at 900°C for 100 h, Al_2O_3 formed on the $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ alloy besides $\text{Cr}_{13}\text{Fe}_7\text{O}_{30}$. The X-ray diffraction pattern for the scale surface had no NiCr_2O_4 reflections since spinel separated from the scale surface after the thin continuous Al_2O_3 layer formed (being typical of the oxidation of Ni–Cr–Al alloys), so reflections from the fcc phase were predominant (Fig. 3d). After further oxidation at 1000°C for 50 h, the phase composition of the scales was similar to that of the oxide films after annealing for the same time at 900°C. In both cases, the X-ray diffraction patterns had reflections of NiCr_2O_4 , Cr_2O_3 , and fcc phase (Fig. 3e, f), but the amounts of phase constituents somewhat differed: the amount of Cr_2O_3 decreased and that of NiCr_2O_4 increased. This will further improve the high-temperature oxidation resistance of the alloys since diffusion processes slow down significantly in the layer with NiCr_2O_4 . Cross-sectional studies of the $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ alloy samples oxidized at 900°C + 1000°C revealed a wide continuous region of a light phase, identified by X-rays as the fcc solid solution, under the oxide film layer. This explains why there are no reflections of the bcc phase in the X-ray diffraction pattern. Hence, the surface layers are structured as follows: scale, fcc solid-solution region, and matrix with bcc + fcc phases.

Since the papers [17–19] found differences in the phase composition of the FeNiCoCrAl_x alloys (in particular, for $x = 5$ and 10 at.% Al) after annealing at 900, 950, and 1100°C, we conducted additional X-ray diffraction and microstructural analyses of the samples' end surfaces after complete grinding of the oxide layers to specify changes in the structure and phase composition of the alloy matrices (Fig. 4).

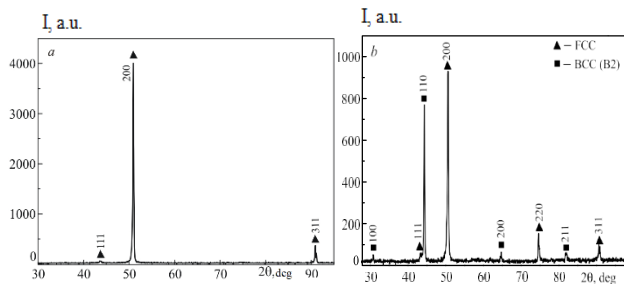


Fig. 4. X-ray diffraction patterns for the $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ (a) and $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ (b) alloy matrices after annealing at 900°C (100 h) and 1000°C (50 h) and complete removal of the oxide layer

After annealing at 900°C for 24 h, two phases were found to form in the FeNiCoCrAl_5 alloy in [17]: fcc and B2-ordered bcc; at 1100°C, there was only fcc phase, the phase composition of the $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ alloy remained unchanged after long-term high-temperature annealing in our case; there was only the fcc solid solution. This indicates that this alloy has high thermal stability since variations in line intensities in the X-ray diffraction pattern are not associated with structural changes but result from significant texture confirmed by the respective texture coefficient along the {200} crystallographic direction. For example, this coefficient τ was 0.2775₍₂₀₀₎ after annealing for the alloy with 5 at.% Al and 0.2553₍₂₀₀₎ for the alloy with 10 at.% Al (note that $\tau = 1$ in the absence of texture) (Fig. 4a).

The phase composition of the $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ alloy somewhat changed (Fig. 4b): the amount of the fcc solid solution sharply decreased from 96 to 46 wt.% and the B2-ordered bcc phase constituted 54 wt.%. Compared to the starting state, the lattice parameter of the fcc phase in the FeNiCoCrAl_5 alloy increased from 0.3571 to 0.3586 nm and that of the FeNiCoCrAl_{10} alloy conversely decreased from 0.3603 to 0.3587 nm after long-term high-temperature annealing. The lattice parameter of the bcc solid solution increased to 0.2870 nm. These changes in lattice parameters occur because of diffusion-controlled redistribution of the alloy components (Table 2) among the phase constituents.

TABLE 2. Phase Constituents and Lattice Parameters of Phases in the Alloy Matrix after Annealing at 900°C for 100h+1000°C for 50h

Alloy	Phase constituents	Phase content, %	Lattice parameter a, nm
$\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$	FCC	100	0.3586
$\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$	FCC	46	0.3587
	BCC (B2)	54	0.2870

Microstructural analysis of the annealed $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ and $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ alloy matrices by scanning electron microscopy (SEM) showed that long-term annealing substantially influenced their morphology. The alloy with 5 at.% Al became homogeneous after annealing, and thus the structure of even a preliminary etched sample was not practically revealed (Fig. 5a). The size of dendrites increased and their shape changed in the $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ alloy, while a dark fine phase precipitated within light grains (Fig. 5b). The annealed alloy matrix and the distribution of elements in characteristic radiation were studied by SEM, which showed that the dendritic phase was enriched with chromium and iron, cobalt was distributed uniformly between the two phases, and nickel and aluminum were mainly in the space between dendrites and fine phase in the $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ alloy.

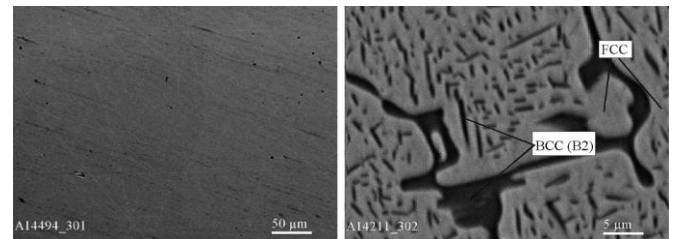


Fig. 5. Structure of the $\text{Fe}_{35}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{20}\text{Al}_5$ (a) and $\text{Fe}_{30}\text{Ni}_{25}\text{Cr}_{20}\text{Co}_{15}\text{Al}_{10}$ (b) alloy matrices after subsequent annealing at 900°C + 1000°C

The mechanical characteristics of the alloys in cast state and after annealing were determined by automated indentation (Table 3).

TABLE 3. Mechanical Properties of the Alloys in Starting State and after Long-Term Oxidation at 900°C for 100 h + 1000°C for 50 h

Alloy	Cast state		Matrix after annealing	
	H_{IT} , GPa	E , GPa	H_{IT} , GPa	E , GPa
Fe ₃₅ Ni ₂₅ Cr ₂₀ Co ₂₀ Al ₅	2	147	1.8	106
Fe ₃₀ Ni ₂₅ Cr ₂₀ Co ₁₅ Al ₁₀	2.5	152	3.1	134

After annealing, hardness of the Fe₃₅Ni₂₅Cr₂₀Co₂₀Al₅ alloy somewhat decreased to 1.8 GPa, which can be attributed to its high homogenization. The elastic modulus sharply reduced to 106 GPa since the lattice parameter of the fcc solid solution increased substantially, which in turn weakened interatomic forces and decreased E . The hardness increased to 3.1 GPa in the Fe₃₀Ni₂₅Cr₂₀Co₁₅Al₁₀ alloy as the B2-ordered bcc phase formed. This indicates that this alloy is a promising high-temperature oxidation-resistant material.

4. Conclusions

A series of studies focusing on the cast and annealed alloys in the Fe_{40-x}NiCoCrAl_x system ($x = 5$ and 10 at.%) has established the following. In oxidation at 900°C for 100 h, thin two-phase oxide films that contain NiCr₂O₄ spinel and Cr₁₃Fe₇O₃₀ oxide form on the Fe₃₅Ni₂₅Cr₂₀Co₂₀Al₅ alloy and Al₂O₃ and Cr₁₃Fe₇O₃₀ oxides on the Fe₃₀Ni₂₅Cr₂₀Co₁₅Al₁₀ alloy. Aluminum oxide in the scale promotes effective protection of the alloy against oxidation. However, when scale annealing temperature increases, Al₂O₃ separates and oxidation proceeds with the formation of NiCr₂O₄ and Cr₂O₃ on the surface. A wide continuous region of the fcc solid solution under the scale on the Fe₃₀Ni₂₅Cr₂₀Co₁₅Al₁₀ alloy has been established to form for the first time. Long-term high-temperature annealing substantially changes the phase composition and mechanical characteristics of the Fe₃₀Ni₂₅Cr₂₀Co₁₅Al₁₀ alloy: the amount of the fcc solid solution sharply decreases to 46 wt.% and an ordered bcc (B2) phase forms. This substantially increases hardness: to 3.1 GPa. This indicates that the Fe₃₀Ni₂₅Cr₂₀Co₁₅Al₁₀ alloy is a high-temperature oxidation-resistant material.

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Structure studding of recycling rubber materials through Infrared with ATR, DSC and Scanning electron Microscopy and energy dispersive analysis (SEM)

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Abstract: Tires are complex objects that consist of many different parts, each with a specific formulation, and include natural or synthetic polymers, carbon black, steel, dispersed oils, sulfur for the vulcanization or bonding process, organic additives and inorganic, and even glass fibers. Their investigation poses a difficulty in identifying them, due to their complex structure. In the Tire Recycling Industry we encounter the problem of quality control, which is difficult due to the lack of solubility of rubber particles, as well as the limited technical means of these industries. The study aimed to investigate the structure and composition of recycled tires, used in artificial turf / grass as fillers.

The study focused on the development of standard investigation methods using three instrumental and analytical techniques, as well as the study of morphological changes they have undergone during the recycling process and the impact of additives on them. The aim of this scientific search is studying the structure rubber these materials are recycled, that is one of the most important issues, especially in Albani. Through FT-IR with ATR Analysis, is a analysis technique that provides information about the chemical bonding or molecular structure of materials, Differential Calorimetry DSC and Scanning Electronic microscope (SEM) equipped with the system of dispersive of energy spectroscopy (EDS).

Keywords: Recycled rubber, FTIR-ATR, Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy and energy dispersive analysis (SEM), Synthetic a artificial grass, heating and cooling

1. Introduction

Polymeric materials have reached a vital position in all branches of science and technology. Because the development of new polymeric materials is expensive, polymers are often mixed to meet the industry need for high-performance materials. Natural rubber can be mixed with styrene-butadiene rubber (SBR) to get an improved performance. Every year, thousands of tires disappear in landfills and landfills, in EU countries today approximately one tire / year is thrown away for every inhabitant, they are a free source from which can be produced crushed tires [1-2-3]. This resilient material provides enhanced durability and safety. Recycling of tire scrap until the 1960s in the US can be taken as an example; about half of manufactured automobile tires were used for recycling and only during the production of tires were synthetic tires used and the tires could be used directly without any major processing. [4] Recycling of used tires was also encouraged by the fact that these materials were also expensive. The increasing use of synthetic rubber, however, reduced production costs and reduced the need for recycling. [5]

Rubber is produced from natural or synthetic sources. Natural gum is obtained from the milky white fluid called latex, found in many plants; synthetic tires are produced from unsaturated hydrocarbons. Recycled tire material, or "rubber crumb", is used as a component of many recreational areas, including artificial turf fields. These crumbs make up up to 90% (by weight) of the fields. Tire crumbs are approximately the size of coarse sand grains and are created from the shredding of used tires. Rubber particle materials are spread two to three inches thick over the terrain surface and packed between strips of green plastic used to simulate green grass [3]. Synthetic tires are classified into general purpose tires and special purpose tires.

Over 16 million of old tires are re-used as coated, i.e., where new tire is formed into an old tire. Tire recycling uses much less oil and other resources than were used to create a new tire. About 56 million tires are used in civil engineering projects such as road slabs and other engineering uses. Vulcanized rubber, like elastomer, is difficult to recycle. Therefore, there is a need to develop direct, rapid and accurate methods to evaluate the composition of such mixtures when the composition is not known. [6].

Eight different types of rubber particles were taken for the study from the fields with artificial grass, which are distinguished by their color and size. The study is to investigate the components of granular tire particles used in the field with artificial grass in Albania. Due to the content of additives in recycled tires, their identification by classical methods, such as flotation or incineration, is inaccurate. Thus, for the identification of crushed tires if they are recycled, the spectroscopic methods of vibration and Fourier transform: infrared (FT-IR with ATR) were initially used, as well as the study of the crystalline structure by means of thermal analysis, differential calorimetry by scanning (DSC). Study of microstructural defects and chemical content of additives by scanning electron microscopy, equipped with SEM-EDX power distribution system.

2. Materials

The present investigation involved eight granulated rubbers from different football fields being used as fillers in artificial grass football fields, received by Albanian and foreign market. Information about color, shape and size of the samples are reposted in Fig1



Fig :1 Studying rubber sample

3. Methods

The paper includes the description of the micrographic structure of the tires, the separation of the constituent phases and the determination of the chemical elements of the additives used. And determining if these rubber particles are from recycled wheels. Rubber itself is different from other polymeric materials, since it is a thermoset material has difficulty in recycling, this lies in the fact that to recycle it in a way similar to plastic often lead to undesirable results. One of the most important issues, not every tire can be recycled and, this poses a serious problem to investigate in proving that these are materials that come from recycled tires.

The first stage of the research involves the study of rubber gills by the method of vibrating infrared spectroscopy and the Fourier FTIR transformation equipped with the ATR system, a method that enables the analysis of thick surface samples without any prior preparation.

Sampling of samples was performed in the wavelength range from 4000-400 cm^{-1} . The research of the structure was then carried out by the method of thermal analysis, by means of calorimetry with DSC scanning that will provide information about the composition in the rubber granules. Thermal analysis is an essential technique for measuring temperature or response depending on the time of physical and chemical changes that occur in materials. The second stage of the work is the research of the structure from the micrographic point of view of the granular tires, the separation of the component phases and the determination of the chemical elements of the additives used. For this purpose we used the electron scanning microscope (SEM).

The information obtained from the FT-IR-ATR spectra identified low-intensity rubber in all eight samples, while the determination of additives was difficult due to the overlap of peaks and their low intensity in the FT-IR-ATR spectrum. and due to the high fluorescence in the recycled materials in the spectra, which indicates the presence of fillers in them. Accurate identification of fillers indicates difficulty due to their low intensity.

Having encountered difficulties in determining the additives with the above method, then we applied two other methods for their determination. To determine the thermal properties, we use differential scan calorimetry (DSC). The temperature range chosen for rubber testing is from -80 $^{\circ}\text{C}$ to +200 $^{\circ}\text{C}$ with a hot heat step of 10 $^{\circ}\text{C}$ / min. The equipment used is the DSC 200 F3Maia rate (Customs laboratory) of 10 $^{\circ}\text{C}$ / min in a nitrogen photo environment.

The technique provides valuable information on softening temperatures (or T_g), melting temperatures, melting heat, percentage crystallinity and recrystallization (temperatures and heat) [8].

