

**PRINCIPLES OF A NEW PHASE NUCLEATION DEVELOPMENT FOR THE MULTY
- PHASE INDUSTRIAL REAL POLY CRYSTALLINE MATERIALS.
PART I: THE PRINCIPLES FOR THE NOMINALLY MONO – PHASE MATERIALS**

*Tkachenko Igor, Miroshchenko Yurii, Tkachenko Olesia, Miroshchenko Victoria,
Miroshchenko Sergii, Tkachenko Svitlana*

Annotation. *Based on thermodynamics, dislocation theory together with own theoretical and experimental results, a new phase nucleation development for the mono - phase industrial real poly crystalline materials was analized. At first, the terms “multy-phase” and “mono-phase” materials were specified and reformulated, introducing an addition one3 “nominally”. The dislocation substructure role in solute chemical elements segregation and subsequent new phase nucleation was analyzed. It was theoretically shown and experimentally verivied possibilities to obtain super fine and homogeneous structure due to isothermal holding at optimal both temperature and duration for the nominally mono-phase metal materials. It was shown that the possibilities may be expanded on other multiphase materials, particularly, Grey and White Cast Irons.*

Keywords: *a new phase nucleation, dislocation substructure, grain boundaries, solute element segregations, ultra fine structures.*

1.1. Evaluation the role of various factors in a formation of microstructures in polycrystalline metallic materials.

As it was shown in [1-3], the most of modern industrial metallic materials are, in principle, multiphase real alloys because they contain the defects of crystal lattices, at first –dislocations, as well as such micro-sized elements of their internal structures (particles, phase conglomerates) which are different from the predominant (main) component of a material volume - the matrix phase. It is **necessary** to special notice here, that according to the commonly accepted principles, the term “real”, contrary to “ideal”, we shall use further to characterize crystals having such linea defects of crystal lattices as dislocations.

Besides, the above mentioned additional (second) phases can be specially created in a material, most often with the aim of its strengthening (harderning phases), but - second phases can also occur arbitrarily in a material during a production process and be undesirable components of the microstructure (non-metallic inclusions). In practice of material science and industrial production, it is conventional to indicate only those phases that are specially introduced in a material with the aim of necessary changes its functional properties.

In addition, it has been experimentally proven that large-sized inclusions of second phases do not cause the expected changes in properties if their volume fraction does not exceed the certain level [3]. Taking into account the above, it is commonly accepted to consider metallic materials that have in their structures no more than 50 % of large-sized particles or conglomerates (non-metallic inclusions, pearlite-like components) of second phases, as **single (mono)-phase materials**. As the examples, low carbon, low perlite steels may be considered. At the same time, materials that contain in their structures even a small volume fraction of particles of strengthening phases are referenced to as **two-phase** materials, without taking into account the possible presence of additional phases there.

Based on the above, we will further consider materials whose properties are determined by the characteristics of the matrix phase – as **nominally mono - phase materials**, despite the possible presence of other phases in their structures. At the same time, as materials of the second group – or **nominally two-phase** materials, we shall consider the ones the properties of which are determined by both the characteristics of the matrix phase structure together with the volume fraction and morphology of the second phase particles. As the corresponding examples of the last type materials, Grey and White Cast Irons, together with particle hardened structural steels (09G2SAF) will be considered further.

It is well known also that dislocations are always presented in a structure of any crystalline real (non-ideal) solid solution, which as a rule is a matrix phase for all industrial metallic materials. Such

linear defects of the internal structure of crystals even in a state of thermodynamic equilibrium [1,4] form **dislocation subboundaries (DS-s)**. Such boundaries are also called **internal phase boundaries** and **low-angle boundaries**

It has been established [1,4] that there can be two types of DS-s : **tilt boundaries** and **torsion boundaries**, which are formed by ordered arrays of edge and screw dislocations, respectively. In the case of tilt boundaries, such an array in a stable state is a dislocation "wall" consisting of edge dislocations oriented parallel each other in one crystallographic plane. A characteristic feature of such a "wall" is the presence of a long-range field of significant elastic deformations, the potential of which is the sum of the corresponding potentials of individual dislocations [1]. As to the torsion boundaries, the corresponding dislocation arrays consist of two sets of parallel screw dislocations that intersect each other. The maximum stability of the just specified dislocations sets can be achieved only if they form a hexagonal network as a result of dislocation reactions between individual ones of both arrays. A characteristic feature of such a network is the absence of a long-range field of elastic deformations in the surrounding volumes of a crystal.

