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Thermal stability of nanomaterials

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Abstract. The main processes and phenomena (grain growth, phase transformations, relaxation, diffusion, and so on) in nanomaterials subjected to heat treatment are considered. Experimental data and theoretical views on the thermal stability of nanomaterials are analysed and generalised. Attention is drawn to unsolved problems. The bibliography includes 152 references.

I. Introduction

At present, the concept of nanomaterials (NM), the development of which has been substantially stimulated by a number of publications,[1–3] is widely known. This is indicated, for example, by the fact that representative all-Russian and international conferences and seminars dealing with nanomaterials have been regularly held for many years; this subject is also actively discussed at the Symposia of the American Materials Research Society (MRS) and the NATO Advanced Study Institute (NATO ASI); monographs, collections of works, and reviews have been published (see, for example, Refs 4 – 24).

The main emphasis in the above-mentioned studies[1–3] was put on the crucial role of numerous interfaces existing in NM. The properties of solids containing such interfaces can be changed appreciably both by structural and electronic modification and by using new doping resources irrespective of the type of bond, size factors, *etc*. When the grain or crystallite size (L) is several nanometers, the proportion of interfaces in the total bulk of the material is at least $\sim 50\%$. This value was approximately estimated from the $3s/L$ ratio, where s is the width of the near-boundary region; for a reasonable value $s \approx 1$ nm, a proportion of 50% is attained when $L \approx 6$ nm. Gleiter and coworkers[1–3] proposed a method for producing nanomaterials, which included preparation of ultradisperse powders by vaporisation – condensation and subsequent *in situ* compaction at high pressures. This procedure gave disk-like specimens 10 – 20 mm in diameter with a height of up to 0.1 – 0.5 mm. In order to obtain high-purity specimens, it is necessary to eliminate contact of the highly reactive powders with the environment (although these specimens usually contain up to 10% – 20% of residual porosity). However, initially, this fact was ignored and gave rise to some erroneous inferences (see, for example, Ref. 21).

This method for the preparation of NM was assimilated by researchers in many countries, first of all, in the USA (Siegel's group in the Argonne National laboratory[25] and research groups in some other universities); this triggered an avalanche-like accumulation of data concerning the properties of NM.

The first Russian session devoted to the research of properties of consolidated NM was held in 1984 and called the first All-Union Conference on the Physical Chemistry of Ultradisperse Systems.†

In an earlier study of NM published in 1983,[27] it was shown that compaction of ultradisperse nickel powders at high pressures and moderate temperatures furnishes NM with a crystallite size of about ~ 60 nm with a hardness exceeding that of usual polycrystalline nickel by a large factor. Unfortunately, the publications cited[26,27] have passed almost unnoticed by both Russian and foreign specialists. Meanwhile, these studies[27] demonstrated one more time, independently of the results obtained by Gleiter and coworkers,[1–3] the validity of the known Hall – Petch relationship, which relates strength (hardness) to the grain size ($H \sim L^{-1/2}$) in the nano-size range, and the expediency of extending this relationship to NM. At present, the greatest L value is taken to be ~ 100 nm.[17,20,21]

In view of the relatively small dimensions of NM crystallites (and, correspondingly, the numerous interfaces they contain), it becomes clear why it is important to study the nanostructure evolution, which is accompanied by changes in the properties of NM, upon heat treatment or other types of treatment. Naturally, these items attract attention of researchers; various aspects of the problem of NM stability have been considered in a number of papers, reviews, and monographs (see, for example publications[14,18,20–22,28–31]); however, generally, this item does not appear to be adequately studied.

In terms of the fields of application, one can distinguish the following main functional types of NM for which thermal stability is especially significant: tool materials and materials for high-temperature friction units; thermal and diffusion barrier components; high-temperature semiconductors, catalysts, and sensors; porous, emission and filter component parts; and refractory materials of various types. The knowledge of thermal stability patterns is also important for NM manufacture technology. In particular, when selecting the optimal conditions for superplas-

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† Proceedings of this conference were published only in 1987.[26]

ticity and when developing the conditions for controlled crystallisation from the amorphous state and for plasma sputtering of nanostructured coatings and high-energy methods for consolidation of ultradisperse powders, specialists should take into account conditions for nanostructure maintenance. The information outlined above accounts for both the theoretical and practical interest in the problems of thermal stability of NM.

II. The key types, structure, and general characteristics of nanomaterials

The concept of NM introduced by Gleiter and coworkers,[1–3] mainly in relation to metal-like materials, has now substantially expanded. Twenty years later, Gleiter[22] considered a broader spectrum of NM, apart from the above-mentioned objects, namely, semiconductors, polymers, diamond-like and supramolecular structures, and biomaterials. This can be supplemented by ceramics, catalysts, nanoporous materials, and a large number of nanocarbon and, generally, nanotubular structures; the scope of investigations of these materials is swiftly extending.

The NM listed above have been prepared by different methods and have different types of microstructure. Table 1 and Fig. 1 present data concerning compact and nonpolymeric NM.[21,22] Classification according to the composition, distribution, and the shape of structural components implies three kinds of structural shapes (layer-shaped, rod-shaped, and equiaxed forms) and four sorts regarding the chemical composition and component distribution, namely, single-phase compositions, statistical multiphase compositions with either identical or non-identical interfaces (*i.e.*, the possibility of segregation is taken into account), and matrix compositions. The number of structural types can be greater due to mixed variants, the presence of porosity and so on. One should

Table 1. Key methods for the preparation of compact NM.

Preparation technique	Main types	Objects
Powder technology	Gleiter method (gas-phase deposition and compaction) electric-discharge sintering hot pressure treatment high static and dynamic pressures at ambient and high temperatures	elements, alloys, compounds
Severe plastic deformation	equal-channel angular pressing high-pressure torsion pressure treatment of multilayer composites phase cold hardening	metals and alloys
Controlled crystallisation from the amorphous state	normal and high pressures	amorphous materials
Film technology	chemical vapour deposition (CVD) physical vapour deposition (PVD) electrodeposition sol – gel processes	elements, alloys, compounds

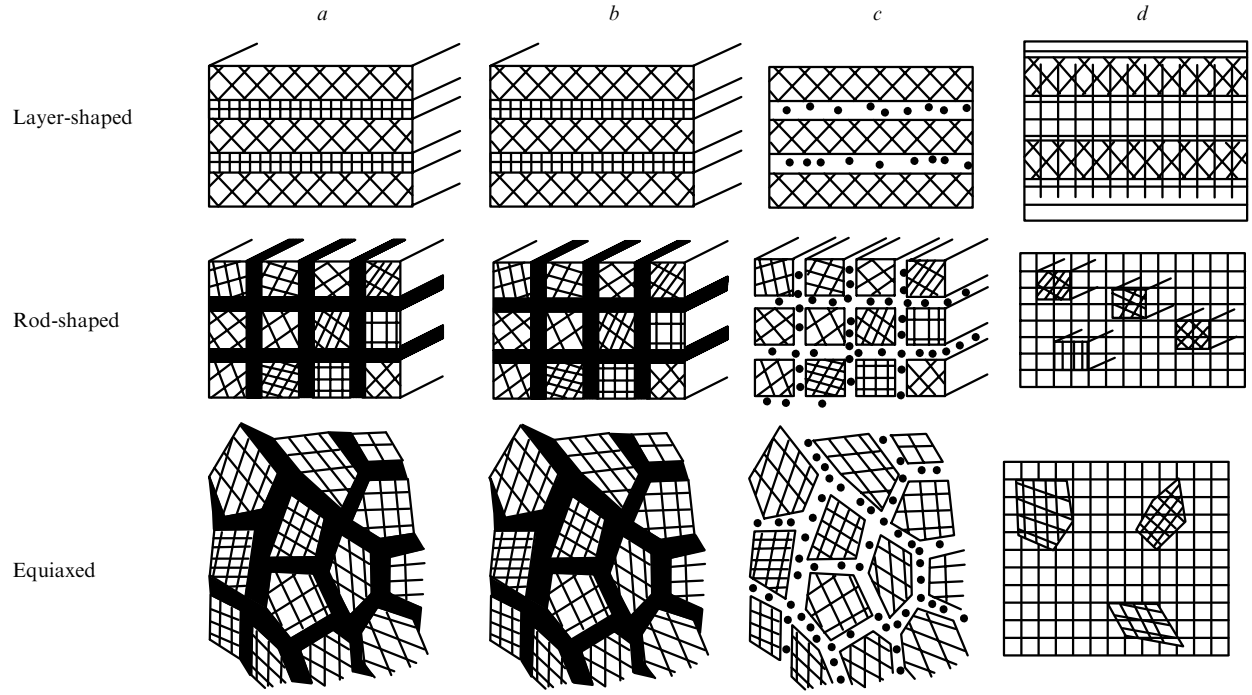


Figure 1. Sketch of single-phase (*a*) and multiphase NM with a statistical (*b*, *c*) and matrix (*d*) distribution of structural components.[22] (*b*) identical interfaces; (*c*) non-identical interfaces.

also take into account the conditional character of the classification of production processes because the borders between particular technological expedients are often blurred. When comparing the thermal stability of different NM, one must bear in mind that the diversity of production techniques and types of macro- and microstructures has an influence on the NM behaviour during heating.