An SEM scanning electron microscope was used for the morphological study of the surface of rubber materials. High-resolution images were obtained, either in secondary electronic mode (SEM) for topography, or in diffuse electron mode (BSE) mode to detect possible component variation.

4. Results

In Fourier transform infrared spectroscopy FTIR-ATR, it is a useful method for the study of polymers when we do not know its structure. Using infrared spectroscopy we can determine if the rubber particles are rubber or any other polymer.

The analysis of the peaks of the FT-IR spectrum revealed the basic material of the tires, as well as the presence of some other peaks with low intensity due to the presence of foreign matter.



Fig: 2 FT-IR spectra for G-1 rubber samples

Fig 2 shows the presence of rubber as the base material was identified across the spectra. Groups of spectrum peaks in the wavelength range 2850 -3000 cm^{-1} resulting from the absorption of C-H3, C-H2 and C-H bonds during deformation. The group of peaks with wavelength 2300 - 2400 cm^{-1} is due to the nitrile group which seems to be present in all tested samples. In addition, the peak frequencies of the 1500-1600 cm^{-1} wave number representing the carbon group and the 900-1000 cm^{-1} wavelength representing the sulfoxide group are present in the tested samples. Different fillers in rubber can be the source of small changes in the wavelength of spectra. The greatest impact on fillers is the intensity of the peaks, as well as their doubling as shown in Fig 3. From the analysis of the FT-IR spectrum with ATR it is noticed the presence of a large number of curves those of the tires, also all the peaks have a low intensity from the base material, this is due to the large amount of fillers.

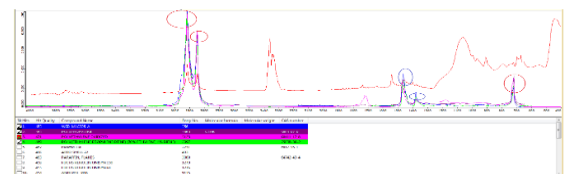


Fig: 3 FT-IR spectra for G-1 and G-6 rubber samples

During the research of rubber particles we concluded and we can say that FT-IR infrared spectroscopy with ATR gives us accurate information for the identification of recycled polymers, but it is not a good method for determining the recycling rate. This is also seen in Fig 4, which shows the FT-IR spectra with ATR for the eight tire samples. Differences in peak intensities for all samples, gives us an overlap from the content of additives in tires, this problematic initially requires a morphological analysis of the elements or substances found in the tire structures.

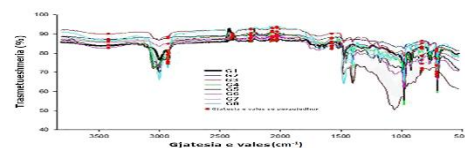


Fig:4 FT-IR spectra for all samples

The DSC results generated from the test are shown in Fig 5. Using the program it was possible to calculate the characteristics of each curve for the second heating and the second cooling. Curves measured from tire particles with heating speed 10 $^{\circ}\text{C}$ / min. This curve shows a glass transition transition occurring at 127 $^{\circ}\text{C}$, an exothermic crystallization peak at about 102 $^{\circ}\text{C}$, and an endothermic peak melting at about -40 $^{\circ}\text{C}$. The results of the glass transition temperatures are very small between samples, which may be associated with limitations due to the interaction between the filler and the rubber matrix.

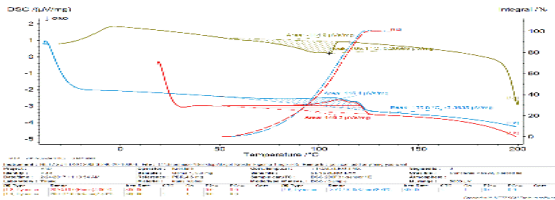


Figure 5: First, second DSC heating and cooling curves, for example G-1. (a), first, second DSC heating and cooling turns,

For sample G-3 and G-4, the first and the second heating are almost identical, as the curves overlap on top of each other. The same behavior is noticed also on the samples G-5 and G-6, G-7 and G-8, as presented in the following figures.

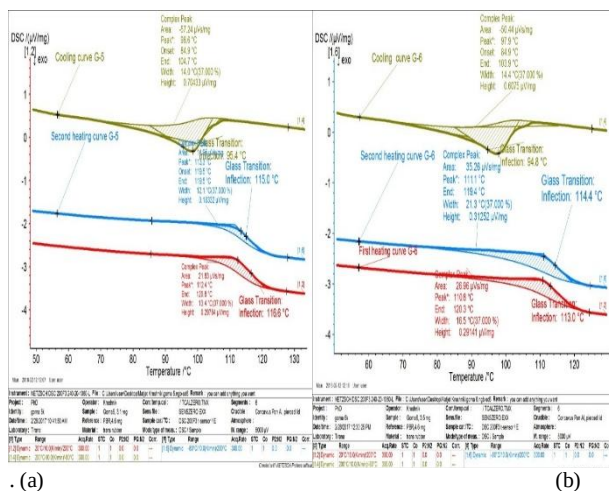


Fig 6: DSC curves of first, second heating and cooling down, for sample G-5. (a), DSC curves of first, second heating and cooling down, for sample G-6

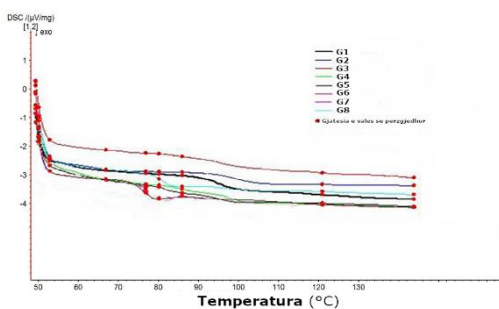


Fig 7: DSC heating and cooling curves first, second, for all example

In the TG derivative (DTG) the rate of data analysis for weight loss is plotted against temperature or time. In a dynamic TGA, the temperature corresponding to the peak weight loss of a rubber derivative depends on the degree of temperature scanning, the average of the environment, the composition, and the thermal history. An increase in the degree of heating shifts the peak of DTG to a higher temperature.

Under nitrogen rubber degrades thermally, but in air or oxygen degradation is thermo-oxidizing in nature. The presence of filler, vulcanizing agent and antioxidant also affect the thermal degradation of rubber. The presence of filler, vulcanizing agent and antioxidant also affect the thermal degradation of rubber. Representative TGA thermograms of a chewing gum and SBR vulcanized carbon black are shown in Fig 7.

After performing the SEM analyses for all seven samples a spectrum was taken as show a figures. Consequently, the provided chemical analyses are shown in the form of spectra [7]. In Figure 7, stains with a lighter color are easily noticed in the BSE image on the surface of the crumb. These stains witness the presence of foreign elements in the matrix of rubber. Chemical

analysis over a number of such stains reveals minor quantities of other elements, such as zinc, silicon, potassium, magnesium, iron, and sulfur. Zinc oxide, together with stearic acid, plays an important role in vulcanization chemistry, called activators. These compounds react together and with accelerators to form a zinc sulfurating compound, which in turn is the key intermediary in adding sulfur to a diene elastomer and creating sulfur interlinks.

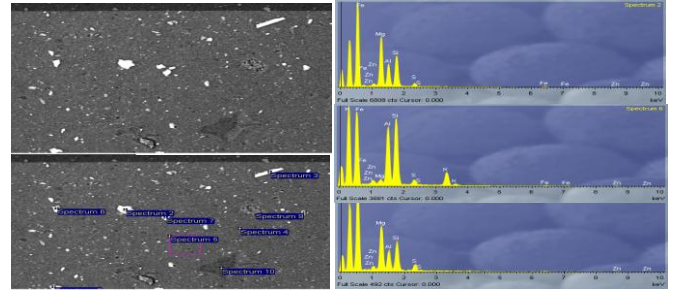


Fig 8. (left) Micrographs of second rubber with crumb, (right) X-ray spectra of 2nd rubber

Reinforcing fillers used in rubber with particles of similar shape and size are finely separated silica. Magnesium oxide is needed to give it resistance during vulcanization, mixed with zinc oxide. Magnesia is included in the formulation to act as a chlorine atom searcher. Iron oxides are active fillers which improve the mechanical and magnetic properties of elastomers. Aluminum silicates are good reinforcing fillers, they create relatively stronger vulcanization than other fillers, such as calcium silicates [8].

5. CONCLUSION

The FT-IR infrared vibration spectroscopy method with ATR enables the accurate identification of rubber particles, even in cases when there is a high content of additives in them and when the tires have a high degree of degradation. Determining the degree of degradation is difficult to determine because the intensities of the molecular bond peaks are almost the same for all the rubber particles analyzed.

The analysis of the peaks of the FT-IR spectrum with ATR revealed the basic material of the tires, as well as the presence of some other peaks with low intensity due to the presence of foreign matter. Due to the Tg glazing temperature of the tires, the mode of crystallization affected to a very large extent the obtaining of FT-IR spectra with ATR. Accurate identification of the diaries was difficult to accomplish due to the low intensity of the peaks and their overlap. Thus, for the accurate determination of additives, in addition to the FT-IR method with ATR, an additional method was required for the qualitative determination of chemical elements in tire structures,

- The DSC Differential Calorimetry Scanning method further confirmed the identification of the tires. Analyzing thermographs shows the differences between the samples as they show different values of heat capacity. Samples G-4 and G-7 show almost the same values of heat capacity for the first heating and for the second heating, unlike the other samples, due to the fact that there is no change in the thermal history. Samples G-6 and G-8 show higher values of heat capacity in the second heating compared to the first heating.

From the results of thermograms obtained from the thermal analysis of rubber particles, from recycling the material does not undergo changes in thermoplastic properties. The thermograms obtained in the thermal analysis of the isothermal kinetics of recycled rubber particles show that in all eight materials there is repetition in the general shape of the thermogram and displacement with the time of melting peaks of the two materials at different crystallization temperatures. This can be explained by the presence

of various additives that can crystallize, however this needs a more detailed analysis which is in further research work. Different shapes and sizes of additive particles were spread all over the surface (and therefore the volume) of the rubber.

- SEM scanning electron microscopy equipped with EDS power distribution system identified different types of tires and identified the additives used in them, but in small quantities. From the analysis of optical images it was concluded that they were minerals. Their presence affects the physico-chemical-mechanical properties of rubber particles. In some cases the determination of additives was difficult to determine due to the small amount used (the apparatus identifies additives in quantities over 5% by mass), as well as the lack of crystallinity.

From the BSE image analysis the basic rubber matrix was highlighted. Different shapes and sizes of additive particles are spread over the entire surface (and volume) of the rubber. In addition to chemical analysis of additives, we can see defects of rubber microstructure presented as holes and microcumulations. From the XDS spectra was determined the chemical content of foreign elements in the structures of rubber particles, to the composition of chemical elements and literature concluded in the content of additives. Thus proved the use of the main additives in tires such as silicon, aluminum, zinc, magnesium, oxide and potassium. In this case the presence of chlorine may define the rubber as chlorinated. Chlorinated rubber is a type of thermoplastic resin in the form of high hardness powder. It is considered as environmentally friendly resin. With perfect adhesion, it can be used for chemicals and abrasives. Due to its high chlorine content, it is non-combustible and thus used

for the production of fire-retardant paints. Her films exhibit excellent resistance to corrosive elements. Throughout the spread of additives in the particle the eight types of gum particles are identified as silicon, aluminum, zinc, magnesium, calcium and potassium. The presence of these elements is mainly due to the use of mineral fillers such as mica talc, which have been used as lubricants and anti-dust agents. We also see some microdefects in the rubber microstructure. Quantitative determination of these additives was impossible to accomplish due to chemical interactions between them, given that polymers are processed at temperatures above 200°C.

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Knowledge for material science. Part I

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Abstract: This article discusses the modern knowledge necessary for materials science. Modern scientific knowledge covers on the basis of the greatest scientific results; complete scientific knowledge: mathematics; mathematical physics; quantum mechanics (not relativistic and relativistic); quantum physics; quantum chemistry. Theory and modern tools for testing and monitoring with increasing resolution. High technologies. A research – type methodology has been obtained, but this methodology is also focused on interactions with business. Business research is not fundamental, but it can be very lengthy.

Keywords: MODERN SCIENCE KNOWLEDG, SCIENCE METHODOLOGY, BUSINESS, HIGH THECNOLOGY

1. Introduction

Industrial aluminum alloys are multicomponent heterophase systems [8, 9, 15]. The modern theory of alloys [15] determines the main factors of interaction and their properties are: the place in the periodic table; their valence; atomic radius and lattice parameter; melting and boiling point; diffuse mobility of atoms, etc. *Structural factors:* defects in the crystal lattice (vacations, dislocations, impurity atoms) and their interaction between them and with the atoms of the alloying elements; the grain size of the solid solution and the condition of their boundaries; quantity and geometry of the eutectic; the quantity, size and geometry of the secondary phases and their interaction with the solid solution in the heating process; sustainability of the solid solution; *Physic-chemical characteristics are:* the main and most stable for an alloy with a certain chemical composition. Example: for the tensility of alloys the main physic-chemical factors are: energy state of the crystal lattice of the solid solution (forces of inter-atomic interaction, nature of the electronic state); coefficient of self-diffusion of the aluminum atoms and diffusion of the atoms of the alloying elements and impurities in the crystal lattice of the solid solution; *The boundaries of the grains are a distorted layer of atoms with different energy states than those in the volume of the grains:* this is caused by the forces striving to move the atoms to a position corresponding to the orientation of one of the neighboring grains. Therefore, the grain boundaries are areas with an increased value of free energy. They play an important role in the mechanism of strengthening the alloy. The existence of a separating surface facilitates the processes of diffusion of atoms of alloying elements and impurities. The sum of the surface energy at the boundary of the solid solution is also an important structural characteristic that determines the mechanical properties of the alloys; *Technological factors:* melting and casting mode; rate of solidification (crystallization) of the castings and the obtained phase composition; heat treatment modes that can strongly change the phase composition; the quantity and nature of the location of the structural components; changes in one or another technological characteristics of alloys determine their final properties.