1.2. Theoretical evaluation the role of the matrix phase dislocation substructure in a new phase nucleation in real poly crystalline nominally mono-phase metallic alloys

Taking into account the inevitable elastic distortions of a crystal lattice around the atoms of dissolved chemical elements and inevitable existence of DS-s in real metallic alloys, the above facts show the possibility of the simultaneous development of two processes: formation of segregations of alloying or impurity elements on DS-s of certain types, as well as changes in the internal structure of DS-s, that affect their ability to form segregations of chemical elements. Besides, it's evident that poly-crystals contain another internal defect type in microstructures which donot have strain fields in their vicinity. It is about **grain boundaries (GB-s)** or **high angle internal interfaces (HAIIn-s)** which also strongly effecting the solute atom distributions [5] due to decreasing free energy of the atoms forming segregations on GB-s.

In addition to the above definitions, the role of DS-s, as one type of the defect configurations in real crystals, should be considered as important [4,5] in the process of nucleation of new phases in real crystals. However, the simultaneous contribution of DS-s and segregations of chemical elements formed on them in the formation of the microstructure of metal alloys has not been studied in detail either theoretically or experimentally so far.

1.2.1. Theoretical identification the features of a new phase nucleation in real polycrystalline mono-phase metallic alloys

In the text below, we identify theoretically some features of the processes of nucleation of a new phase in polycrystalline metal alloys on DS-s for substitutional element segregations there, and to experimentally verify the results of theoretical analysis.

Theoretical analysis in the current work was performed for double polycrystalline real alloys ***AB***, where ***A*** - is a solvent chemical element that has a polymorphic phase transformation $\alpha \leftrightarrow \beta$ and ***B*** - is a dissolved chemical element. It is well known [1], that there may be two possible types of the phase diagrams low temperature parts of which are shown on Fig.1. Namely, the types correspond,

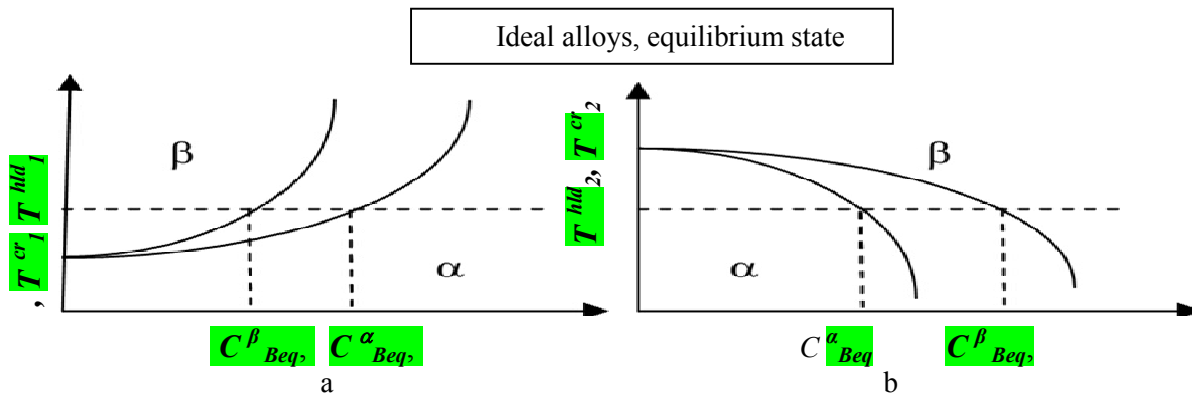


Fig.1. Schematic representation of the typical low temperature parts of the equilibrium phase diagrams for ideal alloys A-B potentially containing α and β -phases. It is necessary to take into account that for the scheme (a) we have: $C^{\alpha}_{Beq} > C^{\beta}_{Beq}$, but, in the region (b): - $C^{\alpha}_{Beq} < C^{\beta}_{Beq}$.

respectively, to limiting equilibrium solubility of the element B in relatively high (β -) and low (α -) temperature phases (see Fig.1a,b). we shall consider the processes occurring in a polycrystal consisting of α - and β - phases during the equilibrium heterogeneous phase transformations: $\alpha A(B) \leftrightarrow \beta A(B)$ at

$T^{eq}_1 = const$ and $\beta A(B) \leftrightarrow \alpha A(B)$ at $T^{eq}_2 = const$, where, in general case, $T^{eq}_1 \neq T^{eq}_2$ at unchanged external parameters. The equilibrium concentrations of the dissolved element B in the α - and β -phases, can be determined based on the parts of the equilibrium diagram (see Fig.1)