The most frequently encountered structural types are single-phase and multiphase matrix and statistical objects, rod-shaped and multilayer structures (so-called superlattices); the latter type is typical of films. Figure 2 shows examples of some typical structures. High-resolution transmission electron microscopy is especially effective for elucidating the NM structure.[32–34] Attention is drawn by the difference between the structures and thicknesses of interfaces for NM prepared by different procedures (see, for example, Figs 2 *a* and 2 *c*). Various opinions have been expressed concerning the nature of interfaces in NM (see, for example, Ref. 21); however, it is clear that the diversity of production methods also leaves a mark on the nature of the interfaces. X-Ray diffraction methods, which allow one to estimate the anisotropy of grain size and to obtain information on structure distortion, are also widely used to study nanostructure (this has been done most comprehensively in investigating the effect of annealing on the rutile nanostructure [35]).

It is evident that the vast majority of NM, except for supramolecular structures (which was first noticed in the review by Gleiter [22]), are non-equilibrium in their nature. A system can move away from equilibrium for several reasons. As regards NM, the most important of these reasons is the abundance of interfaces (grain and phase boundaries and triple junctions), which gives rise to excess free surface energy. Figure 3 sketches a triple junction and Fig. 4 shows the dependences of the overall fraction of interfaces and the fractions of proper grain boundaries and triple junctions on the grain size.‡

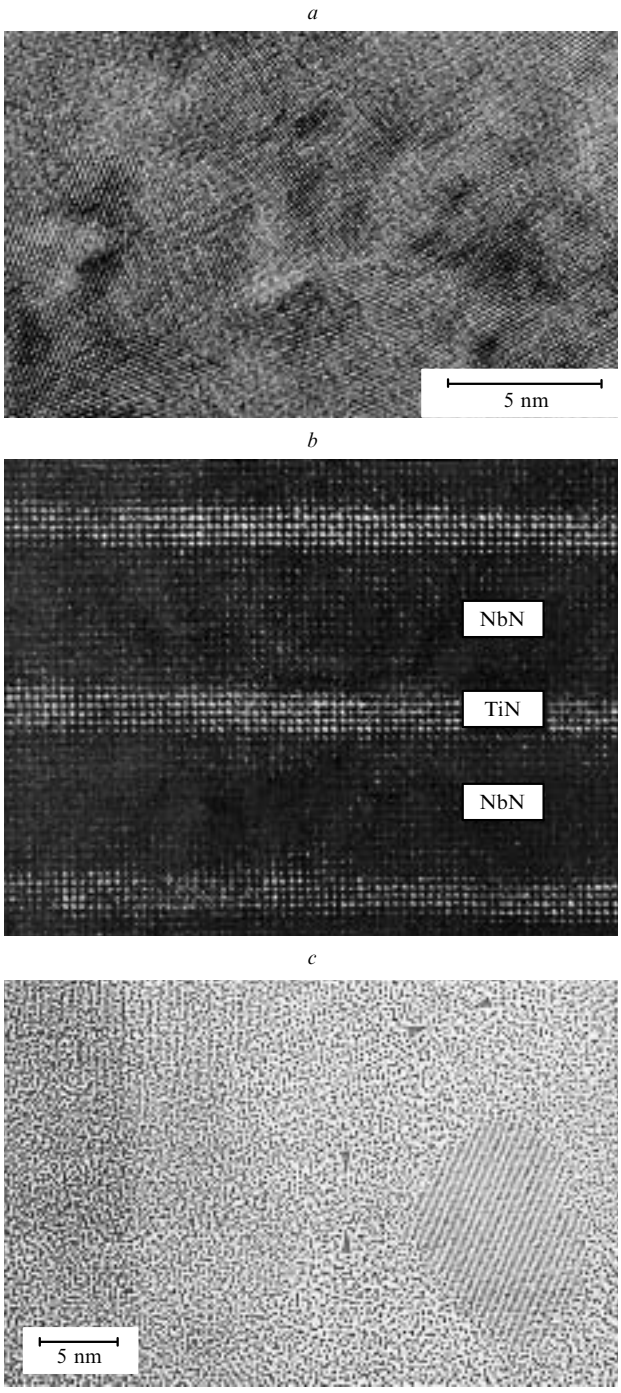


Figure 2. Photomicrographs of the NM structure: (*a*) Ti(N,B) film prepared by magnetron sputtering;[32] (*b*) multilayer TiN/NbN film prepared by magnetron sputtering (the overall thickness of individual monolayers is 4.6 nm);[33] (*c*) 'Finemet' magnetic alloy prepared by crystallisation from the amorphous state followed by annealing at 500 °C (t = 1 h); the arrows mark the grain boundaries.[34]

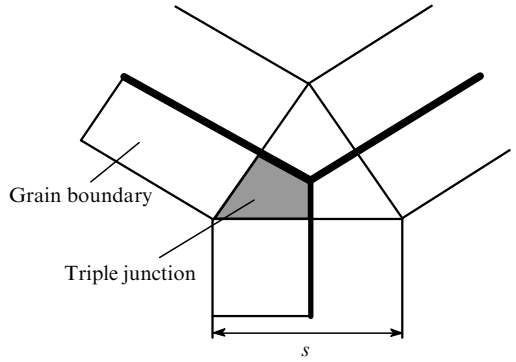


Figure 3. Triple junction formed by grains shaped like tetrahedral dodecahedra.

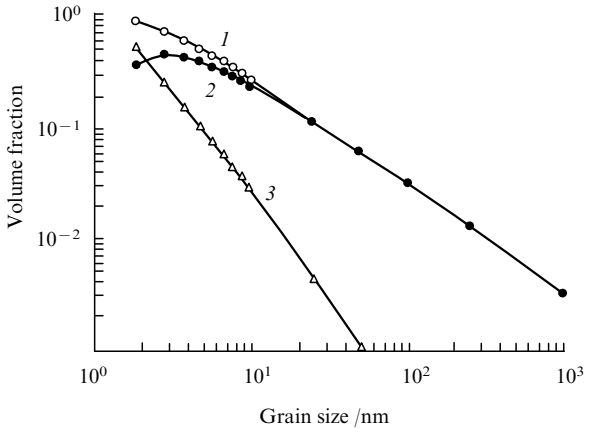


Figure 4. Effect of the grain size on the overall fraction of interfaces (*1*) and on the fractions of grain boundaries (*2*) and triple junctions (*3*) (boundary width 1 nm).[36]

‡ Accordting to estimates,[36] the overall fraction of interfaces amounts to $V_1 = 1-[(L-s)/L]^3 \sim 3s/L$, the fraction of proper grain boundaries is $V_2 = [3s(L-s)^2]/L^3$ and the fraction of triple junctions is, correspondingly, $V_3 = V_1 - V_2$.

As noted above, for grain sizes of less than 5–6 nm, these fractions are rather high and, hence, the excess free surface energy is also rather high; the fraction of boundary segregations also increases.

Note that the values of the interfacial and boundary surface energy can differ from those for usual coarse-crystalline materials; however, reliable experimental data are scarce (see, for example, Ref. 21). It is worth noting that the presence of free space in virtually non-porous NM has been noted in many publications. For example, this was found in densimetric measurements for nanocrystalline nickel [37] and gold [38] specimens (Table 2) and in a study of positron annihilation in palladium.[39] A possible constituent of the free space is the discontinuity of the grain boundaries.

The NM structure often contains non-equilibrium phases; therefore, phase equilibrium diagrams can markedly vary. Nanomaterials produced using film technology and high-energy treatment (static and dynamic high pressures, intensive plastic flow, *etc*., see Table 1) occur inevitably under residual stress and contain crystal structure defects; this also influences their energy state.

Table 2. Density of nanocrystalline nickel [37] and gold [38] specimens (γ_t is the theoretical density).