Alloys are solutions and chemical compounds of metals and some cases and non-metals. Definition of the working properties of A. Balevski [8]: **such a combination of mechanical and technological (and in some cases physical and chemical) properties that no pure metal has, regardless of what mechanical and thermal treatment it is subjected to.**

Stability of phases: Concept of free energy. The term 'phase' refers to a separate and established state of a material in which a substance may exist [15]. The phase is part of the material with a boundary specific arrangement of atoms and the same intensity of properties [3]. The Gibbs phase rule [6, 8 and 15] is the basic equation: $P + F = C + 2$, where P is the number of phases represented at equilibrium; F is the number of degrees of freedom; to C the number of components, which is the smaller number of

substances than the independent variables of the composition of the constructed system. Phase diagram [3] - a graphical way of describing phases in equilibrium with a combination of different variables (T, P, C). The condition [15] of each material is characterized by enthalpy H and the specific heat content C_p at constant pressure of the type $C_p = (dH/dT)_p$. The entropy function S is used to describe a material in a phase transition by going through a complete cycle of events $\oint dQ/T = 0$, where dQ is the heat exchange between the system and its environment during each infinitesimal stage and T is the temperature at which the transfer takes place [15 and 6]. The quantity S is defined by [6] $dS = dQ/T$ at the condition $\oint dS = 0$; so entropy determines a *state property* and at constant pressure in system $dQ = dH \Rightarrow$

$$dS = dQ/T = C_p dT/T, \quad \text{and by integration} \quad (S, 1)$$

$$S = S_0 + \int_0^T (C_p/T) dT = S_0 + \int_0^T C_p \delta(\ln T), \quad (S, 2)$$

where integration constant S_0 represents the entropy at $T = 0$ K, which for a crystalline substance is assumed to be zero [6], i.e. third law of thermodynamics. Every reaction or phase transformation in the system is dS; the transition of the old phase α in the new phase β is the difference between their entropies S_β and S_α :

$$dS = S_\beta - S_\alpha. \quad (S, Ch)$$

Each irreversible change in the system increases the total entropy of the system. This is the second law of thermodynamics [6]. For convenient is work with energy than entropy total energy is H with two components free Gibbs energy and multiplication TS [6, 15]:

$$H = G + TS, \quad (\text{Total, Energy})$$

$$G = H - TS, \quad (\text{Gibbs, Energy})$$

$$dG = dH - dT \equiv dE + PdV - TdS, \quad (\Delta G, 1)$$

where G is the part of the system energy causing the transition process; TC is the necessary energy resulting from the change involved; dG is change of free energy accompanying, the process of phase transition is called "driving force". Spontaneous changes in the system are accompanied by a decrease in total G free energy, i.e. the change has a negative sign ($-\Delta G$) and it follows that the conditions for equilibrium are the driving force to be zero: $dG = 0$ *equilibrium criteria*. For a liquid $\leftrightarrow$ solid phase transition at atmospheric pressure (PdV), is very small and the free energy equation used for *equilibrium criteria* is $dE - TdS = 0$; equivalent to defined (E-TS) to be a minimum for equilibrium state, for by differentiation [15 and 6]:

$$\begin{aligned} d(E - TS) &= dE - TdS - SdT, \\ &= dE - TdS \quad (\text{since } T \text{ is constant}), \\ &= 0 \quad \text{for the equilibrium state.} \end{aligned}$$

Quantity (E-TS) defined equilibrium at T=cents and constant volume and is given *Helmholtz free energy* $F = E - TS$ to distinguish it

from Gibbs free energy $G=H-TS$. In the case of a second order phase transition (solid phase transition, i.e. $(\beta \leftrightarrow \alpha)$) it is reasonable to work with the approximation F instead of G , because H as a sum of internal and external energies, then the external energy PV is negligible and $H \cong E$.

Stability of phases [15]: Free energy and temperature. In metals, and especially alloys, they undergo a structural change from one phase to another (see Fig. 1 of the Al-Mg-Si triple alloy); and transition $L \rightarrow (L+\alpha-Al) \rightarrow \alpha-Al$ and so on. As the temperature decreases between the lines L and S there is a liquid phase with free energy G_L and a solid phase with free energy $G_{\alpha-Al}$; below the line S - solid phase with $G_{\alpha-Al}$.

Stability of phases: Free energy and composition [15]. Depending on the type of phase diagrams, for example, a binary case of a solid solution from statistical physics we have: The probability W for the distribution of two types of atoms A and B in a crystal with a total number of places in the lattice N let n be the places of the lattice occupied by atoms A and $N-n$ be the places of the atoms B is given eq.(W) Thermodynamic and statistical definition of entropy [6] is eq. (SW, 1) $\Rightarrow$ entropy is a property that measures the probability of configuration, the greater the probability W , the greater the entropy S . Using Stirling's theorem (at large $N \Rightarrow \ln N! = N \ln N - N$) eq. (SW, 2) is obtained:

$$W = N! / (n! (N - n)!), \quad (W)$$

$$S = k \ln W, \quad (S, W1)$$

$$S = k \ln [N! / (n! (N - n)!)]$$

$$= k [N \ln N - n \ln n - (N - n) \ln (N - n)]. \quad (S, W2)$$

Principle of alloy theory [26]. Primary substitution solid solution. 1. The Hum - Rothery rules for Phase diagrams representing primary solid solutions and intermediate phases. In short, the rules for primary solid solution are as follows [15]: **1.1 The effect of the atomic size factor** - if the atomic diameter of the solute differs by more than 15% from the atom of the solute, the degree of primary solid solution content is small. In this case, the size ratio is said to be unfavorable for a broad solid solution; **1.2 Electrochemical effect** - the more electro-positive one component is, the more electro-negative the other, the greater the tendency for two elements to form (create) a chemical compound than to create a broad solid solution; **1.3 Relative valence effect** - A metal with a higher valence is more likely to dissolve to a greater extent in one with a lower valence than vice versa. **2.1 The effect of the atomic size factor** due to the distortion obtained in the native lattice deviation around the atom of the solute [29]: Two metals are able to form a continuous row of solid solution only if they have the same crystal structure (Cu and Ni). When the difference in size between the atoms of two metal components A and B approaches 15%, the changes in the equilibrium diagrams change from the fact that the dimensions limit the primary solid solution; for example, a Cu - Ni type system goes to a eutectic system with a limited primary solid solution; **2.2 Electrochemical effect:** General principle: the solubility of phase decreases with increasing stability, and many also be used to show that the concentration of solute in solution increases as the radius of curvature of the precipitate particle decreases. Precipitate small particles are relatively stable than many particles and vary the solubility with particle size is reported in the Gibbs-Freundlich:

$$\ln[c(r)/c] = 2\gamma\Omega/k_B T r, \quad (\text{Gibbs - Freundlich})$$

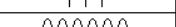
where $c(r)$ is the concentration of solute in equilibrium with small particles of radius r ; c is the equilibrium concentration; γ is the precipitate/matrix interfacial energy; Ω is the atomic volume; k_B and T are constant of Boltzmann and temperature; **2.3 Relative valence effect:** Generalized rule for alloys of monovalent metals, Cu, Ag and Au with those with high valence (valence). Copper dissolves 40% zinc, but the solubility of copper in zinc is limited. For solvent elements with high valence, the application is not so general, but for the magnesium-indium system the rule is

applicable; **2.4 the primary solid solubility boundary [15]:** The solubility limit of α -solid solution increases or decreases with temperature due to the increase in entropy S from the mixing of different atoms. Entropy is a measure of the additional disorder of dissolution compared to pure metal. The high temperature helps the structure with high entropy because TS is a member of the eq. (Gibbs, Energy) $G=H-TS$. A complex alloy system, such as containing intermediate phases of secondary solid solution (Cu-Zn, Cu-Ga, Cu-Al, etc.), the area of the primary solid solution decreases with increasing temperature. The solubility limit of alloys is represented by a ratio of electron (e) to atom (a), i.e. e/a [15]. For example, a Cu-Zn alloy containing 40 at. % Zn has $e/a = 1.4$, i.e. for every 100 atoms, 60 are Cu, each contributing one valence electron and 40 are Zn, each contributing two valence electrons, so that $e/a = (60 \times 1 + 40 \times 2) / 100 = 1.4$. The solubility in alloys for some elements according to their valence is [15]: 1. Monovalent Cu or Ag is $e/a = 1, 4$; 2. Divalent Zn, Cd and Hg have a solubility of up to 40 at. %. In Cu-Zn, Ag-Cd, Ag-Hg; 3. The trivalent elements are approximately 20% at. % (e.g. Cu-Al, Cu-Ga, Ag-Al, Ag-In); 4. The tetravalent elements about 13% (e.g. Cu-Ge, Cu-Si, Ag-Sn), respectively. The limit of solubility has been explained by Jones in terms of the Brillouin zone structure [15].

1.1. Solid State Physics Basis of Materials Science

Phonons and lattice oscillation [4]. The energy of vibration of the crystal lattice or the energy of elastic wave is a quantum value [4]. The quantum energy of an elastic wave is called a *phonon* by analogy with a photon (quant electromagnetic wave energy). Planck - the energy of each type of oscillation of an electromagnetic field in a cavity (gap) is proportional to $h\nu$. Important definitions are given in Table 1:

Table 1. Some important elementary excitations in solid

DEFINITION	NAMING	FIELD
	Electron	—
	Photon	Electromagnetic wave
	Phonon	Elastic wave
	Plasmon	Collective electronic wave
	Magnon	Premagnetization wave
—	Polaron	Electron + elastic deformation
—	Exciton	Wave of polarisation

Phonon energy quantum energy (Photon, QE); phonon impulse (or quasi-impulse) (Phonon, I or QI); wave vector selection phonon rule (Phonon, WVSR)

$$\varepsilon = h\nu, \quad \text{for } n \text{ photons} \quad \varepsilon = n h\nu, \quad \text{or } \varepsilon = n h\omega, \quad (\text{Photon, QE}),$$

$$hK, \quad \text{Phonon Impulse (or Quasi)}, \quad (\text{Phonon, I or QI}),$$

$$k' = k + K + G, \quad \text{Wave vector selection rule}, \quad (\text{Phonon, WVSR}).$$

h is Planck's constant; ν is photon oscillation frequency; ε is energy per photon; n is the number of photons; angular velocity $\omega \equiv 2\pi\nu$; k and k' are wave vectors of an incident and scattered photon; K is phonon wave vector; G is inverse lattice vector.

Assumption [4] two phonons with wave vectors K_1 and K_2 interact anharmonically: Anharmonic interaction of two phonons with wave vectors K_1 and K_2 form an anharmonic term of the third order in the expression of the elastic energy and a third phonon with wave vector K_3 is formed. There are other mathematical relations, such as selection rules for lattice of probability W of collision of three phonons with wave vectors K_1, K_2, K_3 ($W, K_i = (1, 2 \text{ and } 3)$) and for the continuum (Continuum):

$$W \sim \sum_n e^{-iK_1 \cdot r_n} e^{-iK_2 \cdot r_n} e^{iK_3 \cdot r_n} = \sum_n \exp[i(K_3 - K_1 - K_2) \cdot r_n], \quad (W, K_i = (1, 2, 3))$$

$$\sum \rightarrow 0 \Rightarrow \text{the conditions } K_3 = K_1 + K_2 \text{ or } K_3 = K_1 + K_2 + G \text{ are no met}$$

$\sum \rightarrow 0 \Rightarrow$ the conditions $K_3 = K_1 + K_2$ or $K_3 = K_1 + K_2 + G$ are not met. The condition $K_3 = K_1 + K_2$ is a special case of $K_3 = K_1 + K_2 + G$ condition. If these conditions are met for the continuum the matrix element contains the delta function of Dirac then we have:

$$\int d^2x \exp[i(K_3 - K_1 - K_2) \cdot r] = (2\pi)^3 \delta(K_3 - K_1 - K_2). \quad (\text{Continuum})$$

Inelastic scattering of photons by acoustic waves [4]: photon with frequency $\omega = ck/n$ or $\lambda v = c/n$ and impulse $p = \hbar k$ propagate in a continuous crystal medium with refractive index n ; condition for energy storage and rule for selection of the wave vector are [4] in the $v_s K \approx (2v_s \omega / c) \sin(\varphi/2)$ case of photon scattering, the release or condition for energy storage $\hbar\omega = \hbar\omega' + \hbar\Omega$ Fig.1a and the rule for selection of the wave $k = k' + K$ vector; from Fig.1b at $k' \approx k$ we have $K \approx 2k \sin(\varphi/2)$ or as far as $k = \omega n/c$ can write $v_s K \approx (2v_s \omega / c) \sin(\varphi/2)$. And since $\Omega = v_s K$ the phonon formed by inelastic scattering of photons at an angle φ to the beginning direction of incidence of the beam there will be a frequency Fig.1c

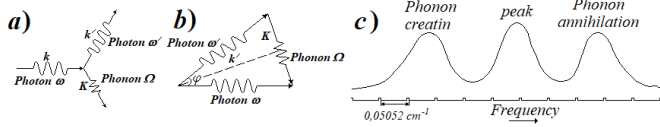
$$\Omega \approx \frac{2v_s \omega n}{c} \sin(\varphi/2). \quad (F, Ph)$$


Fig. 1 by work [4]: a) Non-elastic scattering of a photon with wave vector k and a phonon with wave vector K is formed. The scattered photon has a wave vector k' ; b) Wave vector selection rule for the process presented in a). If $k = k'$ the triangle is isosceles, whose base is the wave vector of the phonon $K = 2k \sin(\varphi/2)$; c) Generating phonons of frequency is eq. (F, Ph). Spectrum of inelastic scattering of monochromatic light. The scattering of light by photons in solids and liquids is a scattering of Brillouin.

No elastic scattering of neutrons by phonons: Rule for selection of a wave vector when scattering a beam of neutrons on a crystal lattice is: $k + G = k' \pm K$, a sign (+) in front of K is the formation of a phonon, and a sign (-) is the disappearance of a phonon; G is an arbitrary vector of the inverse lattice; The kinetic energy of a neutron incident on a crystal is: $p^2/2M_n$, where M_n is neutron mass; impulse of the neutron is $p = \hbar k$, where k is neutron wave vector. Thus the kinetic energy of the neutron is $\hbar^2 k^2 / 2M_n$. If the neutron undergoes scattering there is a wave vector k' and energy $\hbar^2 (k')^2 / 2M_n$. The condition for energy storage is: $\hbar^2 k^2 / 2M_n = \hbar^2 (k')^2 / 2M_n = \hbar^2 (k')^2 / 2M_n \pm \hbar\omega_K$ sign (+) in front of the phonon energy $\hbar\omega_K$ corresponds to the formation of a phonon, and a sign (-) is the disappearance of the phonon. To determine the dispersion law, it is necessary to experimentally measure the increase or loss of energy in the scattering of neutrons depending on the direction of scattering $k - k'$.

Oscillations in a lattice of identical atoms (short elastic waves with a wavelength comparable to the crystal lattice constant):

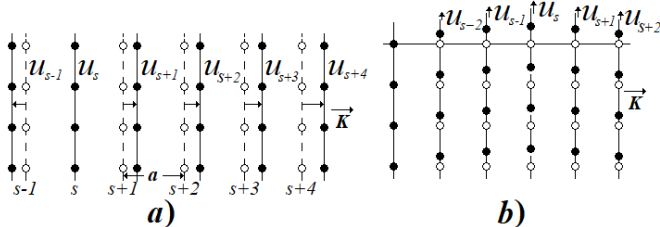


Fig. 2 Propagation of short elastic waves with lengths comparable to the crystal lattice constant (with a primitive basis of one atom, complete displacement of the atomic planes at a distance u_s from the equilibrium position s) [4]: a) purely longitudinal waves (displacement of the atomic planes parallel to the wave K), a is distance between the atomic planes; b) purely transverse waves (displacement of the atomic planes perpendicular to the wave K).