Mandatory processes that develop during the nucleation and growth of crystals of a new phase are the formation and evolution of their dislocation substructure. As is known [1,5], these processes are developed by the limited multiple sliding and annihilation of individual mobile dislocations under the influence of the forces of their long-range elastic interaction. As a result of the interactions, the groups ("walls") of parallel direct dislocations of the same sign are formed in individual crystallographic planes. Under such conditions, one should expect, first of all, the formation of groups of parallel screw dislocations, which have the highest mobility according to the known mechanism [1,4], due to the absence of strictly defined slip planes for them. The specified process has a significantly lower speed in the case of edge dislocations due to the need for limited development of the creep process. The main features of a separate group consisting of parallel screw dislocations are a high level of elastic deformations in the surrounding volumes of a crystal and its extremely high mechanical instability [4,5]. In this regard, on a certain stage of the evolution of the dislocation substructure, dislocation networks arise, which include two sets of straight, parallel each other screw dislocations located in the same plane, but misoriented on a certain angle, which leads to a mutual rotation of two parts of a mono- crystal.

The characteristic features of such a dislocation torsion boundary are the presence of a significant field of elastic deformations in the surrounding volumes of mono-crystal, as well as increased energy of the considered network, which leads to its mechanical instability[1,4]. Complete stabilization of the torsion boundaries occurs only as a result of the formation of hexagonal configurations by the components of dislocations due to dislocation reactions, which requires significant thermal activation.

It is well known that the sliding speed of dislocations in a crystal under the influence of only long-range elastic fields is much higher than the speed of their thermally activated movement (compare the slip and the creep) and approaches the speed of sound. So, we can propose the following development sequence for the above processes depending on their speed. Besides, the same sequence is assumed to be valid to describe the evolution of the dislocation substructure, during the formation of the alloy structure in result of an equilibrium heterogeneous phase transformation:

- formation of isolated groups of parallel each other screw dislocations in one of the crystallographic slip planes, with significant long-range fields of elastic deformations, in result of multiple sliding of the dislocations, under the influence of the long-range interaction forces of individual dislocations;
- formation of dislocation "networks" with enhanced fields of elastic deformations (unstable torsional boundaries), which are formed due to the pairwise intersecting, previously formed groups of parallel screw dislocations, because of the influence of long-range interaction between them;

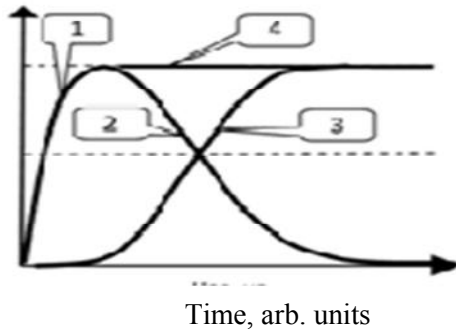


Fig. 2. Proposed schematic illustration of the holding-time effect on the elastic energy produced by various dislocation substructure components during its formation in a mono-crystal: (1) - “walls” or “networks” formed from arrays of parallel screw dislocations (unstable torsion DS-s); (2)- stable torsion DS-s; (3)- tilt DS-s; (4) – overall elastic energy

- formation of completely stable torsion boundaries (without elastic deformation fields) due to the close-range interaction (thermally activated dislocation reactions) of screw dislocations of the different previously existing groups,

- formation of dislocation tilt boundaries with significant surrounding fields of elastic deformations, by forming “walls” of parallel edge dislocations with the participation of thermally activated processes of their creep. Taking into account the equilibrium nature of the phase transformations considered in this work and the absence of changes in the external parameters of such an alloy (mechanical work under the polycrystals), the total density of dislocations in any mono-crystal of such an alloy should be considered as unchanged. Taking into account the fact [2] that the energy of dislocations is concentrated, mainly, in the form of a field of elastic deformations within

the entire mono-crystal, we may conclude that a constant level of elastic energy is reached in a crystal during the formation of its quasy-equilibrium microstructure. At the same time, under the effect of the above-considered processes of dislocation interaction, a redistribution of elastic energy within each individual mono-crystal is possible.

Based on the above, the sequence of reorganization for the dislocation substructure in a mono-