Specimen	Preparation method	L /nm	γ_t /g cm^{-3}	γ /g cm^{-3}
Nickel	pulse electrodeposition	11 ± 1	8.897	8.34 ± 0.02
		18 ± 2		8.32 ± 0.02
Gold	magnetron sputtering	19	19.299	19.0 ± 0.5

Thus, heat treatment, exposure to force fields or radiation, or long-term operation of NM even at usual temperatures induce recrystallisation, segregation, homogenisation and relaxation processes; phase transitions; phase formation and destruction; amorphisation, sintering, and nanopore (nanocapillary) closing. For a long period, these processes have been the subjects of numerous studies related to material science and the physics and chemistry of solids. For example, the theoretical views on the stability of colloids and thin films have been surveyed in a monograph.[40] However, the mechanisms of many of these processes as applied to NM have not been adequately studied. Currently, it is still difficult to differentiate between them and to evaluate their role but, generally, almost all of the above phenomena have an appreciable effect on the properties and the service performance of NM. In the limiting case, degradation of NM is possible, although in many cases, an additional heat treatment of NM proves useful for stabilising their properties.

III. The main processes in nanomaterials during heat treatment

1. Grain growth

a. Experimental data

The experimental curves that illustrate the effect of temperature and duration of the annealing on grain growth in various types of NM are shown in Figs 5–12.[41–53] The general regularities based on the data presented here and other data on grain growth in nanocrystalline specimens are outlined below.

1. The lognormal or normal grain size distributions remain virtually the same for the initial and annealed specimens. Numerous kinetic studies gave diverse results. For example, in the general case, a power law holds for grain growth (see Fig. 5) but it is often rather difficult to prefer either a relation like $L^2 \sim t$ or some other ($L^{1;3;4} \sim t$).[41] Using experimental results (isothermal annealing) for $NbAl_3$ nanocrystals prepared by mechanical doping [47] and for $Fe_{33}Zr_{67}$ and $(Fe,Co)_{33}Zr_{67}$ alloys prepared by crystallisation from the amorphous state,[48] the relationship $L^3 \sim t$ was found.

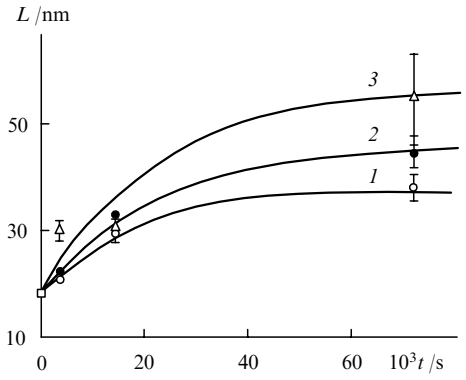


Figure 5. Kinetics of the grain growth in nanocrystalline copper prepared with sliding friction.[41]
T/K: (*1*) 575, (*2*) 625, (*3*) 675.

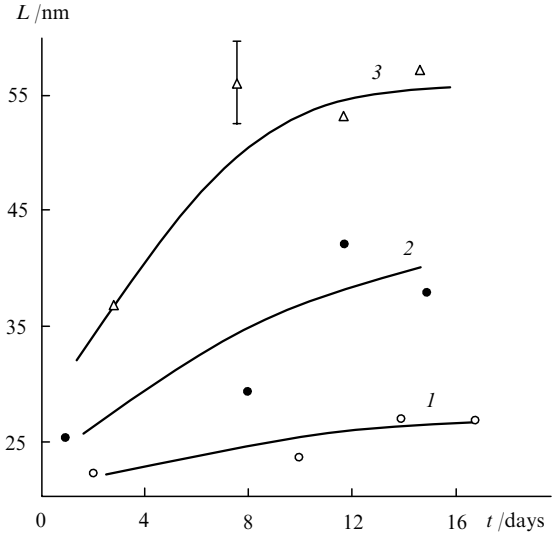


Figure 6. Kinetics of the grain growth in nanocrystalline copper prepared by compacting an ultradisperse powder in a vacuum.[42]
Porosity (%): (*1*) 7, (*2*) 4, (*3*) 3; T = 298 K.

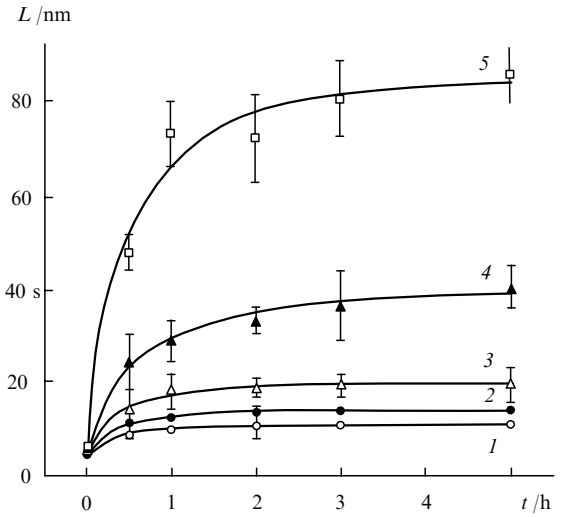


Figure 7. Kinetics of nanograin growth during annealing of RuAl powders prepared by mechanosynthesis.[43]
T/K: (*1*) 873, (*2*) 973, (*3*) 1073, (*4*) 1173, (*5*) 1273.

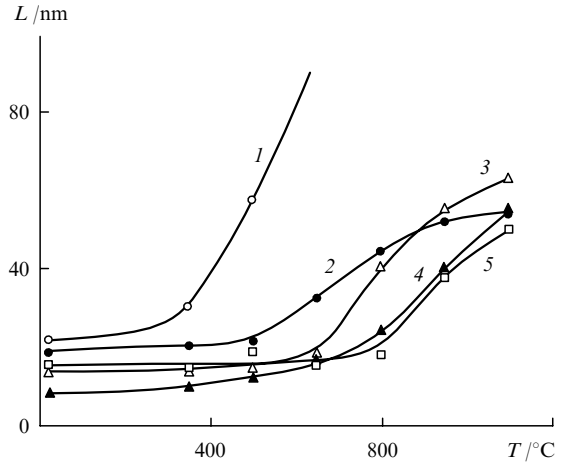


Figure 8. Effect of temperature (t = 1 h) on the nanograin growth in iron (*1*) and iron–aluminium alloy (*2–5*) powders prepared by mechanosynthesis with attritor milling under nitrogen (*1–4*) or argon (*5*) at low temperatures.[44]
Aluminium content in the alloy (mass %): (*2*) 2.6; (*3*) 10; (*4*) 10 (milling for a longer period); (*5*) 10.

The exponential quantity n can depend not only on the object of investigation but also on the temperature range ($1/n$ = 0.05–0.5).[20, 22] The experimental data obtained in kinetic measurements of the growth of nanograins during annealing of ruthenium monoaluminide powders were found to be in good correspondence with the following expression:

$$\frac{L^2(t) - L_{\max}^2}{L^2(0) - L_{\max}^2} = \exp\left(-\frac{2qt}{L_{\max}^2}\right), \qquad (1)$$

where indices t and 0 refer to the current and initial time, $L_{\max}$ is the maximum grain size at the given annealing temperature dictated by factors restricting the grain growth (for example, boundary segregations) (see Fig. 7), and q is a kinetic constant.[43]

In a study of the grain growth ($L_0 \sim 8$ nm) in iron powders treated in a high-energy attritor and annealed at 350–600 °C in a dynamic vacuum ($\sim 10^{-3}$ Pa, annealing time from 5 min to 142 h), a dependence of the exponential quantity on temperature was found and the correspondence of the experimental kinetic data to both the dependence of the $\sim t^n$ type and relation of type (1) was established.[29]

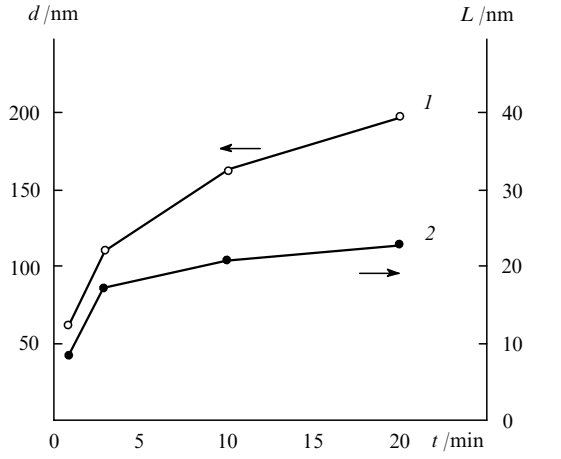


Figure 9. Effect of the duration of deposition from a $[Cd(CH_3COO)_2 \cdot 2H_2O + H_2NCSNH_2 + (HOCH_2CH_2)_3N + NH_4OH]$ solution at 75 °C on the CdS film thickness (*1*) and crystallite size (*2*).[45]