The force F_s acting on the plane s is proportional to the displacement $u_{s+p} - u_s$ (linear displacement function) and therefore eq.(1, 1) is written in the form of Hooke's law, C_p is force constant;

Important: The constant C_p is the force constant for planes at a distance p . **Methodological scheme of [4]:** The force constant C_p is also related to the potential energy of two atoms and often this is the Lennard-Jones potential; The motion of the plane is eq.(1, 2) with solution of the type eq.(1, 3) and (for a see Fig. 1); and **dispersion law** (DL) eq.(DL); The tangent of the angle of inclination of the curve described by the function $\omega = f(K)$ is equal to zero at $K = \pm\pi/a$ [4]: and we have eq.(1, 4); eq.(1, 4, 1) show the wave vector of the phonon lying at the boundary of the Brillouin zone; When interacting only between the first adjacent planes, we have eq.(1, 5), equal.(1, 5, 1), eq.(1, 5, 2); the independent values of K are the interval (1, B, zone) and the maximum value is (1, B, Boundary zone) (Fig. 3 a and b); K values outside the first Brillouin zone: condition (1, B, K') and solution by eq.(1, B, K'_{sol}); Up to the boundary of the 1st zone of Brillouin, the solution is not described by the eq.(1, B, RW) of a running wave, but by the eq.(1, B, SW) of a standing wave. (Fig.3 c); the difference between a discrete structure and an elastic continuous medium; **Mathematical scheme:**

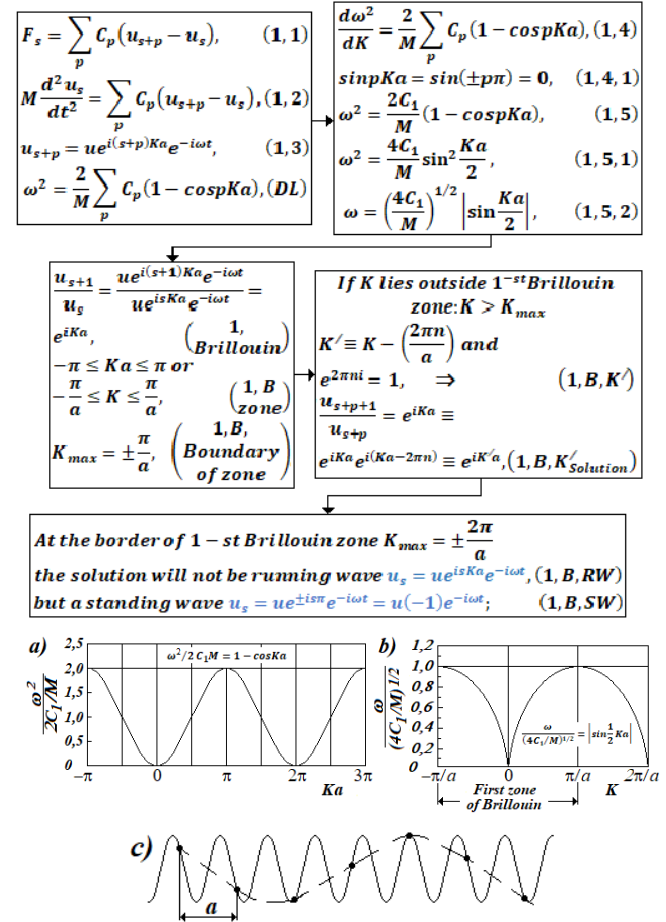


Fig. 3 The tangent of the angle of inclination of the curve described by the function $\omega = f(K)$ is equal to zero at $K = \pm\pi/a$ [4]: a) Dependence of ω^2 on K for a lattice in interaction only between the first adjacent planes; C_1 is the force constant between the planes; and the distance between the planes is a ; b) The definition domain for $K \gg 1/a$ or $\lambda \gg a$ corresponds to a continuum approximation; here ω is directly proportional to K ; c) A solid line represents a wave that contains the same information as the wave described by a dotted line for which $\lambda \gg 2a$. The wave described by the dotted line represents the displacement of the atoms.

Neighboring atoms in standing waves move in antiphase because $\cos s\pi = \pm 1$ it depends on s whether it's an even number or not. The wave does not move either left or right, i.e. it is standing. Analogy of standing wave and Bragg reflection in X-rays: the traveling wave cannot propagate in the lattice as long as there is a right and back reflection and a standing wave is established in the crystal. Critical values of the wave vector $K_{max} = \pm\pi/a$ if the Bragg condition is satisfied $2d \sin \theta = n\lambda$ if $\theta = \pi/2$, $d = a$, $K = 2\pi/\lambda$, $n = 1$ it is accepted so that $\lambda = 2a$. n can be not only 1, since the concept

of amplitude of a wave makes sense in the space between atoms, and the concept of amplitude of displacement of an elastic wave makes sense only in the vicinity of the atoms themselves. Group velocity: equations (GV, 1) and (GV, 2); eq. (Large Long Waves or Continuum approximation); experimentally found dispersion law eq. (Dispersion law, Experiment) for determination of the force constant eq. (C_p):

Group speed
Calculation of force constant from
Dispersion law, Experiment

$v_g = d\omega/dK$ or
 $v_g = \text{grad}_K \omega(K)$, (GV, 1)
 $v_g = (C_1 a^2/M)^{1/2} \cos \frac{Ka}{2}$, (GV, 2)
 $\omega^2 = K^2 \sum_{p>0} p^2 C_p \cdot \left(\text{Large Long Waves or Continuum approximation} \right)$

$$M \int_{-\pi/a}^{\pi/a} dK \omega_K^2 \cos Ka =$$

$$2 \sum_{p>0} C_p \int_{-\pi/a}^{\pi/a} dK (1 - \cos pKa) \cos rKa =$$

$$= -2\pi C_r/a. \quad \left(\text{Dispersion law Experimental} \right)$$

$$C_p = -\frac{Ma}{2\pi} \int_{-\pi/a}^{\pi/a} dK \omega_K^2 \cos pKa. (C_p)$$

Two atoms in primitive cell of the crystals lattice [4]: experimentally found dispersion law eq. (Dispersion law, Experiment) for determination of the force constant eq. (C_p) new features in the oscillation spectrum in crystals with several types of atoms: for each type of displacement (longitudinal and transverse) in the direction of propagation in the law eq. (dispersion law), i.e. in the function $\omega = f(K)$ two branches called **acoustic and optical branch**. (Fig.4 a) By analogy, the corresponding phonons are also called. Symbols: **LA are the longitudinal and TA transverse acoustic phonons; LO and TO are the longitudinal and transverse optic phonons** (Fig.4 a). Interaction only between first neighbor atomic planes: next mathematical scheme equations (2, 1)-(2, 1, 2) and (Fig.4 b); eq.(2, 1, 2) results optical $\equiv$ L eq.(2, 1, L) acoustic $\equiv$ T eq.(2, 1, T); Interaction only between first neighbor atomic planes: eq.(2, 1, 2) is solved exactly with respect to ω^2 , but simply in the boundary case $Ka \ll 1$ and $Ka = \pm\pi/a$ at the boundary of the zone. In $Ka \ll 1$ we have $\cos Ka \approx 1 - 0.5K^2a^2$ and two roots of eq.(2, 1, roots): eq.(2, 1, optical) and eq.(2, 1, acoustic); Values of K in the 1st zone of Brillouin is $-\pi/a \leq K \leq \pi/a$, where a is the lattice period; The 2nd case is for the boundary of 1st, where K is max, i.e. $K_{\max} = \pm\pi/a$ then eq.(2, 1, frequency) (Fig.4); The oscillations of the particles in the transverse acoustic (TA) and transverse optical (TO) branches are presented in Fig. 4 c. For optical branches at $K = 0$ of eq. (2, 1, and 2) and eq. (2, 1, L) eq. (2, 1, oscillate) can be found:

Two atoms in the primitive cell of the crystal lattice

$$M_1 \frac{d^2 u_s}{dt^2} = C(v_s + v_{s-1} - 2u_s),$$

$$M_2 \frac{d^2 v_s}{dt^2} = C(u_{s+1} + u_s - 2v_s), (2, 1)$$

$$u_s = u e^{iKs} e^{-i\omega t},$$

$$v_s = v e^{iKs} e^{-i\omega t}, (2, 1, \text{solution})$$

$$-\omega^2 M_1 u = Cv(1 + e^{-iKa}) - 2Cu,$$

$$-\omega^2 M_2 v = Cu(e^{-iKa} + 1) - 2Cv, (2, 1, 1)$$

$$M_1 M_2 \omega^4 - 2C(M_1 + M_2) \omega^2 + 2C^2(1 - \cos Ka) = 0, (2, 1, 2)$$

$$\omega^2 \approx 2C \left(\frac{1}{M_1} + \frac{1}{M_2} \right), (2, 1, L)$$

$$\omega^2 \approx \frac{C/2}{M_1 + M_2} K^2 a^2, (2, 1, T)$$

$$\omega^2 = 2C/M_1,$$

$$\omega^2 = 2C/M_2, (2, 1, \text{roots})$$

$$\frac{u}{v} = -\frac{M_2}{M_1}, (2, 1, \text{oscillate})$$

Fig. 4 Diatomic crystal structure in primitive cell of the lattice [4]: **a)** Optical and acoustic phonon branches in the dispersion law for a diatomic linear lattice. Frequency limits at $K = 0$ and $K = K_{\max} = \pi/a$, where a is the lattice constant; **b)** A diatomic crystal structure (in equilibrium and $M_1 = M_2$) and the displacement of the atomic planes are connected by a force constant C: the displacement of atoms with mass M_1 is u_{s-1}, u_s, u_{s+1} ; the displacement of atoms with mass M_2 is v_{s-1}, v_s, v_{s+1} ; a is period of repeatability in the direction of the wave vector K ; **c)** Transverse optical and transverse acoustic waves of equal length in a diatomic linear crystal lattice showing two types of particle oscillations (optical and acoustic).

The atoms move against each other as the center of their masses in the cell remains fixed. If the crystal absorbs a photon with the formation of a phonon, the storage condition of the wave vector leads to $k_{\text{photon}} = K_{\text{phonon}}$. From Fig.4 an it follows that there is no solution of the wave equation for waves propagating in a diatomic lattice when the frequencies are in the interval between $\sqrt{2C/M_1}$ and $\sqrt{2C/M_2}$. This is a characteristic feature of the propagation of elastic waves in a multi-atom lattice, i.e. we have a forbidden zone of frequencies located at the boundary $K_{\max} = \pm\pi/a$ on the 1st Brillouin zone. In this region there is no solution for the real value of K and the wave vector is a complex quantity; and any wave with frequency in this region is strongly absorbed. A long solution other than (2, 1, oscillation) corresponding to small values of K corresponds to an equality of amplitudes: $u = v$.

Optical properties in infrared region of the spectrum Fig. 4 and Fig. 5 [4]: How electromagnetic radiation acts in the infrared part of the (infrared) spectrum of (on) a crystal composed of two types of ions with charges $\pm e$ is. For large wavelengths or $K = 0$ the displacement is u_s, v_s does not depend on the index s. The equations of motion in a local electric field are: eq. (2, 2); solution eq. (2, 3)-(2, 3, 1), where μ is the reduced mass of the ion pair; ω_T is the frequency corresponding to $K \rightarrow 0$ for an optic branch. The applied local electric field causes a shift of the ions in the opposite direction - polarization of the crystal eq. (2, 3, 2), where N are positive and N negative charged ions. Eq.(2, 3, 2) always $\Rightarrow$ frequency-dependent dielectric constant eq.(2, 4) and at $\omega = \omega_T$ - resonance; Eq.(2, 4) it follows that electromagnetic waves cannot propagate in any (forbidden) frequency range (ω_T, ω_L) eq.(2, 5) and eq.(2, 4) is saved as eq.(2, 5, 1); the ratio between frequency and wave number for electromagnetic waves are eq.(2, 5, 2), eq.(2, 5, 3) and eq.(2, 5, 4); If ω real and $\epsilon(\omega)$ minus $\Rightarrow$ K is imaginary in (ω_T, ω_L); ω_L defined of eq.(2, 5) or Maxwell's eq.(2, 5, 5) it has: 1-st root of condition is $\text{div} E = 0$ at $K \perp E$; 2-nd root $\epsilon(\omega) = 0$ and $D = 0$ for longitudinal optical oscillations; Lydden-Sachs-Teller relation (2, 5, 6), where at small K ω_T is (frequency, transverse optical) and ω_L is (frequency, longitudinal optical) oscillations; In transverse oscillations of polarization P is $\gg$ E electric field at $\perp$ wave electric field, because E arises with an electromagnetic field eq.(2, 5, 7); and Fig. 5 [4]:

$$-\omega^2 M_1 u = 2C(v - u) + eE,$$

$$-\omega^2 M_2 v = 2C(v - u) - eE, (2, 2)$$

$$u - v = \frac{eE/\mu}{\omega_T^2}, (2, 3)$$

$$\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2}, \omega_T^2 = \frac{2C}{\mu} (2, 3, 1)$$

$$P = Ne(u - v) = \frac{Ne^2/\mu}{\omega_T^2} E, (2, 3, 2)$$

$$\epsilon(\omega) = \epsilon(\infty) + \frac{\omega_T^2}{\omega^2 - \omega_T^2} = [\epsilon(0) - \epsilon(\infty)], (2, 4)$$

$$\omega_T^2 < \omega^2 < \omega_L^2 = \omega_T^2 \frac{\epsilon(0)}{\epsilon(\infty)}, (2, 5)$$

$$\epsilon(\omega) = \epsilon(\infty) \frac{\omega_L^2 - \omega^2}{\omega_T^2 - \omega^2}, (2, 5, 1)$$

$$(CGS) c^2 K^2 = \epsilon(\omega) \omega^2; (2, 5, 2)$$

$$(SI) K^2 = \epsilon(\omega) \epsilon_0 \omega^2; (2, 5, 3)$$

$$\epsilon(Ks) \rightarrow \epsilon^{-1}(Ks), (2, 5, 4)$$

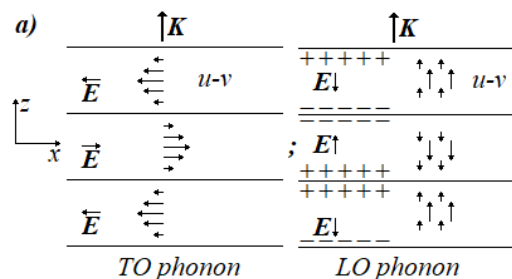
$$\epsilon(\omega_L) = 0, (2, 5, 4)$$

$$\text{div} D = 0 \text{ or } \epsilon(\omega) \text{div} E = 0, (2, 5, 5)$$

$$\frac{\omega_T^2}{\omega^2} = \frac{\epsilon(\infty)}{\epsilon(0)}, (2, 5, 6)$$