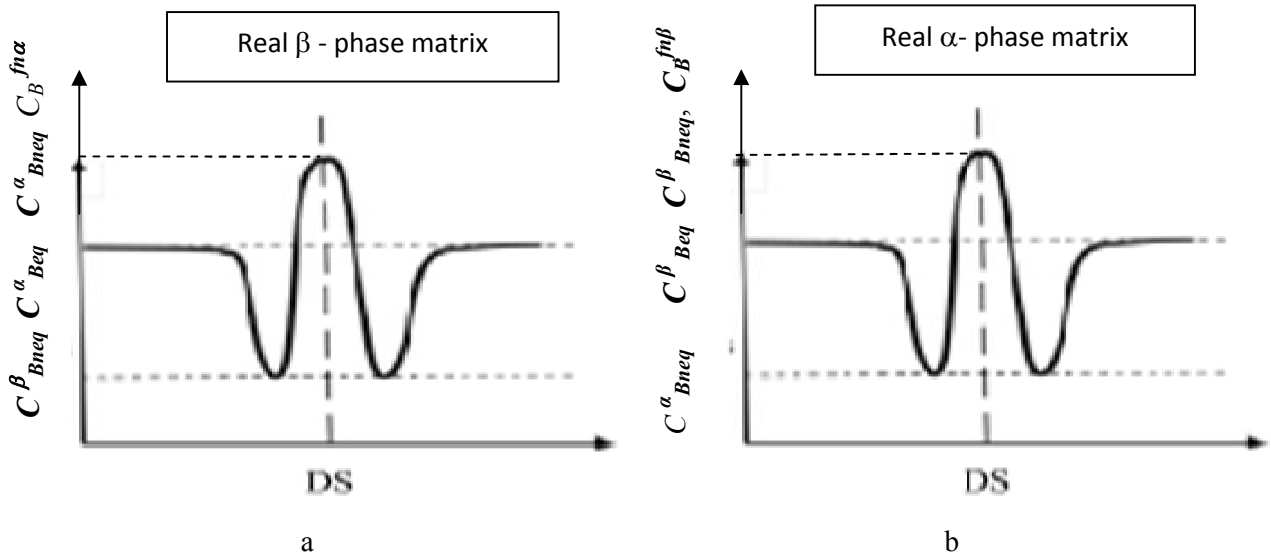


Fig.3. Schematic representation of the solute chemical element B distribution in both real (a) β - and (b) α - matrix phases near a DS. Nonequilibrium low concentrations are not shown on the scheme due to their practical coincidence with the equilibrium ones (compare solid and dotted lines near the coordinate origin on Fig.4)

crystal being in a quasy-equilibrium state considered above, can be illustrated by the scheme shown in **Fig.2**. The scheme shows time dependences of the energy of the elastic deformation fields arising around individual groups of dislocations and dislocation subboundaries (curves 1, 2, 3), together with the total energy of the elastic field in a mono-crystal (curve 4). In particular, it follows from the

scheme that at the initial stages (curve 1) of the formation of an “equilibrium” or quasy-equilibrium dislocation substructure, the elastic energy of a mono-crystal is associated mainly with the fields that arise around the "walls" or "networks". Such dislocation configurations are formed, respectively, by intersecting pairwise arrays of parallel screw dislocations (by unstable torsional DS-s). In their turn, such unstable DS-s are formed, as is known, by motion of dislocations, which occurs practically without the participation of thermal fluctuations, i.e., at high speed, due to the long-range elastic interaction of individual screw dislocations. Subsequently, under the action of thermal fluctuations and therefore with the close average velocities, (curves 2, 3), there is a simultaneous formation of stable torsion DS-s. Such DS-s, have a hexagonal configuration of the constituent dislocations, as well as tilt DS-s, consisting of groups of parallel edge dislocations. These processes of torsion and tilt DS-s formation are accompanied by alternative changes, i.e., redistribution, of the energies of the eigenfields of long-range stresses around such DS-s, which ensures the conservation of an unchanged level of the total elastic energy in a mono-crystal (curve 4).

Thus, at the final stage of microstructure evolution, the decisive role in ensuring a constant level of elastic energy in a mono-crystal is played by tilting DS-s with high energies of their own elastic deformation fields. Such DS-s are parts of the dislocation substructure, together with stable torsional DS-s, which do not have corresponding long-range fields.

Based on the known data [5] regarding the interaction of DS-s with atoms of dissolved chemical elements, the distribution of their concentrations near and along such DS-s should to occur due to long-range fields of elastic deformations in a mono-crystal which are formed by such DS-s. The distribution can be modeled using the scheme shown in **Fig.3**.

The scheme particularly shows, that an isothermal holding for a long time providing approaching equilibrium conditions, during heating or cooling at temperatures $T^{hld}_{1(2)}$ exceeding (Fig. 4a) or lesser (Fig. 4b) than equilibrium critical temperatures $T^{cr}_{1(2)}$: $T^{hld}_1 > T^{cr}_1$ and $T^{hld}_2 < T^{cr}_2$, respectively, gives the formation of crystals of a new (α or β) phase having all the quasy-equilibrium characteristic values.

