

Inorganic Chemistry

Chemical Bonds in Changing the Hardness of Nanomaterials

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ABSTRACT. Nanomaterials consisting of nanoparticles, in contrast to conventional materials, during loading behave in a special way. The value and sometimes even the direction of the change initiated by the loading process depends on the size of their constituent nanoparticles. Despite many attempts the explanation of these facts does not still exist. In this paper, we propose a new mechanism of changing the magnitude and direction of change initiated by a loading process in nanomaterials, depending on the size of the constituent nanoparticles. This mechanism is based on the new ideas about changing the atom position in the material, which is determined by the change of quantum state of the chemical bonds of the atom. This change can be realized in different ways: by temperature, light, pressure, electric and magnetic fields, reduction of the particle size of the material. This mechanism qualitatively explains all the experimental facts taking place during the loading of nanomaterials. © 2016 Bull. Georg. Natl. Acad. Sci.

Key words: nanomaterials, hardness, plasticity, fluidity, quantum state of chemical bonds

Materials of macroscopic size in the solid state (compact materials) at mechanical loading first experience elastic deformation, then inelastic deformation transferred into flexibility and later fluidity bringing to their mechanical destruction [1-3]. Depending upon the nature of the material, some of these processes can be of such small intensity that it is very hard to detect them experimentally, for example, during brittle fracture of the material. In compact materials as the load is increased, the inelastic deformation, plasticity, fluidity are also increased and mechanical destruction occurs [2-3]. Nanomaterials composed of

nanoparticles behave quite differently: the volume and sometimes even the direction of change initiated by a loading process depends on the size of their constituent nanoparticles [4,5]. It was found that the decrease of grain size to nanometer levels causes an increase of the microhardness (MH) values in nanomaterials and yield point (YP) in 4-5 times. This tendency in case of the MH is described by the empirical Hall–Petch relation (H-P): $H=H_0+KL^{-1/2}$, where H is nanomaterial hardness at a given value, H_0 is the hardness of substance, K individual constant for each material, the so-called Hall–Petch coefficient, L is an

grain size, nm

Fig. 1. The dependence of the hardness of nanomaterial from the grain size of the constituent nanoparticles:
1-area, complying with the law Hall-Patch relation
2-anomalous range (anti Hall-Patch)

average size of nanoparticles [4, 5]. Similar expression also describes the dependence of the yield stress on nanoparticles size. With decrease of nanoparticles size the yield stress first increases similar to H-P law: $\delta_T = \delta_0 + KL^{-1/2}$ (δ_T is yield point and δ_0 - internal stress which hinders plastic shift in the material) and then decreases [4, 5]. For numerous researched nanomaterials the Hall-Petch relation is fulfilled up to a certain grain size and for smaller grain sizes the inverse effect is observed: the values of hardness and yield stress are decreased with the reduce of nanograins size (Fig.1). The latter is considered an anomaly and called “anti H-P”. The increase in the microhardness and yield stress values with a decrease in grain size to a nanosize is explained by a decrease in the number of dislocations in particles with reduction of their size which is proved by X-ray and electron microscopic investigations [4, 5].

It is believed that due to the fact that in the range of “anti- H-P” dislocation activity is not observed, reduction of hardness and yield point is caused by different mechanisms. The fact that in case of brittle substances (oxides, nitrides, carbides, intermetallids), changing the grain size the value of hardness changes insignificantly [6, 7]. It is also known that