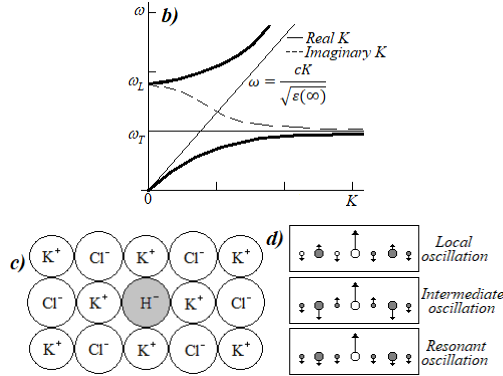
$$(CGS) P = \frac{\epsilon(\omega) - 1}{4\pi} E; (2, 5, 7)$$

$$(SI) P = \omega^2 [\epsilon(\omega) - 1] \epsilon_0 E; (2, 5, 7)$$



a) The relative displacement of the positive ions at a time point in the direction of the z axis is indicated by a set of arrows. Atomic planes have zero displacement; the atomic wounds for long-wave phonons are separated from each other by many atomic planes. **Left side:** transverse optical phonon mode, particles shift $\perp$ to wave vector K; the macro-electric field in an infinite medium acts only in the $\pm x$ direction for the mode shown, the symmetry of the problem is given by $\partial E/\partial x = 0$. It follows that $\text{div} E = 0$ for transverse optical phonons; **Right side:** the longitudinal optical phonon mode, the particle displacement and, therefore, the dielectric polarization P

is parallel to the wave vector. Macro-electric field $\mathbf{E}$ satisfies the ratio $\mathbf{D}=\mathbf{E}+4\pi\mathbf{P}=0$ in CGS and $\epsilon_0\mathbf{E}+\mathbf{P}=0$ in SI; the symmetry is conditioned by $\mathbf{E}$ and $\mathbf{P} \parallel$ on the z axis, and $\partial E_z/\partial z \neq 0$. Thus $\text{div}\mathbf{E} \neq 0$ for longitudinal optical phonons, and $\epsilon(\omega)\text{div}\mathbf{E}$ is equal to zero only if $\epsilon(\omega)=0$;



b) Related oscillations of phonons and transverse optical phonons in an ionic crystal: oscillation with frequency $\omega_T = 1$ without interaction with electromagnetic field - thin horizontal line; thin line marked with $\omega = cK/\epsilon(\infty)^{1/2}$ - electromagnetic wave in the crystal, not related to the oscillations of the lattice ω_T ; **thick lines are dispersion ratios in the interaction between the lattice oscillations and the electromagnetic wave:** thick lines are dispersion ratios in the interaction between the oscillations of the lattice and the electromagnetic wave, which increases the dielectric function according to the expression $\omega_T^2(\omega_T^2 - \omega^2)^{-1}[\epsilon(0) - \epsilon(\infty)]$ (see eq.(2.4)). One consequence is the appearance of a forbidden interval of frequencies between ω_T and ω_L : inside this interval the wave vector is a purely imaginary quantity - a dotted line. In the forbidden interval the wave vector is an imaginary quantity; the wave subsides according to the law $\exp\{-|K|x\}$ and the graphics shows a much stronger attenuation near the boundary ω_T than near ω_L . The region of variation of K corresponds to the left end region of the values of Fig. 4 a [4] for dispersion dependences; the corresponding oscillations do not depend on the electromagnetic waves; neither acoustic nor longitudinal optical phonons that are not associated with transverse electromagnetic fields are shown. A quantum coupled photon-phonon oscillation is called a **Polariton**; **c)** the hydrogen ion H^- , replacing Cl in the crystal of KCl : this impurity center is called the U-center. The high frequency local oscillations are caused by the ions H^- ; **d)** Amplitudes of oscillation of particles in a crystal with two atoms in the primitive cell: impurity atom is denoted by the light circle; intermediate, and resonances

Fig. 5 Zeros, poles of dielectric function and local phonon oscillations [4]:

Local phonon oscillations [4]: The phonon spectrum of the crystal can be altered by lattice defects and impurity atoms. In Fig. 5 c is the defect - an impurity atom called a U-center. The light ion H^- oscillates with high frequency in the vicinity of the heavier ion K^+ ; an electric dipole moment is formed; the crystal lattice to the H^- ion is slightly deformed in the process of motion, but the magnitude of the deformation must decrease rapidly with increasing distance from the H^- ion: this oscillation is called a *local phonon*. The ion of H^- is at the beginning of the coordinate system $s = 0$. The description solution is applied not with a traveling wave, but with a standing wave, which is the solution at the border of the Brillouin. The motion of an ideal lattice is represented by eq.(2, 6, Ideal lattice) and Solution to the boundary of the zone for undisturbed lattice eq.(2, 6, Solution); For broken lattice eq.(2, 6, 1 Real lattice), where α needs to be determined; eq.(2, 6, 2) and eq.(2, 6, 3) are compatible when $e^\alpha = (2M-M')/M'$ whence eq.(2, 6, 4), where $\omega_{\max} = (4C/M)^{1/2}$ is the border - off (threshold) frequency of the undisturbed grid for which $M = M'$. If $M \ll M' \Rightarrow$ eq. (2, 6 and 4) $\rightarrow$ eq. (2, 6 and 5):

$$\begin{aligned} M \frac{d^2 u_0}{dt^2} &= C(u_1 + u_{-1} - 2u_0) \\ M \frac{d^2 u_0}{dt^2} &= C(u_2 + u_0 - 2u_1), \quad \left(\begin{array}{l} 2, 6 \\ \text{Ideal lattice} \end{array} \right) \\ u_s &= u(0) \cos \pi n e^{-i\omega t} \equiv \\ u(0)(-1)^s e^{-i\omega t}, & \quad \left(\begin{array}{l} 2, 6 \\ \text{Solution} \end{array} \right) \end{aligned} \rightarrow \begin{aligned} u_s &= u_0(-1)^s e^{-i\omega t} e^{-|s|\alpha}, \quad \left(\begin{array}{l} 2, 6, 1 \\ \text{Real lattice} \end{array} \right) \\ \omega^2 &= (C/M)(2 + e^{-\alpha} + e^\alpha), \quad (2, 6, 2) \\ \omega^2 &= (C/M)(2 + 2e^{-\alpha}), \quad (2, 6, 3) \\ \omega^2 &= \frac{\omega_{\max}^2 M^2}{2MM' - M'^2}, \quad (2, 6, 4) \\ \omega^2 &= \omega_{\max}^2 (M/2M'), \quad (2, 6, 5) \end{aligned}$$

And the end on Fig. 5 d are shown so-called local, intermediate and resonant oscillations. The frequency of the local oscillation is higher than the maximum frequency of the "pure" (without impurities) crystal. The frequency of the intermediate oscillations lie within the interval between the acoustic and optical branches (see Fig. 5 b and Fig. 4 a). The frequency of the intermediate oscillations lie within the interval between the acoustic and optical branches. Heavy impurities can lead to quasi-local resonant oscillations, the frequencies of which lie in the region of the allowed phonon pairs of the ideal starting crystal; such oscillations are characterized by a greatly increasing amplitude of the oscillation of the impurity atom.

Thermal properties of dielectrics [4]: Heat capacity of crystal lattice Heat capacity at constant volume C_V is more fundamental quantity than heat capacity at constant pressure C_P eq. (3, C). Experimental facts: **1.** at room temperature, the heat capacity of almost all solids is close to $3Nk_B$, i.e. 25 J/mol.grad ; **2.** at low temperatures the heat capacity noticeably decreases and in the region of absolute zero the temperature approaches zero according to the law T^3 for dielectrics and according to the law T for metals. If the metal goes into a superconducting state, then the law of reducing the heat capacity is sharper than the law T for metals; **3.** In solid magnets, at any temperature range where there is an arrangement in the system of magnetic moments, a significant part of the total heat capacity consists of the contribution associated with the magnetic order; **Planck distribution function for the state of oscillators in thermal equilibrium and in excited states:** eq.(3, Planck), at $\hbar\omega < k_B T$ we have eq.(3, Planck, Classic condition) as far as $e^{\hbar\omega/T} \approx 1 + \hbar\omega/T + \dots \Rightarrow$ energy of every oscillator is $\langle \hbar\omega \rangle \approx k_B T$; at $\hbar\omega/k_B T \approx 1$. At low temperatures the relation $\hbar\omega/k_B T \gg 1$ and we have eq.(3, Planck, Low temperature); Einstein's model of heat capacity eq.(3, Einstein), eq.(3, Einstein, C_V), eq.(Number normal oscillation), eq.(Energy of small oscillation in $(\omega + d\omega)$); **Condition density function (CDF) in one-dimensional case** Fig.6 a and b: normal oscillation (modes) is a standing wave and solution is eq.(3, CDF, Sol.), eq.(3, CDF, K); at $K = \pi/L$ eq.(3, CDF, Sol_K); at $s=0$, $s=N$ boundary condition of the case $K = N\pi/L = \pi/a = K_{\max}$ eq.(3, CDF, Sol_{Kmax}); Fig.6 c; d eq.(3, periodic boundary condition, Sol) and at great system solution is running wave eq.(3, The case of great system, Sol) and of K (Allowed values) for two dimensional case Fig.6 e; function number of modes in one length of the frequency interval $\mathcal{D}(\omega)$; and the number of states $\mathcal{D}(\omega)d\omega$ close to ω is eq.(3, $\mathcal{D}$), eq.(3, $\mathcal{D}$, 1); approach to Debye eq.(3, Debye); for Einstein's N oscillators with frequency ω eq.(3, Einstein); Dirac δ -function eq.(Dirac); eq.(Dispersion law, || layers); eq.(Density mode); modes density in the three-dimensional case: eq.(3, $\mathcal{D}$, 3D case) and eq.(3, $\mathcal{D}$, 3D case 1), volume of K -space eq.(Volume, $\mathcal{D}$); function $\mathcal{D}$ in general case eq.(3, $\mathcal{D}$, Volume) and the end equations of the frequency and the wave vector for acoustic phonons in N primitive cells eq.(3, $\mathcal{D}$, 2). Physic-mathematical scheme of theoretical models is **from blocks I to block V, and Fig.6:**

$$\begin{aligned} \text{I} \quad C_p - C_v &= 9\alpha^2 BVT, C_v \equiv \\ T(\partial S/\partial T) &= (\partial E/\partial T)_V, (3, C) \\ \downarrow \\ \langle n \rangle &= (e^{\hbar\omega/k_B T})^{-1} \quad \text{or} \\ \langle n \rangle + \frac{1}{2} &= \frac{1}{2} \coth \frac{\hbar\omega}{2k_B T}, \quad \left(\begin{array}{l} 3 \\ \text{Planck} \end{array} \right) \\ \text{II} \quad \begin{aligned} (n) &= k_B T/\hbar\omega, \quad \left(\begin{array}{l} 3, \text{Planck} \\ \text{Classic condition} \end{array} \right) & u_s &= u(0) e^{-i\omega t} \sin \pi K a, \quad (3, \text{CDF, Sol}) \\ (n) &\approx e^{-\hbar\omega/T}, \quad \left(\begin{array}{l} 3, \text{Planck} \\ \text{low temperature} \end{array} \right) & K &= \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \dots, \frac{(N-1)\pi}{L}, \quad (3, \text{CDF, K}) \\ C_v &= (\partial E/\partial T)_V = \sum_K (n_K) \hbar\omega_K, \quad \left(\begin{array}{l} 3 \\ \text{Einstein} \end{array} \right) & u_s &\sim \sin(\pi s a/L), \quad (3, \text{CDF, Sol}_K) \\ Nk_B &= \left(\frac{\hbar\omega}{T} \right)^2 \frac{e^{\hbar\omega/T}}{(e^{\hbar\omega/T} - 1)^2}, \quad \left(\begin{array}{l} 3 \\ \text{Einstein} \end{array} \right) & u_s &\sim \sin \pi s, \quad (3, \text{CDF, Sol}_{K_{\max}}) \\ E &= \sum_K (n_K) \hbar\omega_K, \quad \left(\begin{array}{l} \text{Number} \\ \text{normal} \\ \text{oscillation} \end{array} \right) & u(s) &= u(s+L), \quad \left(\begin{array}{l} 3 \\ \text{Periodic} \\ \text{boundary} \end{array} \right) \\ E &= \int d\omega \mathcal{D}(\omega) (n(\omega, T)) \hbar\omega, \quad \left(\begin{array}{l} \text{Energy} \\ \text{of small} \\ \text{oscillation} \end{array} \right) & u_s &= u(0) e^{i[sK_0 - \omega t]}, \quad \left(\begin{array}{l} 3 \\ \text{The case} \\ \text{of great} \end{array} \right) \\ & & & \left(\begin{array}{l} \text{system} \\ \text{Allowed} \end{array} \right) \\ & & & K = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots, \frac{N\pi}{L} \end{aligned}$$