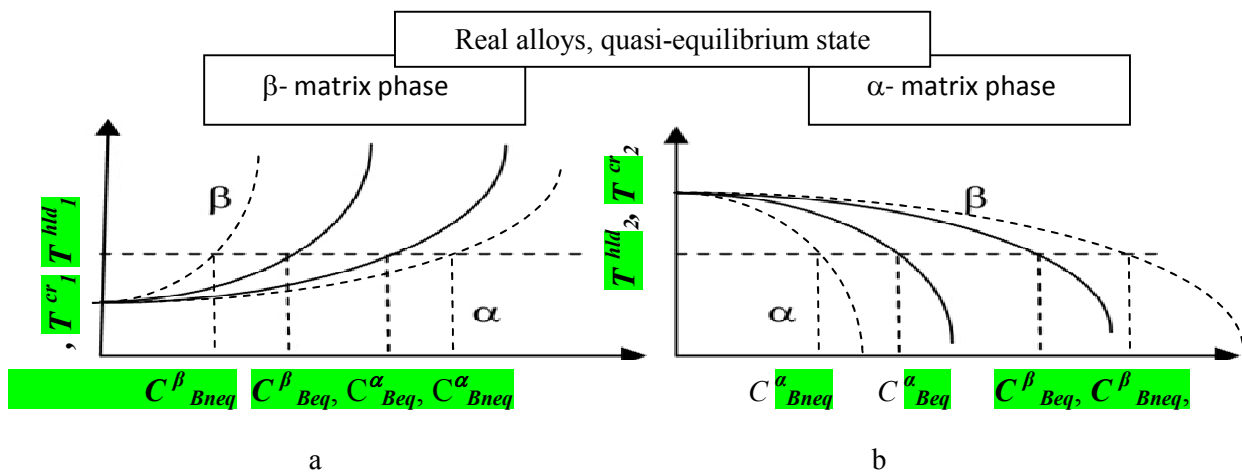


Fig.4. Chematic representation of the low temperature parts of possible phase diagrams for real (quasi-equilibrium) alloys A-B having dislocation substructure (dotted lines) together with equilibrium (solid) lines and potentially containing α and β -phases. Take into account that for the scheme (a) we have: $C^{\beta}_{Bneq} > C^{\beta}_{Beq} > C^{\alpha}_{Beq} > C^{\alpha}_{Bneq}$ but, in the scheme (b): $C^{\alpha}_{Bneq} < C^{\alpha}_{Beq} < C^{\beta}_{Beq} < C^{\beta}_{Bneq}$.

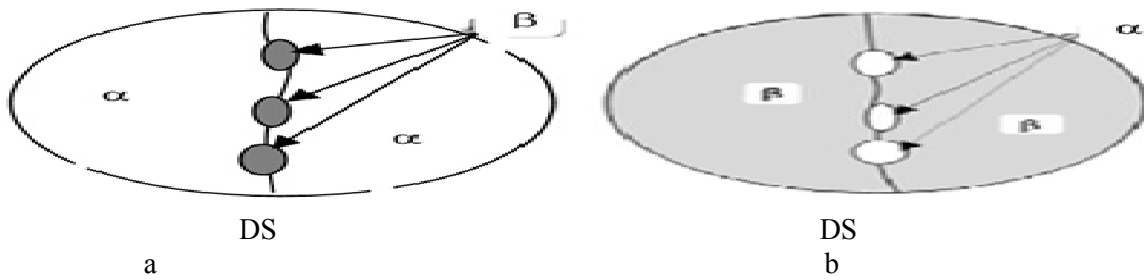


Fig.5. Schematic representation of a new phase non equilibrium nucleation on DS in monocrystals of both quasy-equilibrium (a) α - and (b) β - phases

Meantime, due to inevitable formation of dislocation networks in any quasy-equilibrium initial matrix phases: β (see Fig.4a) or α (see Fig.4b) and the interaction of the solute element B atoms with the DS-s, the lines of the equilibrium phases shift in such a way that expand the regions of the $\alpha + \beta$ coexistence

Scematically the above notions may be illustrated by a scheme shown on Fig.5 [6]

1.3. Experimental verifications of the theoretical results

It should be noted here that above theoretical analisys has some lacks caused by impossibility to take into account theoretically all peculiarities of the processes developed during the holding at the relevant temperatures of real metal polycrystals with various chemical compositions. However the analysis caches the main features of new phase nucleation in such alloys. It may be seen from metallographic data related to the holding durarion effect on the microstructure formation in low alloy steels (see Fig.6) [6].