superplasticity phenomenon in nanomaterials is far higher by value and occurs at lower temperatures than in compact materials that has big practical importance [4, 5]. Besides this, in nanomaterials created from metal alloys, intermetallids and high-melting compounds are revealed higher speed and lower temperatures of deformation processes than in the same materials in polycrystalline state [4, 5]. In nanomaterials of oxides and silicium nitrides the lowest temperature, after which superplasticity occurs, is higher than in nanomaterials of other substances. In various works the results quantitatively different from each other, nevertheless it can be stated that changes of hardness characteristics (MH, plasticity, yield point and mechanical destruction) in nanomaterials are connected with the decrease of nanoparticles size. In spite of numerous attempts, there is no explanation to these facts [4, 5]. On the basis of new ideas about the change of the location of an atom in the material which allowed to create elementary act of decreasing the hardness of the compact material, this work offers the mechanism of changing in nanomaterials the value and direction of the change initiated by loading of the processes depending on the sizes of nanoparticles constituting them [8]. All above-mentioned processes on microscopic level are determined by the change of initial location of atoms in the material which has been described till now from the viewpoint of molecular-kinetic theory (MKT) [9]. However, the MKT is valid at temperatures $T=0.7 T_{mp}$ (T_{mp} – temperature of melting) and even at these temperatures cannot explain many experimental facts connected with the change of the location of the atom in the substance and totally powerless in interpretation of the phenomena taking place at low temperatures [10]. This explains non-existence of the elementary act of beginning the processes developing in the loaded compact materials [8] and announced in nanomaterials as “anomaly”, dependence of the changes of directions and value initiated by loading processes on the size of nanoparticles [4, 5].

In the paper [8] it has been shown that the change

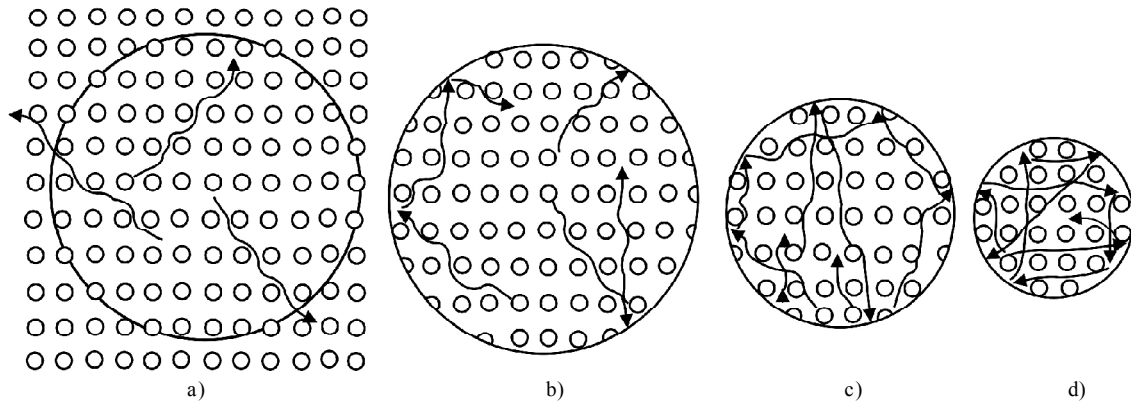


Fig. 2. Schematic illustration of growth in ABQPs' concentration with reducing in nanoparticles size at given temperature. Increasing in AQPs the calculated real concentration for fixed concentration with decreasing in sizes: a) AQP trajectory in compact solid's region with volume equal to the nanoparticle volume: two of them are leaving the volume; b) in connection with the reflection from the boundary surface of the nanoparticle trajectory three AQP is in it and they will be around more the number of atoms in this volume than in the case of a compact solid body; c) and d) with decreasing size of nanoparticles of the same three AQP will be near a larger number of atoms.

of the hardness of the usual materials as a result of mechanical loading at a constant temperature is determined by decreasing the energy of chemical bonds between the atoms (molecules) composing given material. The energy of chemical bonds is decreasing due to the appearance of additional antibonding electrons due to the approach of bonding and anti-bonding zones under the pressure [10]. The magnitude of this approach depends on the ratio direction of the pressure force and crystallographic direction [8]. Therefore, the concentration of additional antibonding electrons is unequal in all areas of material. The probability W_A of change of atom location in the substance is determined by the expression $W_A = A(n_{ABQP} / N_a)^\beta W_{ph}$, where A is almost constant value, n_{ABQP} - concentration of AQP (antibonding quasi-particles – electrons in antibonding zone and holes in the bonding zone), N_a is concentration of atoms (molecules) of the substance, β is number of AQP near the given atom necessary for reduction of the height of potential barrier to zero, W_{ph} is the probability of the phonons presence of definite energy close to the given atom [8-10]. Clearly, the more n_{ABQP} concentration of the AQP, the easier the change of atom location in the material and beginning of the processes of decreasing hardness of the material. In case of nanomaterials it is

necessary to consider the specifics of the energy (quantum) states of the electrons participating in creation of chemical bonds in nanoparticles.