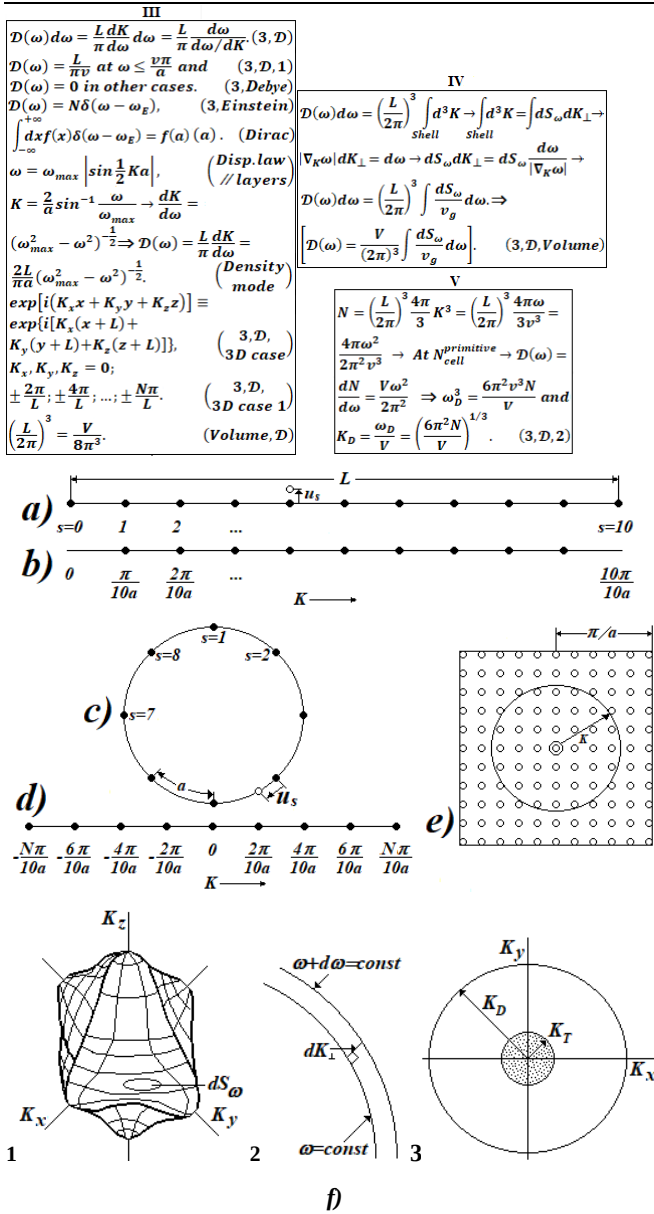


Fig. 6 [4] a) Linear lattice (chain) of $N + 1$ atoms at $N = 10$. Boundary conditions for attachment of terminal atoms, i.e. atoms in $s = 0$ and $s = 10$. In normal oscillations, longitudinal or transverse displacement; the displacement is described by the function $u_s \sim \sin sKa$; and boundary conditions: at $s = 0$ $u_s = 0$, and the value of K is chosen so that the offset at $s = 10$ is reversed to zero; b) The boundary condition of attachment: $\sin sKa = 0$ at $s = 10$ can be satisfied by choosing values of $K = \pi/10a, 2\pi/10a, \dots, 9\pi/10a$, where $10a = L$ is the length of the chain i.e. image of K -space for a chain. The points (*) are not atoms, but admissible values of K . Only $N-1$ particles can be moved from $N+1$ particles on the chain and in the most general case the motion can be described by $N-1$ values of K . Quantization of K has nothing to do with quantum mechanics; this is simply a classic consequence of the boundary conditions for the case of fixed terminal atoms of the chains. For each value of K we have three types of polarizations: two transverse (one - when the particle moves up and down in the plane of the drawing, the second - perpendicular to this plane) and (the third) is longitudinal when the particle moves to the left or right in the direction of the length.; c) N particles at equal distances from each other are located on a circle and vibrate around the equilibrium position only on the circle; the normal oscillation is the displacement at a distance u_s of the atom s ; two independent oscillations: longitudinal oscillation described by the function $\sin sKa$ and transverse oscillation described by the function $\cos sKa$; from the periodicity in the direction of the circle the boundary conditions are: $u_N = u_s$, i.e. the number of NKa is a multiple of 2π , at $N = 8$ the values of K are: $0, 2\pi/8a, 4\pi/8a, 6\pi/8a, 8\pi/8a$. Values $K = 0$ and $K = 8\pi/8a$ are only for $\cos sKa$ as long as $\sin s0a = 0$, and $\sin(s8\pi/8a) = \sin(s\pi) = 0$. The values $2\pi/8a, 4\pi/8a, 6\pi/8a$ for K give for $\sin$ and $\cos$ eight permissible normal oscillations (modes) for eight particles. The periodic boundary conditions for a circle give equality between the admissible normal oscillations and the number of particles, i.e. coincidence with the result of (b). If the function of

the normal oscillations is written in complex form: $\exp(isKa) \Rightarrow$ the boundary conditions again lead to eight normal oscillations with values of K : $0, \pm 2\pi/Na, \pm 2\pi/Na, \pm 2\pi/Na, \pm 2\pi/Na$ (for $N = 8$) same result eq. (Allowed values); d) The admissible values of the wave numbers K for periodic boundary conditions here for a linear chain of length L (1D lattice) at $N = 8$ (of eight atoms). The solution $K = 0$ corresponds to a homogeneous mode. The points $\pm N\pi/L$ correspond to the same solution ($e^{i\pi}$ coincides with $e^{-i\pi}$); for this we have eight permitted modes; displacement of the atom with number s are described by the functions: $1, \exp(\pm i\pi/4), \exp(\pm i\pi/2), \exp(\pm i3\pi/2), \exp(\pm i\pi)$; e) Permissible values of the wave vector of the phonon K in the Fourier space for a planar square lattice with constant a . Periodic boundary conditions here only inside the square with side $L = 10a$. A mode corresponding to the value of K is marked with a double circle. On an element of the surface with area $(2\pi/10a)^2 = (2\pi/L)^2$ corresponds to one allowed value of K , so that inside the circle with area πK^2 we have rounded $\pi K^2 (L/2\pi)^2$ allowed points; f) 1 - Elementary site dS_ω on the surface of the constant frequency in K -space. The volume of the layer between two surfaces with constant frequencies ω and $\omega + d\omega$ is equal to $dS_\omega d\omega / (\text{grad}_K \omega)$; 2 - The quantity $dK_\perp$ is the distance between the surfaces with constant frequencies ω and $\omega + d\omega$ taken in the direction of the normals to them; 3 - Visual explanation of Debye's T^3 law. Assumption: All phonon modes with wave vectors $K < K_T$ have classical energy $k_B T$, and the modes with wave vectors in the interval $K_T < K < K_D$ are not excited at all. Part of the excited modes of the possible $3N$ is $(K_T/K_D)^3 = (T/\theta)^3$, insofar as this quantity is equal to V_T/V_D , where $V_T = (4/3)\pi(K_T)^3$ and $V_D = (4/3)\pi(K_D)^3$. For the energy in the atom for this case we have $E \approx k_B T \times 3N(T/\theta)^3$ and for heat capacity $C_V = \partial E / \partial T \approx 3Nk_B(T/\theta)^3$. In addition for 3 we have $\hbar\omega_D = \hbar v K_D = k_B \theta; \hbar v K_T = k_B T$.

Debye's theory of the heat capacity lattice (HCL) [4]: energy of every type of polarization eq.(3, E, HCL), full energy at total energy at equal phonon velocities for the three types of polarization eq.(3, E, HCL 1), Debye's temperature eq.(3, θ , Debye) and eq.(3, θ , Debye 1), for energy is eq.(3, E, HCL 2) and heat capacity of lattice eq.(3, C_V , HCL) Values for Debye's theory are presented in the reference books [4]; Debye's T^3 Law: eq.(3, Law T^3 , 1), energy eq.(3, E, Law T^3) and heat capacity of lattice eq.(3, C_V , Law T^3):

$$\begin{aligned}
 E &= \int_0^{\omega_D} d\omega \mathcal{D}(\omega) n(\omega) \hbar\omega = \\
 &= \int_0^{\omega_D} d\omega \left(\frac{\omega^2}{2\pi^2 v^3} \right) \left(\frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \right). \quad (3, E, HCL) \\
 E &= \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \frac{\omega^2}{e^{\hbar\omega/k_B T} - 1} = \\
 &= \frac{3V k_B^4 T^4}{2\pi^2 v^3 \hbar^3} \int_0^{\omega_D} dx \frac{x^3}{e^x - 1}, \quad (3, E, HCL 1) \\
 \text{at } x \equiv \hbar\omega/k_B T &\equiv \hbar\omega_D/k_B T \rightarrow \\
 x_D &\equiv \frac{\hbar\omega_D}{k_B T} \equiv \frac{\theta}{T}. \quad (3, \theta, Debye) \\
 \theta &= \frac{\hbar v}{k_B} \left(\frac{6\pi^2 N}{V} \right)^{1/3} \text{ and } \rightarrow (3, \theta, Debye 1) \\
 E &= 9Nk_B \left(\frac{T}{\theta} \right)^3 \int_0^{\omega_D} dx \frac{x^3}{e^x - 1}. \quad (3, E, HCL 2) \\
 C_V &= \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} d\omega \frac{\omega^4 e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} = \\
 &= 9Nk_B \left(\frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2}. \quad (3, C_V, HCL)
 \end{aligned}$$

$$\begin{aligned}
 \int_0^{\omega_D} dx \frac{x^3}{e^x - 1} &= \\
 \int_0^{\omega_D} dx x^3 \sum_{n=1}^{\infty} e^{-nx} &= \\
 &= 6 \sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{\pi^4}{15}, \quad (3, Law T^3, 1) \\
 \text{at } T \ll \theta, \\
 E &= \frac{3\pi^2 N k_B T^4}{5\theta^3}, \quad (3, E, Law T^3) \\
 C_V &= \frac{12}{5} \pi^4 N k_B \left(\frac{T}{\theta} \right)^3 = \\
 &= 234 N k_B \left(\frac{T}{\theta} \right)^3. \quad (3, C_V, Law T^3)
 \end{aligned}$$

Equation (3, CV, Law T3) is the approximate Debye law of T3; at very low temperatures only acoustic oscillations are excited; are considered as elastic oscillations of a continuous medium (continuum), described by macroscopic constants [4]. Shortwave phonons at low temperatures: The energy is so great that no matter how inconspicuous their number of eq. (3, Planck, low temperature) they can fill the corresponding levels [4]. Debye's law of T^3 is explained on the basis of Fig. 6, f, 3. At low temperatures, only those lattice modes whose energy is $\hbar\omega \leq k_B T$ are excited in a noticeable amount. These modes is close to the classics, insofar as their energy is close to $k_B T$ and is described by law $\langle n \rangle \approx k_B T / \hbar\omega$. The volume of the K -space containing points corresponding to these excited modes occupies the part of the order of $(K_T/K_D)^3$, where K_T is the magnitude of the wave vector defined by the ratio $\hbar v K_T = k_B T$, and K_D is the magnitude of the wave vector characterizing the approximation of Debye is defined eq. (3, D, 2). This part is $(T/\theta)^3$ of the volume of K -space. The number of excited

modes will be of the order of $N(T/\theta)^3$, and the energy of each state $\sim k_B T$. Then the internal energy $\sim Nk_B T(T/\theta)^3$, the heat capacity $\sim 4Nk_B(T/\theta)^3$. The large numerical multiplier equal to 234 in (3, C_V , law T^3) appears for these reasons, as well as the multiplier $(6\pi^2)^{1/3}$ in determining the Debye temperature T^3 in eq. (3,0, Debye 1). Important [4]: 1. Temperature selection method θ for a suitable speed of sound at which the approximation to the law T^3 is true: It is $T < \theta/50$. C_V is a little sensitive to the change of the function of the density of the mode $\mathcal{D}(\omega)$; 2. Computer the best way to determine the function of the mode density $\mathcal{D}(\omega)$: 2.1 measurement of elastic scattering of neutrons in the crystal is used; 2.2 these data theoretical considerations and analytical methods can be used, a dispersion law for a chosen direction in the crystal is obtained.

Anharmonic interactions in crystals [4]: The potential energy in the lattice oscillation theory is limited to quadratic terms at interatomic distances, i.e. harmonic approximations; with consequences and peculiarities: 1. No thermal expansion; 2. Equality between adiabatic and elastic constants; 3. The elastic constants do not depend on pressure and temperature; 4. The heat capacity at high temperatures ($T > 0$) remains constant; 5. Two elastic waves in the lattice do not interact with each other, the individual wave does not break up over time and does not change its shape. **None of these consequences are fulfilled in real crystals:** the reason is that the anharmonic terms (i.e. higher than the quadratic ones) are not taken into account in the interatomic displacements:

Three phonons interaction – classic example
 $\omega_1 + \omega_2 = \omega_3$
 $U_{cub} = Ae_{xx}e_{yy}e_{zz}$, (4, Potential [anharmonic Energy] interaction)
 $U(x) = cx^2 - gx^3 - fx^4$, (4, thermal extension)
 $\langle x \rangle = \left(\int_{-\infty}^{\infty} dx x e^{-\frac{U(x)}{\tau}} \right) / \left(\int_{-\infty}^{\infty} dx e^{-\frac{U(x)}{\tau}} \right)$, $\tau \equiv k_B T$, (4, Boltzmann distribution possible function values)
 $\int dx x e^{-U(x)/\tau} \approx \int dx x e^{-cx^2/\tau} \left(x + \frac{1}{\tau} gx^3 + \frac{1}{\tau} fx^4 \right) =$
 $\frac{3\pi^{1/2}}{4} \frac{g}{c^{5/2}} \tau^{3/2}$, at $(gx^3 - fx^4) < k_B T$, (4, decomposition in order)
 cx^2 is in the exponent and we have decomposed
 $\exp\left[\frac{1}{\tau}(gx^3 + fx^4)\right] \approx 1 + \frac{1}{\tau}gx^3 + \frac{1}{\tau}fx^4 + \dots$
 $\int dx x e^{-U(x)/\tau} \approx \int dx x e^{-cx^2/\tau} = \left(\frac{\pi\tau}{c}\right)^{1/2}$, (4, decomp. 1 in order)
 $\Rightarrow$ in the classical case for $\langle x \rangle$ we receive:
 $\langle x \rangle = \frac{3g}{4c^2} k_B T$. (4, x)

COEFFICIENT OF LINEAR EXPANSION OF METALS
 $\alpha = \frac{1}{l} \frac{\partial l}{\partial T}$, (4, CLEM)

Mechanism of heat distribution is [4]: random process; similar to the diffusion process; energy in its path in the physical (material) environment, experiences multiple collisions. Flow of heat energy (FHE) Q in a long rod in which a temperature gradient dT/dx is eq. (4, Q, FHE), where K is coefficient of thermal conductivity; for description thermal conductivity (K) of solid dielectrics, Debye propose [4]: C is the heat capacity of a **phonon gas**; v is the **average velocity of phonon propagation**; l is the **average free path length of the phonons**. Flow of particles (molecules) in the direction of the x -axis is $(1/2)n\langle |v_x| \rangle$, where n is the number of molecules per unit volume; $\langle \dots \rangle$ mean average. Particle energy change here is eq. (4, ΔT , Particle energy loss), where c is particle heat capacity; τ is mean time between collisions; full flow of energy is eq. (4, Q, full flow particles energy) and for the case of phonons is eq. (4, Q, full flows phonons energy) and the end for K coefficient of thermal conductivity (CTC) we have eq. (4, K, CTC)

Debye: thermal conductivity of solid dielectrics

Flow of heat energy
 $Q = K \frac{dT}{dx}$, (4, Q, FHE) $\Rightarrow \Delta T = \frac{dT}{dx} l = \frac{dT}{dx} v \tau$, (4, ΔT , energy loss)

$K = \frac{1}{3} C v l$, (4, K, CTC)
 where $l \equiv v \tau$; $C = n c$.