Given the tendency of the most chemical elements which are dissolved in metal alloys to form segregations on GB-s, one should expect the development of the processes similar to the above considered ones (on DS-s) with the formation of corresponding distributions of dissolved elements

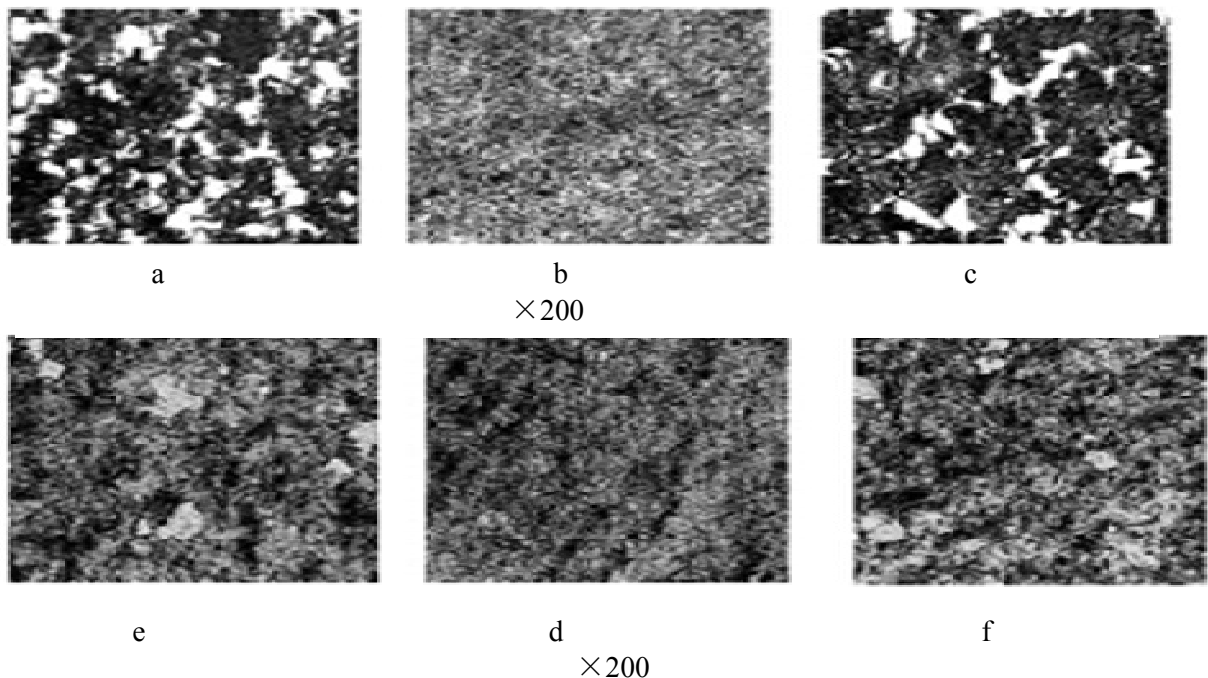


Fig.6. Effect of isothermal holding duration at 830°C on microstructure formation in hipo-eutectoid (a,b,c) and hyper-eutectoid (c,d,f) steels: a,e – 10 min, b,d – 30 min, c,f -120 min

and, subsequently, crystals of α - and β -phases nearby or directly on GB-s [9]. According to [15], an important additional factor determining the nuclei distribution for a new phase by potential places of their formation: GB-s or DS-s, is temperature. This leads to the possibility of refining and homogenizing the distribution of crystals of a new phase and chemical element concentrations in the microstructure of polycrystals. As it should be concluded from the above, such situation may be created by making the conditions during the heat treatment providing the formation of segregations of dissolved elements on DS-s in the interiors of grains of an initial matrix phase.

So, based on the theoretical results obtained and experimental data shown on **Fig. 6**, confirming the results, we can formulate the following conclusions regarding the time-stages formation of the quasy-equilibrium microstructures in polycrystalline real metallic alloys with a well developed dislocation substructure, taking into account the elastic interaction effects:

- at the initial time-stage, the nonequilibrium formation of new phase crystals should be expected exclusively on DS-s, in local volumes near or on isolated groups of parallel screw dislocations