Unlike compact solid bodies, during creation of which from the multiplicity of the atoms, energy levels of atoms split and create bonding and anti-bonding zones, during the formation of the nanoparticles (clusters), the splitting of electronic levels of atoms to discrete bonding and anti-bonding energy levels (orbitals) occur. It will be recalled that electrons located in the bonding orbitals increase the energy of chemical bond apart from electrons located on antibonding orbitals which decrease it. Therefore, the electrons located on the antibonding orbitals and vacant places on the bonding orbits on bonding orbitals (holes) are the AQP. In big clusters the levels are less split. A small cluster is similar to the molecule with its discrete set of energy levels, bonding and antibonding orbitals. In nanoparticles the energy distances between discrete levels are of such value that electrons can freely transit to the higher energy levels and move along the nanoparticle. Beginning from the certain sizes of nanoparticles, during its motion the AQP reaching the surface of nanoparticle, are mostly reflected from them and remain in its volume raising the AQP concentration unlike the compact solid body of the same volume from which the AQP

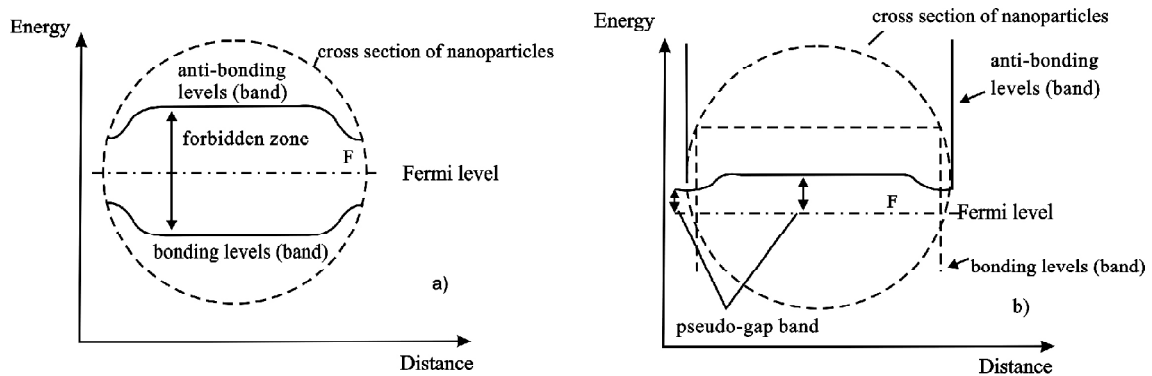


Fig. 3. Energy levels distributions in nanoparticle surface layer and bulk. Due to reflection from surface the probability of AQPs appearance near atoms in the surface layer is higher than that in bulk, what a) decreases energy-difference between bonding and anti-bonding levels in semiconductor; b) in metals these levels are overlapped and pseudo-gap near the surface is smaller than in the bulk and the concentration is incomparably higher.

can transit freely into the neighboring region (Fig.2). This can be described by real concentration of the AQP which is bigger as compared with the calculated at the given temperature. The lesser nanoparticles size, the bigger real concentration. Due to the fact that AQP (during one period of atomic oscillation) appears near atoms more frequently in nanoparticles than in compact solid body [10, 11] and weakening of their chemical bonds will be bigger. Thus, with the decrease of nanoparticles size the real concentration of AQP increases, chemical bonds weaken more, the probability of atoms motion grows and hardness decreases correspondingly.

It should be mentioned that in the near-surface range of the nanoparticle the AQP more frequently appear near the atoms, than in its volume due to the direct and reverse direction of the AQP motion in the reflection process which will cause additional increase of the real concentration of the AQPs. In its turn as a result of increasing electron-hole screening will decrease the distance between bonding and anti-bonding orbitals that will contribute to further increase of the AQPs because of thermal transitions and correspondingly further decrease of the distance between bonding and anti-bonding orbitals [11]. Thus, in the near-surface range of the nanoparticle the real concentration of the AQP (Fig.3) and respectively the probability of the movement of atom is more than in the volume. Thus, unlike compact materials during

loading of nanomaterials and increase in the AQP concentration occurs not only as a result of pressure caused by pressure but because of decreasing of nanoparticles size.