$Q = n(v^2/c) \tau \frac{dT}{dx} = \left(\frac{1}{3} n(v^2) c \tau \frac{dT}{dx} \right)$, (4, Q, particles energy)
 full flow

$Q = \frac{1}{3} C v l \frac{dT}{dx}$, (4, Q, phonons energy)
 full flow

Crystal lattice thermal resistance: Two processes determine the magnitude of the average free path length of phonons l : 1. Influence of an-harmonic connections on the thermal resistance of the crystal

lattices; 2. Geometric scattering - from boundary surfaces and from defects in the lattice. Possible situations when these effects are dominant: An-harmonic interactions of the type eq. (3, Planck Classical condition): there is an interaction between the phonons, limiting l . Then the exact modes of anharmonic systems no longer resemble the usual phonons. Then the exact modes of anharmonic systems no longer resemble the usual phonons. Influence of anharmonic connection on thermal resistance due to lattice interactions. An approximate solution is given by Debay; it was later examined in detail by Pierrel. It is known from experiment: at high temperatures l is proportional to $1/T$. Explanation: A number of phonons interact with certain phonons; at high temperatures the total number of excited phonons according to eq. (3, Planck Classical condition) is proportional to T . The frequency of collisions of a given phonon must be proportional to the number of phonons it can collide with, therefore $l \sim 1/T$. **Need for thermal conductivity providing local thermal equilibrium in the distribution of phonons:** mechanism providing limitation of the average free path length; mechanism of collision of a phonon with statistical defects or boundaries of the crystal without changing the energy of the individual phonons: the frequency of the scattered phonon ω_2 is equal to the frequency ω_1 of the incident (initial) one: next equations of anharmonic plus geometric effects and Fig. 7

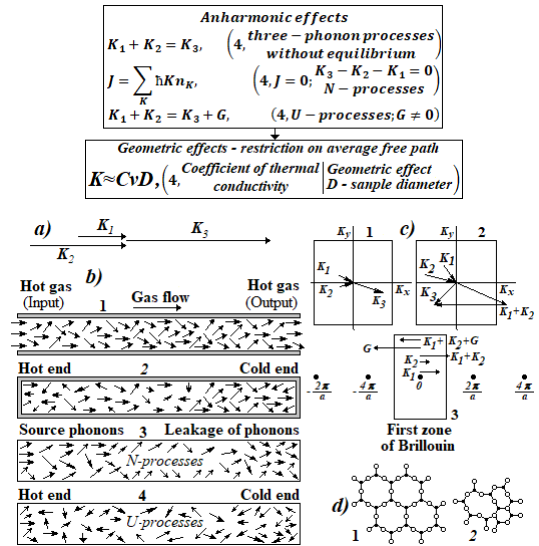


Fig. 7 [4] a) Collinear interaction of two longitudinal phonons K_1 and K_2 , and as a result a third longitudinal phonon K_3 is created (arises). In this part of the spectrum, where no dispersion occurs, the two laws can be satisfied: for energy conservation $\omega_1 + \omega_2 = \omega_3$ and for the conservation of wave vectors $K_1 + K_2 = K_3$; **b)** Schemes of transmission of particle flow in a long cylindrical volume (pipe): 1 - particle flow (gas molecules) without friction in the walls of the volume. Storage of full momentum and total particle energy: elastic collisions do not change the total momentum and total energy, with each collision the velocity of the center of mass of the particles and the total energy remain unchanged. Therefore, the energy is distributed from the hot to the cold end not due to the temperature gradient. The thermal resistance is zero and the thermal conductivity is infinitely large (∞); 2 - determination of the thermal conductivity of the gas without mass transfer (both ends of the pipe are closed): with a temperature gradient (average velocity is introduced $v_{average}$) - the velocity of the centers of mass of the colliding particles ($v_{particles}$) is greater, equal to or lower than $v_{average}$; if $v_{particles} > v_{average}$ the particles will tend to move to the left (hot) end, and if $v_{particles} < v_{average}$ the particles will tend to move to the right (cold) end. The small concentration gradient (of course the larger one on the right) is a means to help reduce the total mass transfer to zero, while creating the resulting energy transfer from the hot to the cold end.; 3 - stream of phonons in long crystal: Take the left end as a «phonon lamp» we get a stream of phonons to the left end. Only normal scattering processes (N-processes) take place in the crystal, in which $K_1 + K_2 = K_3$ the flux of phonons is kept unchanged by a full pulse and part of the phonons pass through the crystal along its entire length. Much of the phonon energy flowing from the right end can in principle be converted into radiation, creating a flow of phonons there. As in case (b, 1), the thermal resistance is equal to zero; 4 - Scattering with displacement processes (U-processes), in which $K_1 + K_2 = K_3 + G$ ($G \neq 0$) in each act of scattering the momentum of the phonons can change greatly. The primary flow of phonons when moving to the right will quickly

disintegrate. The ends of the crystal can be either a source or a drain. The result of energy transfer in the presence of a temperature gradient will have a place analogous to (b 2); c) Wave vectors in scattering processes: 1 - normal scattering process (N-process) $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$; 2 - Displacement process in which $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 + \mathbf{G}$; for a simple example, we work with a 2D rectangular grid in $\mathbf{K}$ -space. The square shows the first Brillouin zone in the $\mathbf{K}$ -space of the phonons. The points inside this zone correspond to all possible independent wave vectors of the phonons. The wave vectors directed to the center of the zone describe phonons of absorption; wave vectors directed from the center of the zone describe detachment phonons in collisions. It is clear that in the case of (c 2) in the processes of displacement in the direction of the $-x$ coordinate the flux of phonons is reversed. The vector of the inverse lattice $\mathbf{G}$, is shown in fig. 7 (c 2) has a length of $2\pi/a$, where a is the distance between adjacent atoms of the crystal lattice (lattice constant); the vector $\mathbf{G}$ is parallel to the axis $\mathbf{K}_x$. For both types of processes (N- and U-processes) the energy is stored, and for this $\omega_1 + \omega_2 = \omega_3$; 3 - Points from the inverse lattice in a polyatomic one-dimensional crystal (linear chain) with lattice constant a . A typical example of a displacement process (U-process): collision of two phonons with wave vectors $\mathbf{K}_1$ and $\mathbf{K}_2$. The vector sum $\mathbf{K}_1 + \mathbf{K}_2$ is a vector in the inverse lattice ending outside the first Brillouin zone; from eq. (1, Brillouin) such a vector is equivalent to the vector $\mathbf{K}_1 + \mathbf{K}_2 + \mathbf{G}$, lying inside the first zone ($\mathbf{G}$ is any suitable vector in the inverse lattice). Here is the diagram. $\mathbf{G} = -2\pi/a$. For the phenomena of thermal conductivity there is a difference in the processes in which $\mathbf{K}_1 + \mathbf{K}_2$ lies inside the 1st zone of Brillouin and the processes in which $\mathbf{K}_1 + \mathbf{K}_2$ lies outside it, and it is necessary to add a suitable vector $\mathbf{G}$ to obtain the resulting wave the vector lies inside the 1st zone; d) Differences between 2D schemes of crystal and glass shown by W.H. Zachariasen (1932): 1 - a regularly repeating structure of atoms in a crystal; 2 - chaotic arrangement of atoms in glass (quartz, the lines indicate the directions of the bonds; black circles are the atoms of oxygen).

Anharmonic effects eq.(4, three-phonon processes without equilibrium), eq.(4, $J=0$, $\mathbf{K}_3-\mathbf{K}_2-\mathbf{K}_1=0$, N-processes), eq.(4, U-processes, $\mathbf{G}\neq 0$) and the geometric effects eq.(4, Thermal conductivity coefficient, Geometric effect of the D sample diameter) and (Fig. 7) of phonon scattering at the thermal resistance of the lattices are important information for us for mathematical description of the processes of formation of structures during casting.

Free electrons. Fermi gas [4]: The models of free electrons are used to explain a number of very important physical properties of metals and especially of *simple metals*: 1. The least bound electrons are the valence ones that make up the metal atoms and can move freely enough in the volume of the crystal lattice; 1.1 The valence electrons in metals are carriers of electric current and are called 'conduction electrons'; 2. In free electron models: the forces of interaction between valence electrons and ionic skeletons can be neglected; the calculations are such that, as if the electrons were indeed free, they can move freely in any area of the sample; 3. The total energy of the electrons can be assumed equal to the kinetic energy, and the potential energy can be neglected; 4. But free electrons experience a strong electrostatic potential from ionic skeletons. Free electron models are convenient for experimental evaluations of their kinetic properties; 4.1 but in general it is necessary to take into account the effects of the interaction of conduction electrons with the lattice. *Simple metals*: these are the alkali metals (lithium, sodium, potassium, cesium and rubidium). In all of them, the conduction electrons are almost like free electrons; Exception: These are metals in which there is an overlap of the d-shells or where the energy of the electrons is close to the conduction band. The electrons in the d-shells are usually less mobile than the s- and p-electrons; They are added to simple metals (except alkali) Be, Mg, Ca, Sr, Ba, Al, Ga, In, Tl, Zn, Cd, Hg and Pb. Precious metals (Cu, Ag, Au), transition metals, lanthanides are not simple metals. (An example of a simple (alkali) metal is: sodium (Na) [4]. The valence electron of the Na atom is in the 3g state, in the metallic state this electron is established as a conduction electron and travels freely in the crystal. A monovalent metal crystal consisting of N atoms and N positive ionic skeletons. Ten electrons of Na + ions are located successively in the states 1s, 2s and 2p of the free ion. The distribution of electrons by states in the ionic skeleton is exactly the same as in the metal atom. **Important comment:** The classical theory, the models of free electrons is well

developed; and the interpretation of the properties of metals has led to the following [4]: **Successes:** Derivation of Ohm's law, establishing the connection of current with the magnitude of the electric field and the derivation of the ratio between electrical conductivity and thermal conductivity; **Difficulties:** classical theory is not able to explain: 1. The behavior of heat capacity by temperature and para-magnetic susceptibility by conduction electrons; 2. Why are the free path lengths of the conduction electrons so large. It is known from experiments that free electrons move freely without collision with other conduction electrons or ionic skeletons and do not deviate from the *straight path* at distances consisting of many lattice constants. In the purest samples at low temperatures, the average free path length can reach $10^8 \div 10^9$ between-atomic distances (more than 10 cm), which is much larger than the expected classical estimates. The answers to the questions are sought: Why is the condensed medium so transparent to conduction electrons? Why do conduction electrons behave like a gas of non-interacting particles? The answer to these questions consists of two parts: a) Conduction electrons do not deviate from ions because the ions are located in a regular periodic lattice in which the waves (in this case the electron waves), as in any periodic structure, propagate freely; b) Conduction electrons rarely scatter from other conduction electrons. This property of electrons is a consequence of Pauli's principle. A gas of free, non-interacting electrons that obeys Pauli's principle, we will call *Fermi gas of free electrons* [4]. Schrödinger's equation is the **«law»** of physics, explaining physical phenomena; if applicable, it should lead to the prediction of experimental data. Schrödinger proposed his equation for the final explanation of the atomic structure using wave function $\Psi(x, t)$ [3].

$$\Psi(x, t) = \Psi(x)e^{(-2\pi i/\hbar)Et}, \quad (\text{Wave Function})$$

$$\frac{-\hbar^2}{8\pi^2 m} \frac{\partial^2 \Psi(x)}{\partial x^2} + V(x)\Psi(x) = E\Psi(x), \quad \left(\begin{array}{l} \text{Schrödinger} \\ \text{1D case} \\ \text{without } t \end{array} \right)$$

Wave functions of free particles		Energy quantization: a particle in a potential box
$\frac{\partial^2 \Psi}{\partial x^2} + \frac{8\pi^2 m E}{\hbar^2} \Psi = 0, \quad \left(\begin{array}{l} \text{Schrödinger} \\ V(x) = 0 \end{array} \right)$	$\Psi(x) = \exp[ix\sqrt{8\pi^2 m E/\hbar^2}], \quad (4, \text{Solution})$	$\Psi(x) = \frac{\sin kx}{\cos kx}, \quad \left(\begin{array}{l} \text{4, } \Psi \text{ is some} \\ \text{combination} \end{array} \right)$
$\Psi(x, t) = \exp\left[\frac{-2\pi i}{\hbar}(Et - x\sqrt{2mE})\right], \quad \left(\begin{array}{l} \text{4, Running} \\ \text{wave} \end{array} \right)$	$y = \sin(kx - \omega t), \quad \left(\begin{array}{l} \text{4, Description} \\ \text{oscillating} \end{array} \right)$	$\Psi(L) = \sin kL = 0, \quad (4, \Psi, L)$
$y = e^{i(kx - \omega t)}, \quad \left(\begin{array}{l} \text{4, string} \\ \text{movement } y \end{array} \right)$	$\Psi = e^{i(kx - \omega t)}, \quad \left(\begin{array}{l} \text{4, wave} \\ \text{formula} \end{array} \right)$	$k = \frac{n\pi}{L}, \quad n = 1, 2, \dots, \infty, (4, \Psi, k)$
$E = \frac{\hbar\omega}{2\pi}, \quad \left(\begin{array}{l} \text{4, Einstein's} \\ \text{ratio} \end{array} \right)$	$k = \frac{2\pi p}{\hbar}, \quad \left(\begin{array}{l} \text{4, de Broglie} \\ \text{ratio} \end{array} \right)$	$E = \frac{\hbar^2 k^2}{8\pi^2 m}, \quad n = 1, 2, \dots, \infty, (4, E)$
		$(\Delta x)(\Delta p) = \hbar, \quad \left(\begin{array}{l} \text{particle uncertainty} \\ \text{min } E \end{array} \right)$
		$E = \frac{\hbar^2}{8mL^2}, \quad (4, \text{quantization } E)$

$$\Psi(x, t) = \Psi(x)e^{(-2\pi i/\hbar)Et}, \quad (\text{Wave function})$$

$$\frac{-\hbar^2}{8\pi^2 m} \frac{\partial^2 \Psi(x)}{\partial x^2} + V(x)\Psi(x) = E\Psi(x), \quad (4, t)$$

$$\frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{8\pi^2 m E}{\hbar^2} \Psi(x) = 0, \quad \left(\begin{array}{l} \text{4, } \Psi \\ V(x)=0 \end{array} \right)$$

$$\frac{-\hbar^2}{8\pi^2 m} \Delta \Psi + V(x, y, z) \Psi = E \Psi, \quad (4, t, 3D)$$

$$V = \begin{cases} 0 & 0 < x < L \\ 0 & 0 < y < L \\ 0 & 0 < z < L \end{cases} \quad \left(\begin{array}{l} \text{General} \\ \text{4, potential} \end{array} \right); \Psi = 0 \quad \left(\begin{array}{l} \text{Boundary} \\ \text{condition} \end{array} \right)$$