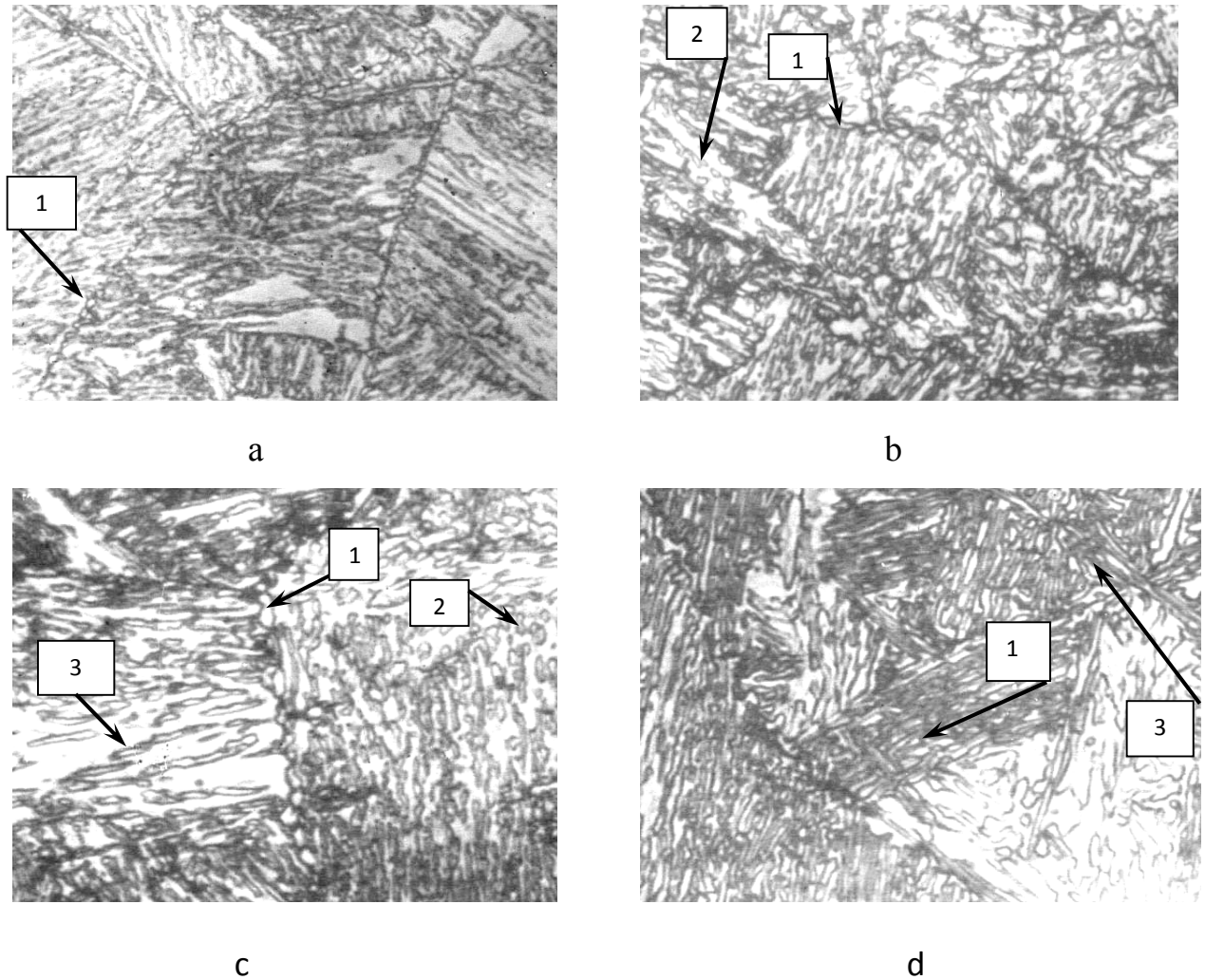


Fig.7. Typical microstructure areas of the Cr-Ni-Mo-V-Cu steel formed after isothermal holding during 18 hours at temperatures: (a) 660 °C, (b) 690 °C, (c) 710 °C, (d) 725 °C. [6], $\times 1000$

- 1- new phase “islands” on high angel boundaries separating martensite packets;
- 2- new phase “islands” on low angel boundaries separating martensite plates withing the packets;
- 3- elongated new phase “islands” along low angel boundaries separating martensite plates

and unstable torsion sub-boundaries;

- the transition time-stage corresponds to the simultaneous formation of new crystals on all existing types of DS-s;
- at the final stage when the elastic interaction between DS-s and solute atoms is practically absent, new crystals form in any potential places.

In other words, extra long holding at the constant temperature providing a new phase nucleation on DS-s within quasy-equilibrium matrix phase leads finally to formation of conventional microstructures typically observed in a material as a result of ordinary heat treatment. Such conclusion is very well known from numerous ordinary industrial technology application results.

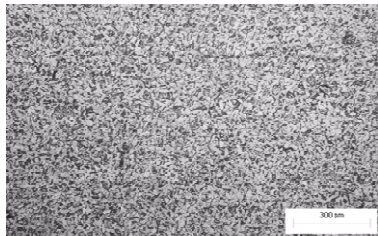
Experimental verification of the above conclusions in the work was carried out by the metallographic analysis of some samples of hypo- and hyper-eutectoid steels after heat treatment regimes that provide different conditions for the nucleation of a new phase in grain interiors [5,6]. (See **Fig.6**)

Besides, the analysis conducted does not take into account, for example, the fact of beginning the phase transformation in a low carbon alloy Cr - Ni – Mo – V- Cu steel at holding during heating at about 660 instead of 710 C deg., according to equilibrium data. However, the feature does not effect on the final results due to effective holding at 690 C deg.(See Fig.7) [6].