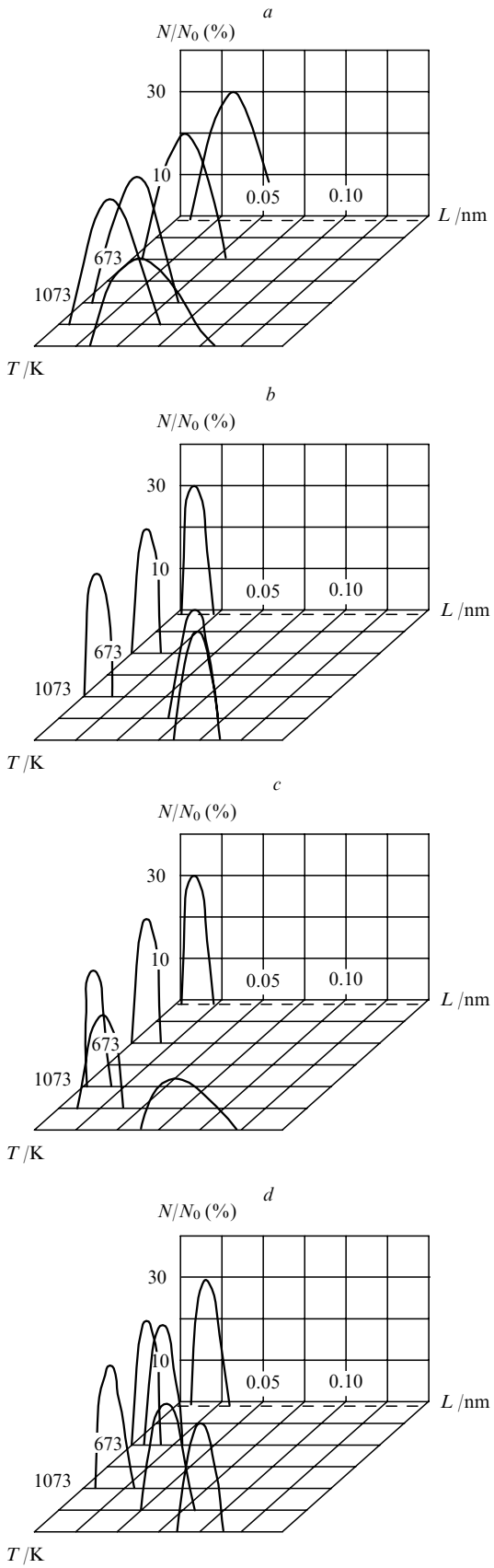


Figure 10. Statistical size distributions of crystallites in ZrN films (*a*, *b*), a ZrN + TiN 20-layer film (*c*) and a doped (Zr,Ti)N film (*d*) annealed at different temperatures.[46]
Film thickness /μm: (*a*, *c*) 2, (*b*) 0.1, (*d*) 1.

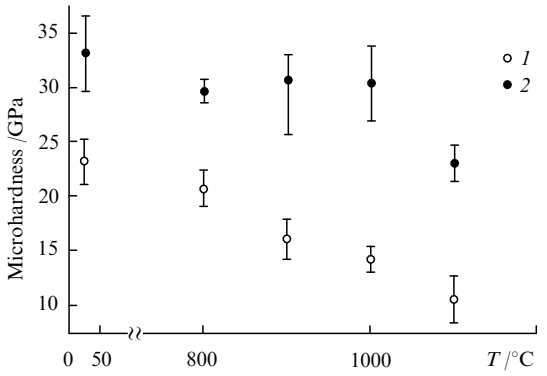


Figure 11. Change in the microhardness of TiN/AlN multilayer films after annealing in an argon atmosphere for 2 h.[53]
The total thicknesses of TiN and AlN individual layers are 16 (*1*) and 2.9 nm (*2*); the total film thickness is 300 nm.

2. When NM are kept for a long time even at room temperature, growth of grains takes place.[22,42,49,50] This so-called anomalous growth of grains occurs if the grain size distribution is inhomogeneous (in this case, large grains serve as seeds for the anomalous growth).[22] The activation energies for grain growth in NM and for the grain-boundary diffusion are close.[21,22] Measurements over a broad temperature range showed an increase in the activation energy for boundary growth with temperature rise; for example, for RuAl nanocrystals, the activation energies were found to be 39, ~72 and 213.5 kJ mol^{-1} for temperatures of 873–1073, 1073–1173 and 1073–1273 K, respectively. This dependence could be due to the progressive effect of the boundary segregation temperature on the retardation of grain growth.[43] The activation energy for grain growth in iron at low temperatures is 125 kJ mol^{-1} (which is close to the activation energy of the boundary self-diffusion in iron), while at higher temperatures, this value is 248 kJ mol^{-1} (which is approximately equal to the activation energy of bulk self-diffusion).[29] These results can be

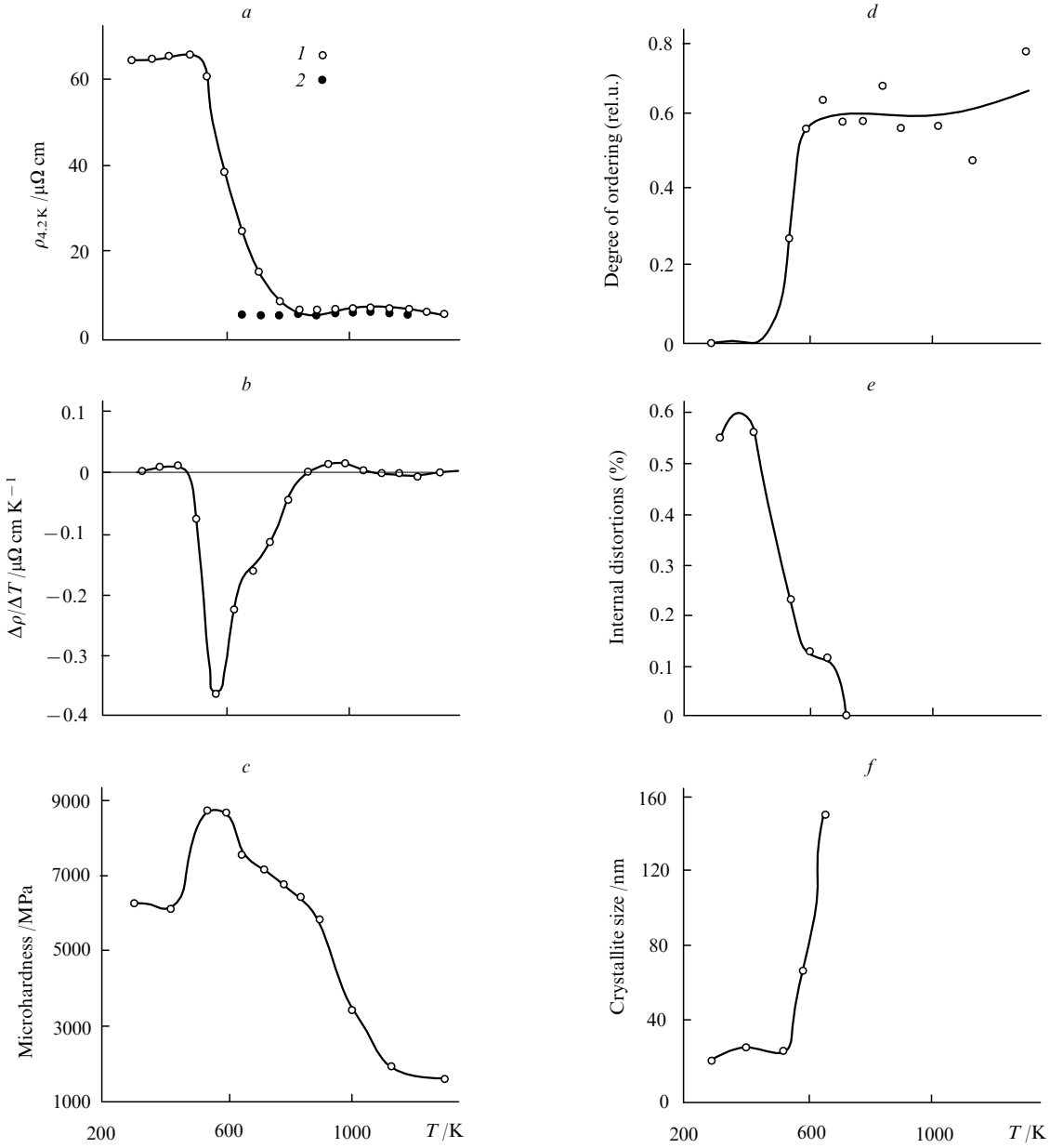


Figure 12. Effect of the annealing temperature on the electrical resistivity at 4.2 K $\rho_{4.2\,K}$ (*a*) during temperature increase (*1*) and decrease (*2*); temperature gradient $\Delta\rho/\Delta T$ (*b*); microhardness (*c*); degree of ordering (*d*), internal distortions (*e*); and crystallite size (*f*) of nanocrystalline Ni_3Al.[18]

explained by assuming different growth mechanisms for low- and high-temperature ranges.