$$\Delta \Psi + \frac{8\pi^2 m E}{\hbar^2} \Psi = 0, \quad (4, t, 3D, 1)$$

$$\Psi(x, y, z) = \Psi_1(x) \Psi_2(y) \Psi_3(z), \quad (4, t, 3D, 2)$$

$$1/\Psi_1 \Psi_2 \Psi_3 \quad (4, t, 3D, 2, 1)$$

$$\left(\frac{1}{\Psi_1(x)} \frac{\partial^2 \Psi}{\partial x^2} + \frac{1}{\Psi_2(y)} \frac{\partial^2 \Psi}{\partial y^2} + \frac{1}{\Psi_3(z)} \frac{\partial^2 \Psi}{\partial z^2} \right) + \frac{8\pi^2 m E}{\hbar^2} = 0, \quad (4, t, 3D, 3)$$

$$\Psi_1^2 \frac{\partial^2 \Psi}{\partial x^2} = -k_1^2, \quad \Psi_2^2 \frac{\partial^2 \Psi}{\partial y^2} = -k_2^2, \quad \Psi_3^2 \frac{\partial^2 \Psi}{\partial z^2} = -k_3^2,$$

$$k_1^2 + k_2^2 + k_3^2 = \frac{8\pi^2 m E}{\hbar^2}, \quad (4, t, 3D, 4)$$

$$(4, t, 3D, 5)$$

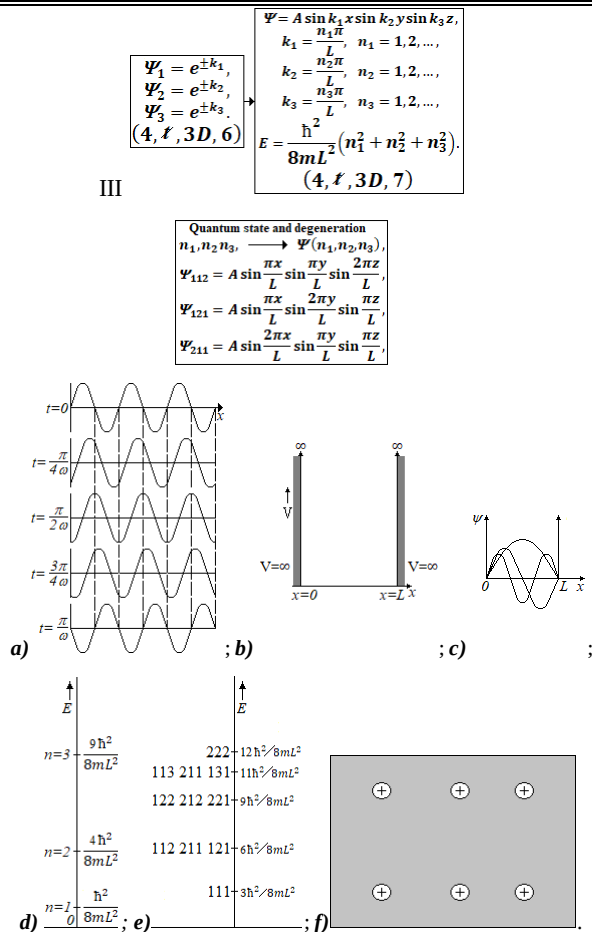


Fig.8 Quantum Mechanics [3]: a) Wave functions of free particles: running wave eq.(4, Description running wave); over time, the phase of a point moves evenly to the right at the phase speed ω/k ; b) Particle potential energy in a one-dimensional potential box; c) Some wave functions of a particle moving in a one-dimensional potential box; d) Energy spectrum particle moving in a one-dimensional potential box; e) Energy levels of a particle moving in a three-dimensional potential box; f) Crystal sodium model. The light circles are the ionic skeleton of Na^+ ; they are ((immersed)) in an electron fluid formed by conduction electrons. Electronic conductivity is the former valence electrons of Na. In isolated atoms, these electrons are in $3s$ -states. The ion skeleton stores 10 electrons in the $1s^2 2s^2 2p^6$ configuration. The total volume of the ionic skeleton of the alkali metals is a small part ($\approx 15\%$), but in the noble metals (Cu, Ag, Au) the ionic skeleton is relatively large (the ions touch each other). At room temperature, alkali metal crystals have a volume-centered cubic structure, and precious metals have a wall-centered cubic structure.

Stefan's task describes the nonstationary field solidification with the motion of the interfacial surface of the first-order phase transition [12] and it is 1st task; 2nd task is [13], which describes the first-order phase transition of the system cast-mold with contact temperature between them. Third Stefan's task is [1], where we have a moving a moving volume in which the latent heat of melting is dissipated. Work [7] is also of great importance for the circular economy. With the zone melting method; and the results in [7] are also associated with a significant environmental effect. Engineering studies are important for the phase stability and performance of casting [7]. The use of modern testing tools in [7] and even more so in mathematical experiments based on quantum [2 and 5] it will be studied as [7] will be very simplified. There is a very good methodological coincidence between: [8] and [11]; and between [8] and [9]. In [9] it is measured supercooled per melt. Thus develop Stefan's task [1] of taking into account the latent heat of melting connects fundamental theory and engineering research. Now can use heuristic methods. I [14] a very good study of heuristic rules for the formation of laws was made. A basic cycle [14] is proposed: **problem-method-solution**, respectively **hypothesis-conclusions-verification**. Heuristics rules by American physicist Holton and Roller present seven steps for formulating laws [14]. 1. Knowledge

of modern science; 2. Close knowledge of natural experience and observation; 3. Reaching the question or problem; 4. Preliminary knowledge of the type of expected solution; 5. Specific concepts that analyze the problem situation; 6. Emergence of a working hypothesis, by trying the simplest hypothesis, various independent checks are made; before accepting an experimental result of significance, never consider the hypothesis as beyond and necessarily reevaluate an reformulate the old knowledge in the light of the new; 7. Design and perform experiments that are more specific and better specific and better controlled.

Everything written is well known. But the great difficulties come from the need to work very quickly and especially professionally with modern scientific and engineering knowledge.

3. Conclusions – Materials Science Knowledge

Working with modern knowledge requires continuous learning and orientation in many contradictory cases.

Working with modern knowledge leads to the creation of more or less, very difficult negotiations of the fundamentally known and with a strict mathematics, mathematical physics and the best patents.

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Habits of nanocrystals of cubic and hexagonal systems

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Abstract: habits of coordinational polyhedras are considered as forms of nanocrystals. Habits for coordination polyhedra with numbers from 1 to 30 are given. It was analyzed the cubic and hexagonal lattices. There are the next nanocrystals: primitive, cubic and inter-centered and face-centered and diamond-like (all cubic) and hexagonal close packed.

KEYWORDS: NANOCRYSTALS, HABITS, COORDINATION POLYHEDRONS, CUBIC LATTICES, HEXAGONAL CLOSE PACKED

1. Introduction

The forms of nanocrystal polyhedra (habits) depend on the crystallographic system. The surface of habit polyhedra (HP) of various sizes has different reticular densities. This affects to some technological parameters, for example, the modifying activity of the filling agent in polymer composites.

Knowledge about the habits of nanocrystals (HNC) is needed not only for solving technical problems, but also for diagnostics and medical treatment, and other [1, 2].

The vertices of the GNC are the atoms of the same coordination sphere (CS). At the same time, the number of faces can exceed the order of the point group, since atoms (vertices) can belong to planes with different groups linked by point symmetry. For example, planes (5 0 0) and (4 3 0).

2. The results of computer simulation

The object of the study was crystals with equal spherical shapes. It was analyzed the lattices with next unit cells:

1. Primitive cubic (PC).
2. Volume-centered cubic (BCC). This unit cell is a combination of two PC cells when the original coordinate of the 2-nd cell is shifted to the point $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$ of the first unit cell.
3. Face-centered cubic (FCC). It is a combination of four PC cells. If the first cell is taken as zero, then the origin of coordinates of other cells will shift to the first cell, and as follows – the second cell to the point $[\frac{1}{2}, \frac{1}{2}, 0]$, the third to the point $[\frac{1}{2}, 0, \frac{1}{2}]$, fourth to point $[0, \frac{1}{2}, \frac{1}{2}]$.
4. The diamond-like system (DL). The unit cell of DL is complex from two FCC-cells when the original coordinate of the 2-nd cell is displaced to $[\frac{1}{4}, \frac{1}{4}, \frac{1}{4}]$ of the first cell.
5. Hexagonal close-packed system (GPU). This system is a two-layer closest packing of spherical atoms [3, 4].

HP with numbers for all these lattices are shown in Figures 1 – 5.

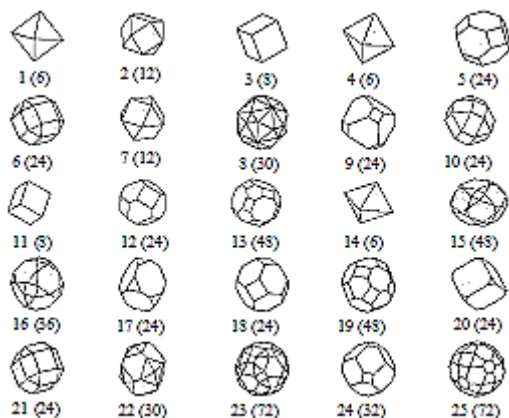


Fig. 1. Habit polyhedra of primitive cubic (PC)

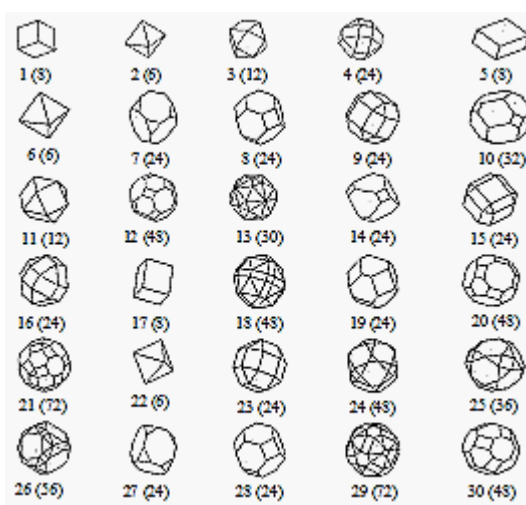


Fig. 2. Habit polyhedra of volume-centered cubic (BCC)

All vertices of a single polyhedron are located on the same coordination sphere. Coordination numbers are indicated in brackets.

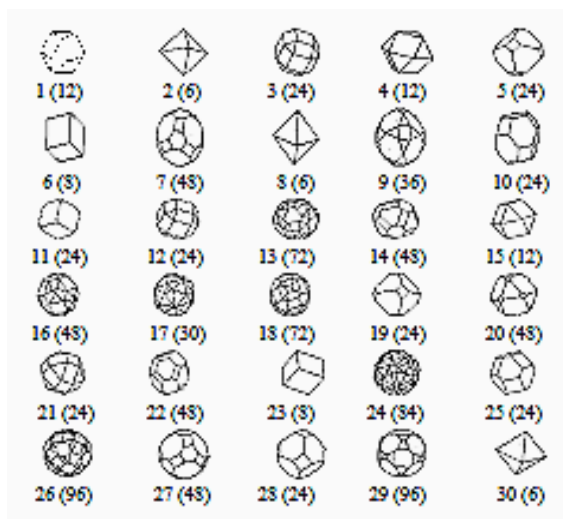
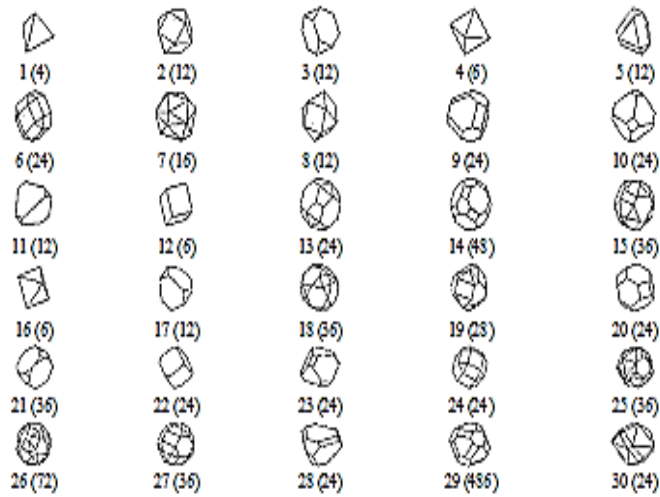


Fig. 3. Habit polyhedra of face-centered cubic (FCC)



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Fig. 4. Habit polyhedral of diamond-like system (DL)

The polyhedron ($n - 1$) is inside the polyhedron (n) and these polyhedra do not have common vertices (atoms).

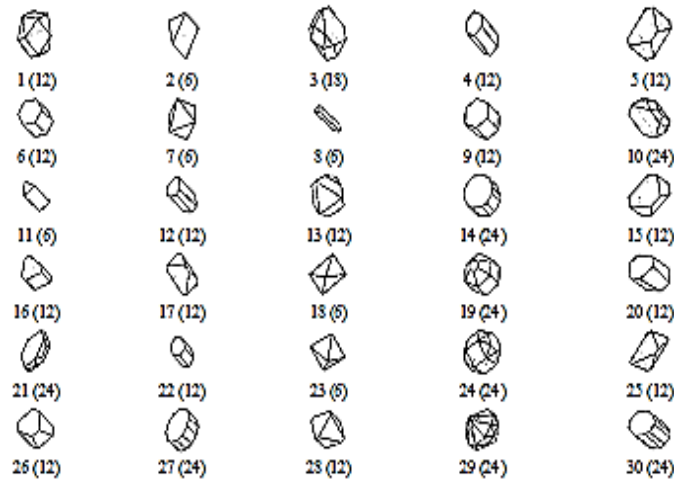


Fig. 5. Habit polyhedral of hexagonal close-packed system (GPU)

The polyhedrons in Figures 1–5 are shown at different scales.

The number of atoms in a particle is equal to the sum $\sum_{j=1}^n n_j$, where n_j is the number of vertices of the j -th polyhedron. All polyhedra are ideal models.

In real nanoparticles certain polyhedra (especially external) can be unfinished. But everyone can see that there are differences in the reticular densities of the n -th and $(n - 1)$ -th polyhedra.

3. Conclusion

A computer program has been developed to determine the structural forms of polyhedra for crystals. The vertices of the polyhedra are atoms of the same coordination sphere with number (n). As an example it was given the polyhedrons with n from 1 to 30 for P, I, F cubic and hexagonal lattices.

The technological properties of nanocrystals depend not only on the structural - chemical parameters and sizes of nanocrystals, but also on their surfaces, because the reticular densities can be different even for two neighboring (n -th and $(n - 1)$ -th) polyhedra of a nanocrystal. The program can be used to obtain an image of the cells of n - polyhedra, as well as to calculate the number of vertices and atoms in them.