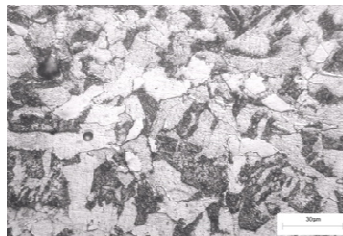
The steel of the above chemical composition was, probably, first developed in former USSR to provide the hardening particles precipitation of two types: cutted Cu based particles and bypassed V-based carbonitrides. Namely combination of these types particles was hoped to provide the highest strength of Cr-Ni-Mo war shipbuilding steels which was known as AK-35(36). However, in reality, the impact strength of such steels was sporadically decreased, that is why the researches were conducted to eliminate the problem by new heat treatment development. The researches were conducted by one of the author of this paper and the obtained results show that the main reason of the low impact fracture work of the steel was spartial inhomogeneous precipitation of hardening particles. Namely, they are formed on the matrix GB-s in the course of high temperature heating for hot rolling and further low speed cooling. Thus, big grain size in the steel was fixed and cannot be changed by any further relatively low temperature heating for quenching, due to decreased diffusion speed of the steel alloy substituting chemical elements. So, many time heating the steel for example for quenching cannot gives any positive effect on the impact resistance of the steel. The technical problem of the Cr-Ni-Mo-V-Cu embrittlement was solved by the heat treatment application [6] which provides precipitation of hardening particles not on the matrix phase GB-s but – in interior of the grains. (See Fig.7). The technology was implemented in “Azovstal” I&S works and was used in 1980-1990 for production some volumes of thick sheets for war ships building.

An additional verification was made on the both industrial E36 and 35Cr-Mo cast steel. Despite the fact of hardening particles possible appearance in the steels structures, during the optimal isothermal holding the microstructures were formed shown on **Fig.8** [7].

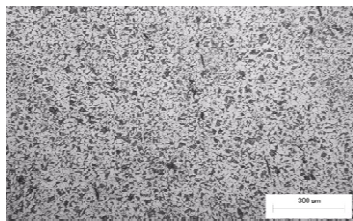
It should be noted here that the above results relate to binary or more complex metallic alloys able to have heterogeneous phase transitions $\alpha \leftrightarrow \beta$, where the phases are solid solutions with the dislocation substructures. Meantime, there are numerous industrial metallic materials microstructure of which contains matrix phase as a solid solution together with particles of “second” phases of various forms and sizes. We mean, first at all, White and Grey Irons together with particle hardend alloys. The application of the principles, which are the basics of the novel proposed heat treatment regimes or regenerative heat treatment technology, to the last type of the metallic materials will be considered below. It is necessary to emphasize that the all peculiarities, revealed during the analysis, we will take into account during the industrial technology development further.



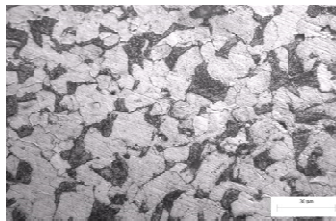
a (x100)



b (x1000)



c (x100)



d (x1000)

Fig.8. Microstructures of the E36(a,b) and 35Cr-Mo cast (c,d) steels after isothermal holding at the time-temperature conditions providing realization of the above discussed principles.[7]

REFERENCES

1. J. Christian, *The theory of transformations in metals and alloys*. Part 1, (London, EN: Pergamon Press, 1975), 786
2. R.W.K. Honeycombe, *The Plastic Deformation of Metals*, Edward Arnold, London (1984)
3. Tkachenko I.F., Tkachenko K.I. and Miroshnichenko V.I.(2016) Some features of the heterogeneous diffusive nucleation and their use to form new type microstructures and eliminate chemical nonuniformities in bulk industrial product made of alloy structural steels. Svidotstvo № 68323 dated 25.10.2016. Application №68903 dated 25.08.2016, Ukraine
4. J. Hirth and J. Lote, *Theory of Dislocations*, Krieger Pub. Co., (1992)
5. J. Martin, *Micromechanisms in particle hardened alloys*. (Cambridge, EN: Cambridge Univ. Press, 1980)
6. Tkachenko I.F. Dissertation Dr. Technical Sciences, Mariupol, 1998
7. Tkachenko I.F. Formation of identical fine grained microstructures with high impact resistance in as cast and as hot rolled conventional low alloy structural steels/ Tkachenko I.F., Miroshnichenko V.I., Tkachenko K. I. // Contributed Papers from Materials Science and Technology 2018 (MS&T18) October 14–18, 2018, Greater Columbus Convention Center, Columbus, Ohio, USA