3. The low-temperature milling of Fe – Al alloys reduces the tendency of the resulting NM for recrystallisation, which is attributed to the formation of fine $FeAl_2O_4$ particles and boundary segregations (see Fig. 8). The temperatures of the onset of active grain growth are mainly correlated with the melting points. In the presence of interstitial impurities (oxygen, nitrogen, *etc.*) and with formation of oxides and nitrides in the system, the grain growth starts at higher temperatures. This was confirmed for the Ag – O,[49] Ti – N [50] and Mo – N [51] systems. Their thermal stability was demonstrated in relation to two-phase nanosystems, Cu – Ag and TiN – Si_3N_4.[49, 52]

4. In film specimens, the size of crystallites is much smaller than the film thickness but is correlated with the latter (see Figs 9, 10). A decrease in the film thickness promotes the growth of grains (see Fig. 10); in multilayer films, thermal stability increases with a decrease in the thickness of layers (Fig. 11).[53]

5. It was noted in several publications (see, for example, the studies [21, 22, 53, 54]) that the thermal stability of grains increases as the grain size diminishes.

6. The growth of grains is accompanied by not only changes in structural parameters such as microdistortions, the degree of ordering, *etc.*, but also by changes in physicochemical properties of NM (Fig. 12).[18]

The features noted above were established using electron microscopy, diffraction and calorimetric techniques.

b. The models and theoretical concepts

The problem of maintenance of the nanostructure of NM has been discussed in several reviews and original studies (see, for example, the publications [20 – 22, 28, 30, 31, 50 – 56]). The main factors considered to favour the production of thermally stable NM include the presence of nano- and micropores, boundary segregations and two- or multi-phase nanostructures, a decrease in the grain-boundary surface energy, the formation of supersaturated solid solutions, an appropriate grain morphology, and homogeneity of the grain size distribution. The stagnation of grain growth in nanocrystalline films and ultradisperse powders has been discussed in the literature.[57]

The research into grain boundaries and, generally, interfaces has been the subject of numerous publications (including monographs, see for example, Refs 58 – 62). However, these works barely touch upon the specificity of nano-objects. In recent years, the structures of grain boundaries have been calculated and the NM properties and the probability of vacancy generation during boundary migration have been predicted using molecular dynamics techniques (see for example, the studies [21, 22, 28, 63 – 69]). In particular, it was shown that one-component NM can be simulated by two-phase models (the grain body and grain boundaries). In estimating the properties that depend little on the structure, this approach provided satisfactory results.[21, 22] The contribution of triple junctions to the excess energy of NM was found to be rather weighty.[67]

The molecular dynamics simulation proved to be useful for confirming the generation of vacancies upon grain boundary migration.[66] This process is related to elimination of the free space existing as interface discontinuity; the 'injection' of vacancies inside the grain body should increase the free energy of the system and hamper the boundary migration. An increase in the vacancy concentration during recrystallisation of ultradisperse powders has been recorded experimentally by positron-annihilation analysis.[68]

The following relation was obtained for the critical size of crystallites:[69, 70]

$$\frac{L_c}{2} = \left[24NkTZ(\beta sd)^2 \frac{m}{D}\right]^{1/3}, \qquad (2)$$

where N is the number of atoms in unit volume; k is the Boltzmann constant; Z is the coordination number; β is the excess relative free volume of the grain boundaries; d is the distance between the vacancy sources and sinks; m is the boundary mobility; and D is the self-diffusion coefficient. When $L_0 < L_c$, excessive vacancies retard the migration of grain boundaries, and when $L_0 > L_c$, the grains grow in the usual way, for example, in conformity with the law ($L^2 \sim t$). If the number of dislocations as vacancy sinks is relatively low, the grain boundaries or film surfaces mainly act as the sinks. In this case,

$$\frac{L_c}{2} = 24NkTZ(\beta s)^2 \frac{m}{D}, \qquad (3)$$

where $L_c/2 \approx d$. For example, for aluminium ($m = 2 \times 10^{-14}$ m^4 J^{-1} s^{-1}; $T = 273$ K; $D = 1.3 \times 10^{-17}$ m^2 s^{-1}), the L_c value amounts to $\sim$100 nm, *i.e.*, this is a typical value for an NM structure.[70]

When using relation (2) [or (3)], one should take into account the estimates of the typical grain sizes in NM made in a publication.[71] In crystallites with dimensions of less than L^*,

$$L^* = \frac{\alpha Eb}{2\tau_{PN}}, \qquad (4)$$

where α is a coefficient dependent on the dislocation geometry and ranging from 0.1 to 10, E is the shear modulus, b is Burgers vector, and τ_{PN} is the Peierls – Nabarro stress, the existence of dislocations is unlikely. For example, for linear edge dislocations, the following L^* values (nm) were found for some metals [71] and for titanium nitride:[32]

Cu	Al	Ni	Fe	TiN
25	10	10	2	$\sim$1

When $L_c < L^*$, relation (2) should be used, while for $L_c > L^*$, the use of formula (3) is preferred. However in both cases, one should bear in mind that these relations are approximations.

Yet another interesting conclusion concerning triple junctions has been drawn in a study of grain boundary migration. Triple junctions can be considered as a sort of impurity at interfaces but they mainly play an important role at relatively low temperatures. It has been shown for zinc and aluminium [72 – 74] that the migration velocity of grain boundaries with triple junctions is lower than that for grain boundaries without the junctions at low temperatures. This is due to different activation energies for migration of these boundaries. A temperature rise entails an inversion: the boundaries with junctions become more mobile and the grain growth is controlled by the grain boundary migration. In the case of 99.995% pure zinc, the upper limit of the predominant influence of triple junctions is $\sim$380 °C (tilt boundary grains in the $\langle 10\bar{1}0\rangle$ system) and $\sim$430 °C (tilt boundary grains in the $\langle 10\bar{2}0\rangle$ system). For 99.999% pure aluminium, these temperatures were found to be $\sim$400 °C (tilt boundary grains in the $\langle 111\rangle$ system) and $\sim$510 °C (tilt boundary grains in the $\langle 110\rangle$ system).

The retarding role of triple junctions should be enhanced by a decrease in the grain size (see Fig. 4). Analysis of the variation of the areas of two-dimensional grains showed that, with allowance made for triple junctions, the velocity of grain boundary migration is proportional to the grain perimeter, but the pattern of dependence on topological parameters would be more complex§.[75] However, the general features of switching of the mechanism of the triple junction effect on grain growth and the temperature ranges in which each particular mechanism is effective have not yet been adequately studied.

In investigating the grain growth in metallic films, a thermodynamic approach taking into account tensile stresses has proved to be useful.[76] According to estimates, the boundary migration and injection of vacancies inside the grains create conditions

§ Number of triple junctions per grain (m); when $m = 6$, grains exist in an equilibrium form; when $m < 6$, smaller grains disappear and when $m > 6$, larger grains grow (anomalous growth situation).

where recrystallisation is thermodynamically unfavourable and the grain growth is retarded. The incubation period depends on the grain size (or the distance between the sinks) and on the temperature

$$t_{\text{inc}} = \frac{(\beta s d)^2 NkT}{\gamma D L_0 c_{\text{eq}}}, \quad (5)$$

where γ is the grain-boundary surface energy, L_0 is the initial grain size, c_{eq} is the equilibrium concentration of vacancies. For example, for $T/T_{\text{M}} \approx 0.3$ and $L_0 = d \approx 10$ nm, the t_{inc} value would be $\sim 10^7$ s, *i.e.*, ~ 150 days. From general considerations, this appears reasonable, although somewhat overestimated. One should bear in mind that relations (2) – (5) are approximations and also the fact that the residual stresses in the crystalline films are not necessarily tensile but can also be compressive.

The thermodynamic aspects of the segregation effects have been considered in several studies (see, for example, the publications [21, 22, 28, 56, 77, 78]). The patterns of adsorption at crystallite boundaries have been studied since long ago. It is noted in monograph [59] that a thermodynamic theory that regards the interfacial areas as a separate phase was proposed by Zhukhovitskii back in 1944. The same study presents the thermodynamic relations determining the activity of a component in the interfacial layer as a function of its bulk concentration. Well-known are also Arkharov's studies in which the attention is focused on the role of boundary segregations in the formation of the properties of metal alloys.

The general thermodynamic aspects of boundary segregations in metallic and ceramic alloys have been considered by Ishida;[79] as applied to NM, this topic was discussed in a number of publications.[55, 56, 77, 78, 80] An important result obtained in these works is as follows: calculations performed in different approximations (Langmuir – McLean and Fowler – Guggenheim) showed that the free Gibbs energy (G) varies non-monotonically ¶ as a function of the crystallite size, the minimum G being located in the nano-size region (Fig. 13). Hence, the temperature rise in doped nanocrystals may produce situations where further increase in the grain size becomes thermodynamically unfavourable.

Nanocrystalline nickel alloys with a minor content of phosphorus (2 at.% – 5 at.%) were used to demonstrate the possibility

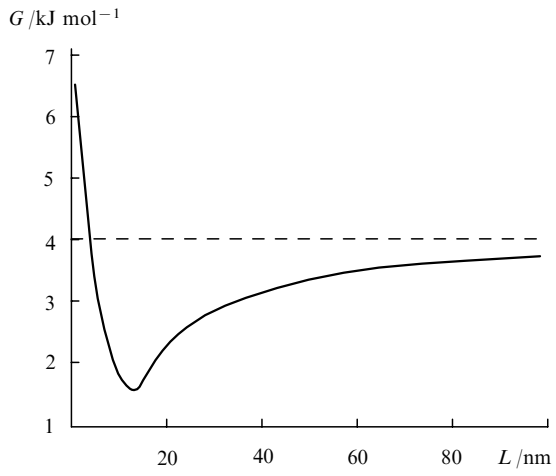


Figure 13. Gibbs free energy for a binary nanostructured alloy with an average concentration of 5 at.% at $T = 600$ K *vs.* crystallite size (for a standard polycrystal, $G = 4$ kJ mol^{-1}).[77]

¶ We would like to note incidentally that this non-monotonic variation is correlated with the views [81] of singular points reflecting the topological transitions in the nanocrystalline state.

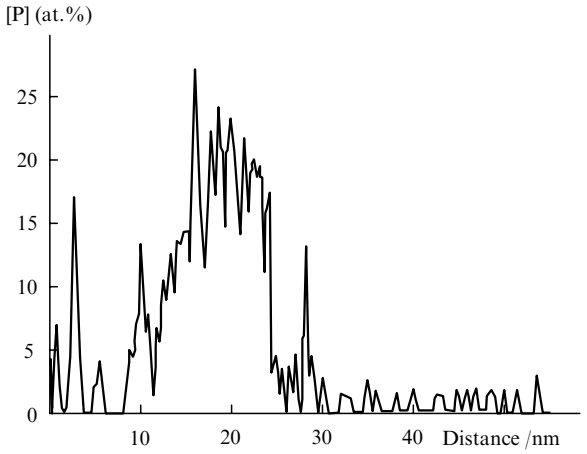


Figure 14. Concentration profile of phosphorus in a triple junction for a nickel – phosphorus alloy (3.6 at.% P) after heating to 400 °C at a rate of 5 K min^{-1} (see Ref. 82).
The alloy containing 25 at.% P corresponds to nickel phosphide (Ni_3P).

of Ni_3P crystallisation *via* boundary segregations (Fig. 14).[56, 82] It was found [55, 83] that during the annealing of palladium – zirconium alloys (grain size 10 – 25 nm), the grain boundaries became enriched in zirconium.[55, 83] In the $Pd_{90}Zr_{10}$ alloy, the grain size increased after annealing at 350 °C, whereas in the $Pd_{80}Zr_{20}$ alloy, no increase in the grain size was noted even after annealing at 500 °C, which was attributed to greater enrichment of grain boundaries in zirconium in this alloy. This fact was determined based on the change in the lattice spacing.

Experimental investigations of the boundary segregations in NM make use of unique analytical equipment (such as atomic tomograph, atomic force microscope) as well as advanced investigation methods (for example, electron energy loss spectroscopy and so on).[82] Interesting features of iron segregation in nanocrystalline iron – yttrium alloys have been followed.[14, 28]

The possibility of crystallisation at compound boundaries due to the inflow of surface active elements has been considered theoretically by Rabkin,[84] who noted the retarding effect of particles (so-called pinning effect) and pointed to low probability of complete stoppage of boundary migration. Nevertheless, stabilisation of the nanograin growth has been observed by many researchers [for example, during annealing of RuAl (see Fig. 7), iron or aluminium powders after milling in an attritor [29, 43, 85]]. Evidently, to take into account numerous factors that govern the evolution of grain ensembles [such as boundary migration, diffusional segregation, phase crystallisation,[84] vacancy injection by moving grains, the possible relaxation of the residual stresses, size effects as applied to the intergrain surface energy and integral free energy (see Fig. 13), and so on], it is necessary to perform a versatile computer simulation of the main processes occurring during heat treatment of NM. An attempt at Monte Carlo simulation of some of these factors has been reported.[86]

2. Phase transformations

The presence in NM of a nanocrystalline structure, supersaturated solid solutions or unusual crystalline phases is due to non-equilibrium conditions of NM preparation.

Experimental and theoretical studies of the thermal stability of these objects are few, although thermodynamic characteristics and the features of phase diagrams as applied to nanoparticles have been the subject of investigation of many researchers (see, for example, Refs 87 – 89). However, phase transitions in compact NM (diffusiveness, shifts, *etc.*) have not been studied systematically.

Several attempts have been undertaken to carry out rough calculations of state diagrams with allowance for the component

dispersity (see, for example, Refs 87, 90–93). Using the relations for the partial free energies of the system in the liquid and solid states (for the latter, the excess component of the boundary surface energy was taken into account), in the simple approximation of regular solutions, relations were derived that reflect the influence of the component dispersity on, for example, the decrease in the eutectic temperature ΔT_E:

$$\Delta T_E = \frac{\Delta G_2}{R\ln x}, \quad (6)$$

$$\Delta T_E = \frac{\Delta G_2}{R\ln x_E - \Delta S_{M2}}, \quad (7)$$

$$\Delta T_E = \frac{\Delta G_1}{R\ln[(1-x_E)/(1-x)] - \Delta S_{M1}}, \quad (8)$$

where G_i is the contribution of the excess boundary surface energy per mole, $\Delta G_i = 6V_i\sigma_i/L_i$ (V_i is the molar volume), σ_i is the grain-boundary surface tension, x and x_E are the limiting solubility and eutectic concentrations; ΔS_{Mi} is the melting entropy.[92]

These relations are equivalent, their practical value being dependent on the presence of particular data for components 1 and 2.

Expressions (6)–(8) lead to a size dependence of the type $\Delta T_E \sim 1/L$. The calculated ΔT_E and T_E values for the TiC–TiB_2, TiN–TiB_2 and TiN–AlN systems are summarised in Tables 3 and 4. It can be seen that a tangible decrease in T_E can start when the dimensions of the dispersed component are several tens of nanometers, although one should remember that the calculations are rough. With more complicated approximations, the estimates cannot be brought to a numerical solution. The available thermodynamic information is inadequate for determining the solubility regions in the phase diagrams.

The phase stability in multilayer films has been considered in terms of various statistical thermodynamic approaches.[94,95]

The presence of metastable structures is especially typical of NM prepared by mechanosynthesis or by film techniques. The formation of supersaturated solid solutions and compounds was detected in the Fe–Cu, Fe–Ni, Fe–Ti, Fe–Al, W–Cu, Ni–Al, TiN–TiB_2, and TiN–AlN systems, *etc.*[14,44,50,95–104] Detailed study of the Fe–Cu and Fe–Ni systems (crystallite site 3–50 nm)[96,98,99,104] showed a pronounced increase in the solubility of the components in each other. Whereas iron dissolution in copper increases the thermal stability, the reverse process has virtually no influence on the grain growth parameters; two-phase Fe + Cu compositions were found to be less stable than single-phase ones.

In multilayer films (superlattices), cubic structures are often formed instead of hexagonal ones due to epitaxy (examples are aluminium and niobium nitrides with the NaCl structure in combination with cubic titanium and zirconium nitrides;[30,50] and titanium with FCC structure in multilayer titanium–aluminium films[105]).

Magnetron sputtering with both single-phase and two-phase TiB_2 + (0%, 25%, 50%, 75% or 100%) TiN targets at moderate deposition temperatures (~150°C) resulted in the synthesis of single-phase nanostructured boride–nitride films of the following composition: $Ti(B_{0.73}N_{0.2}O_{0.05}C_{0.02})_{1.56}$ and $Ti(B_{0.56}N_{0.29}O_{0.05}.C_{0.1})_{1.32}$ with a hexagonal structure and $Ti(B_{0.34}N_{0.49}.O_{0.12}C_{0.05})_{1.49}$ and $Ti(N_{0.6}O_{0.2}C_{0.2})_{1.58}$ with a cubic structure. The composition formulae were determined using Auger analysis. Judging by these formulae, these films were essentially non-stoichiometric because the homogeneity regions of titanium diboride and nitride in the equilibrium state differ from these values ($TiB_{1.89-2.0}$ and $TiN_{0.7-1.2}$). However, the solubility of interstitial elements in films is rather high; therefore, fairly broad homogeneity regions appear in the state diagram of the TiB_2–TiN system.[102,103] The equilibrium state diagram of the pseudo-binary TiB_2–TiN system (see Table 3) is an eutectic type diagram, the mutual solubility of the components in this system being very low. A similar situation is found in the TiN–AlN and NbN–AlN systems. While the equilibrium solubility of Al in TiN at 1000 °C equals ~2 at.%, the cubic equiatomic phase (Ti,Al)N occurs in nanostructured films even at room temperature.[30] Thus, the pattern of state diagrams of nanocrystalline systems† and the homogeneity regions of individual compounds substantially change.

Study of the effect of annealing at 700 and 1000 °C (t = 15 min) on the structure of Ti(B,N) films did not reveal decomposition: the films remained phase-homogeneous and the grain size changed insignificantly (Table 5).[106] Some changes in the microhardness will be discussed below.

An extensive study of the effect of annealing in the temperature range from 850 to 1000 °C on the structure and composition of and the chemical bonding in plasmochemical SiCN films has been reported.[108] Using electron microscopy and X-ray diffraction analysis and resorting to the data of infrared, Raman and photoelectron spectra of the films, it was shown that high-temperature annealing leads to a decrease in the amorphous matrix and yields oblong oriented α-Si_3N_4 nanocrystals (in the amorphous matrix of the initial films, 2–3 nm crystallites were detected).

Interesting examples of spinodal decomposition of nanostructured solid solutions, TiN–ZrN and TiN–AlN, have been reported.[30,50,109,110] The dependences presented in Fig. 15 allow one to follow the influence of the annealing temperature on the change in the microhardness of films of individual titanium and zirconium nitrides and multilayer (TiN–ZrN) and doped [(Ti,Zr)N] films.[110] It can be seen that starting from T > 1000 °C, the microhardness of doped films tends to increase with an increase in the annealing temperature; this is due to evolution of the ultradisperse products of spinodal decomposi-

Table 3. ΔT_E values in TiC(TiN)–TiB_2 and TiB_2–TiC(TiN) pseudo-binary systems with different degrees of dispersity of one of the components.[92]

L /nm	ΔT_E /K	
	TiC(TiN)–TiB_2	TiB_2–TiC(TiN)
200	~45	~35
100	~90	~70
20	~450	~350
10	~900	~700

Note. In the polycrystalline state, T_E for the TiC–TiB_2 system is 2790 K; for the TiN–TiB_2 system, 2870 K.

Table 4. T_E values for the TiN–AlN pseudo-binary systems with different degrees of component dispersity (for macrodisperse specimens, T_E = 2715 K).[91]

Dispersed component	L /nm	T_E /K
TiN	200	2660
	100	2610
	20	2160
AlN	200	2710
	100	2690
	20	2565
TiN, AlN	200	2650
	100	2590
	20	2110

† Unlike the equilibrium state diagrams of usual polycrystalline objects, in the case of nanocrystalline systems, it is appropriate to speak of quasi-equilibrium diagrams to mean their lability and possible variation with time.

Table 5. Effect of annealing on the average size (L /nm) and the microhardness (H_M /GPa) [a] of crystallites in boride – nitride films.[106]

Target	Initial film		T_0 = 700 °C		T_0 = 1000 °C	
	L	H_M	L	H_M	L	H_M
TiB_2	3 – 5	41 – 46	–	40 – 46	–	35 – 39
TiB_2 + 25%TiN	2.3 ± 1.1	40 – 46	4.4 ± 1.4	40 – 45	–	32 – 38
TiB_2 + 50%TiN	2.9 ± 1.1	46 – 52	3.7 ± 1.2	47 – 54	3.4 ± 1.9	38 – 45
TiB_2 + 75%TiN	5.4 ± 4.0	53 – 59	8.1 ± 4.4	52 – 58	7.9 ± 3.8	32 – 42
TiN	9.9 ± 8.8	36 – 40	13.0 ± 6.6	38 – 42	10.2 ± 7.0	33 – 40

[a] The H_M values refer to a procedure [107] largely eliminating the effects of the substrate and film thickness; *i.e.*, here, H_M is the microhardness of the proper films.

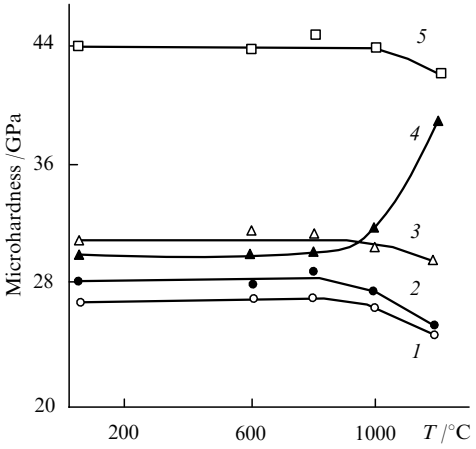


Figure 15. Effect of the annealing temperature on the microhardness of monolayer ZrN (*1*) and TiN (*2*), 10-layer ZrN/TiN (*3*), doped (Zr,Ti)N (*4*) and 20-layer ZrN/TiN (*5*) films.[110]

tion. These films provide an example of so-called 'smart' materials whose properties not only deteriorate during operation but can also be upgraded to a certain extent.

Annealing of the (Ti,Al)N – Si_3N_4 nanocomposition at different temperatures showed a microhardness maximum and a grain size minimum at 800 °C, which should also be attributed to spinodal decomposition of the (Ti,Al)N phase; a substantial decrease in the microhardness and an increase in the crystallite size is observed after annealing at 1200 °C (t = 30 min in an atmosphere of 90 vol.% N_2 + 10 vol.% H_2).[111]

The nanocrystalline cubic phase (Ti,Al)N is highly stable against oxidation.[103, 112] Therefore, it is not accidental that one of the (Ti,Al)N-based layers is highly resistant to change in industrial and pilot multilayer superhard nitride films.[113]

3. Relaxation and diffusion

Relaxation processes in nanocrystalline compounds were analysed in the review;[114] the diffusion processes in nitride films have been characterised.[30] If an NM has been prepared by, for example, severe plastic deformation or vapour quenching and represents a disordered solid solution, a temperature rise restores the short-range order, establishes a long-range order and induces the growth of grains. These regularities were followed for the Ni_3Al intermetallic compound in calorimetric experiments.[114, 115] However, the use of differential calorimeters does not always permit detection of processes related to the relaxation of internal microstresses during low-temperature annealing. The relaxation of residual stresses can be detected in X-ray diffraction studies based on line narrowing and splitting into doublets. Relaxation is believed to precede the grain growth.[114] Turning back to the data of Table 5, we would like to note that some decrease in the microhardness during annealing of boride – nitride films can, apparently, be attributed to relaxation of the residual compressive stresses, where the grain size changed insignificantly.

The residual stresses in nanostructured nitride and other films caused by differences in the linear thermal expansion coefficients and elastic properties in the film – substrate system or in multilayer films can be rather pronounced. For example, in nitride films, the residual compressive stresses can reach 10 GPa and they can contribute noticeably to the hindering of dislocation and fracture migration (and, correspondingly, to the increase in hardness).[30] Stress relaxation processes consisting in migration, redistribution and annihilation of various defects as well as grain boundary migration are known to be diffusional processes. The activation energy of stress relaxation (E /kJ atom^{-1}) and the temperature ranges of this process for the films of some refractory compounds are given below [30]

Compound	TiN	TiN	Ti(C,N)	CrN
T /°C	400 – 900	250 – 430	450 – 900	240 – 670
E /kJ atom^{-1}	~200	~120	200 – 400	200 – 300

The given E values are similar in magnitude to the activation energies of nitrogen self-diffusion in nitrides (which is, more likely, a boundary rather than a bulk process).[116] Comparison of the residual stress relaxation in titanium nitride and carbide – nitride showed that an equal level of compressive stresses in carbide – nitride films is attained at temperatures ~200 °C higher than in TiN; therefore, the high-temperature hardness of Ti(C,N) is higher.[30]

The relaxation processes and the evolution of nanostructures in metals, alloys and intermetallic compounds (Fe, Cu, Ni; Al, Fe, Cu alloys; Ni_3Al, see Fig. 12) subjected to severe plastic deformation have been discussed in detail in a monograph.[18] However, the mechanism of stress relaxation in NM as a whole is not entirely clear.

The information concerning heterodiffusion processes is important for the analysis of the thermal stability of multilayer films. A study of the mutual diffusion in single-crystalline multilayer TiN/NbN films (the thicknesses of separate layers are 4.4 and 12.3 nm for a total thickness of ~1 μm; isothermal maintenance at 750 – 875 °C, non-isothermal heating to 1200 °C) revealed the predominant diffusion of titanium.[117] The activation energies (Q /kJ per atom) for different temperature ranges have been determined.[30, 117]

T /°C	< 830	830 – 875	885 – 930
Q	115	250	430

The last Q value is similar to the activation energy for the self-diffusion of metal atoms in transition metal carbides and nitrides.[116] According to estimates,[117] the duration of homogenisation in multilayer TiN/NbN films and, correspondingly, the working life of this nanocomposite with ~2 nm thick layers is ~10 h at 750 °C or ~2 h at 850 °C. To study heterodiffusion in multilayer films, one should employ high-precision X-ray diffraction and electron-microscopy procedures and also use powerful sources such as synchrotron radiation. The versatile capabilities of

X-ray diffraction for the assessment of In_xGa_{1-x} films with one ~ 10 nm thick quantum well have been demonstrated.[118]

A study of the thermal stability of multilayer Mo/NbN films (the metal has a body-centred cubic lattice and the nitride has a face-centred cubic lattice) showed that the formation of the tetragonal (Mo,Nb)N phase starts after maintenance for 3 h at 1000 °C.[119]

The diffusion of oxygen in films determines the stability of films against oxidation. The abundance of interfaces in NM creates conditions for substantial oxygen streams. Characteristic features of oxidation of nanostructured films have been analysed.[30, 103, 112, 113, 120] The resistance of nitride films against oxidation is markedly increased by chromium or yttrium additives which 'lock up' the crystallite boundaries.[113] Amorphous films have demonstrated both a poorer oxidation resistance (800 nm TiN films) [120] and a higher scale resistance (2–3 μm $AlN-TiB_2$ and $AlN-TiB_2-SiC$ films) [112] compared to the same characteristics of crystalline films or bulk specimens of the same composition.

IV. Other stability aspects of nanostructures

For some types of NM (for example, for nanoporous, nanosemiconducting and nanocarbon materials), studies of thermal stability have started only recently (see, for example, Refs 121–126). It should also be noted that nanoparticle-related problems have been barely considered above, because, in view of the multiaspect character of agglomeration and sintering processes, these topics require separate consideration. We would only like to note that the sintering of nanoparticles and the grain growth in NM have much in common. Figure 16 shows the temperature dependence of the compaction during sintering of ultradisperse powders of metals and metal-like substances and also ionic and covalent compounds.[127] Whereas active sintering (compaction) of metals and metal-like or ionic compounds starts at homological temperatures $(0.3-0.5)T_m$, the powders of covalent compounds (B, Si, Si_3N_4) are actively sintered only at $T \geqslant (0.8-0.85)T_m$, *i.e.*, at much higher temperatures. Aluminium nitride, as an ionic-and-covalent compound, occupies an intermediate position. This difference is due to specific features of the diffusion mobility in objects with different types of chemical bonds. In all probability, the temperatures of the onset of the active grain growth in these materials should lie within the same ranges.

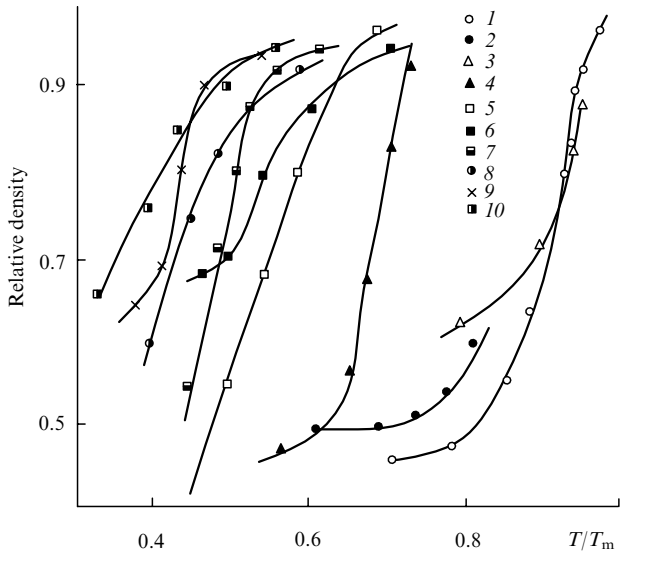


Figure 16. Temperature dependence of compaction during sintering of various ultradisperse powders.[125]
(*1*) Si, (*2*) Si_3N_4, (*3*) B, (*4*) AlN, (*5*) WC, (*6*) ZrC, (*7*) MgO, (*8*) Mo, (*9*) CaF_2, (*10*) Ni.

The aspects of NM thermal stability considered above are far from exhausting the general problem of nanostructure stability. For example, the NM stability is appreciably affected by various fields (force, radiation, *etc.*). In particular, the grain growth upon superplastic deformation of fine-grained ceramic materials has been considered theoretically taking into account the additional driving forces for migration.[128]

The microstructure changes induced by NM implantation or irradiation have been the subject of only a few studies (see, for example, Refs 129–131). The appearance of nanoclusters in metal alloys (Fe–Ni, Cu–Ni, Fe–Cr, *etc.*) at high levels of radiation damage has been noted.[132] The formation of nanocrystalline diamonds ($L = 2-70$ nm) was detected on graphite irradiation with Ar^+ ions (the fluence was $\sim 10^{22}$ cm^{-2}).[133] Amorphisation of nanocrystalline zirconium oxide on exposure to radiation by high-energy Xe^{2+} and Ne^+ ions has been reported;[131] meanwhile, gold nanoparticles with dimensions of 3 nm remained crystalline after irradiation. It is noteworthy that NM based on ZrO_2 are under vigorous research now (see, for example, studies [134, 135]). The behaviour of irradiated NM is an extensive field for further research.

It should be emphasised that the stability of NM largely depends on the process used for their manufacture. A number of techniques such as high-pressure processes, sintering with controlled heating rates, pulse sintering, pulse modes of electrodeposition, moderate substrate temperatures during film deposition, the formation of multiphase structures and boundary segregations and some other are widely used in the preparation of NM (see, for example, the studies [24, 31, 52, 136–142]). However, problems of deliberate selection of conditions for the production of the initial NM with a narrow nanocrystallite size distribution, the optimal content of doping or impurity elements for decreasing the grain-boundary surface energy or for the formation of barrier layers, and many other problems are far from being solved. It is not accidental, therefore, that the Japanese national program 'Material Nanotechnology' pays considerable attention to the development of NM with optimal structures and to the prevention of anomalous grain growth phenomena.[143]

V. Conclusion

When generally evaluating of the state-of-the-art research into the thermal stability of NM, we would like to stress the following points. On the one hand, there exist quite a few experimental and theoretical facts demonstrating the possibility of production of thermally stable NM; on the other hand, examples of anomalous grain growth in NM are documented.

Unfortunately, our knowledge is still inadequate to unambiguously explain many facts and to compare the efficiency of various methods for nanostructure maintenance, say nothing of the possibility of making predictions. Note that the latter depends not only on the theoretical works and availability of reliable experimental information but also on the general level of the nanostructure theory. For example, it is not entirely clear what are the grain dimensions (of phase components) down to which the classical thermodynamics remain valid. The point is that objects with crystallite dimensions of $\sim 1-2$ nm or even less are already involved in NM investigation and application (see Table 5 and the studies [32, 103, 106, 144–146]). A ~ 1 nm grain of titanium nitride with a lattice spacing of ~ 0.424 nm contains ~ 8 ($\sim 2^3$) unit cells, *i.e.*, in essence, it is a cluster-consolidated object (unlike cluster-aggregated materials [16, 147]). In this connection, the points such as the effect of the grain boundary curvature on its energy parameters, the applicability of the concepts of statistical thermodynamics or thermodynamics of irreversible processes, the type of excessive thermodynamic functions, the energy characteristics of triple junctions, and so on have been scarcely studied so far. These aspects have to be thoroughly analysed to be used in estimations.

Note that research into the determination of the energy characteristics of the surfaces of isolated clusters, cluster aggregates and colloids is also in progress.[148–150]

In the long-term American forecasts (for 10–15 years) concerning the arrival of nanotechnological products on the world market, nanomaterials occupy a leading position — of the putative total volume of 1 trillion US dollars, a sum of 340 billion US dollars is predicted for NM.[151, 152] It is clear that substantiation of the operation capacity of NM, including thermal stability characterisation, is among the most important problems facing the science of nanostructured materials.

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