Proceeding from the above-mentioned mechanism of changing at constant temperature, quantum state of electrons participating in the creation of chemical bonds in nanoparticles, it can be easily explained not only the above mentioned experimental data but also the facts announced anomalies from the viewpoint of MKT.

A decrease of the hardness value and yield point with decrease of nanograin sizes is naturally explained by an increase of the AQP concentration and corresponding decrease of the energy of chemical bonds.

The thing that in case of fragile nanomaterials (oxides, nitrides, carbides, intermetallids) with the change of the grains size the value of hardness is changing less than in other nanomaterials [4, 5] is due to the fact that at the uniform sizes of nanograins in fragile nanomaterials of AQP concentration and their mobility is less because of bigger splitting of atoms electron levels which decreases the possibility of electrons transition to the overlying energy levels. Therefore, in materials with big splitting of levels for achievement of the necessary AQP concentration the sizes of nanoparticles must be smaller than in materials with less splitting of levels. Figure 4 shows that the anomaly for NiZr_2 starts from com-

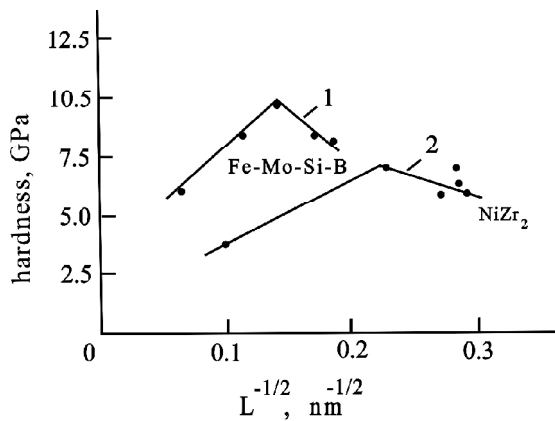


Fig. 4. The dependence the hardness of nanomaterial, which had different melting point, from the size of their respective nanoparticles $T_{m1} < T_{m2}$

paratively smaller nanopartcles size than Fe-Mo-Si-B, the melting temperature of which is less than in NiZr₂ (It is shown that [12, 13] in semiconductors and metals the width of levels splitting is in correlation with melting temperature). The same mechanism explains the fact that in nanomaterials of oxides and silicon nitrides the minimum temperature after which superplasticity occurs is higher than in nanomaterials of other substances.

As was mentioned above, in nanomaterials created from metal alloys intermettalids and refractory compounds are revealed the higher speeds and lower temperatures of deformation processes than in the same materials in polycrystalline state. This is due to the fact that the ratio of bulk and near-surface range of polycrystalline particles by order of magnitude is greater than in nanoparticles and hence the increase of the AQP concentration because of refraction is very small compared with voluminous concentration of AQP and contributes insignificantly in weakening of chemical bonds.

According to a number of authors plastic deformation in materials always starts with athermal grain boundary microsliding [4, 5] which consists in the fact that at a certain loading of the solid body the shift of one of its parts in relation to another along

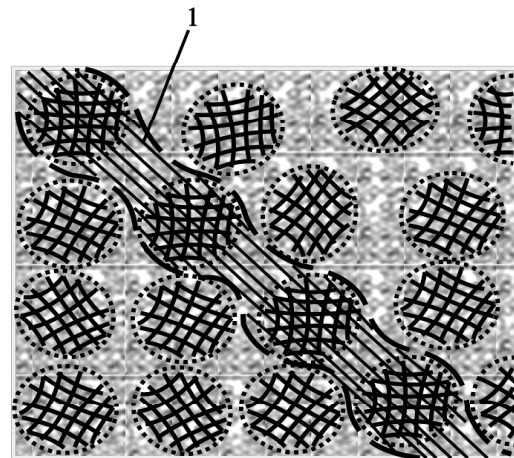


Fig. 5. Disposition of nanoparticles with different crystallographic orientation in the nanomaterial. 1-micro sliding plane.

some plane can take place. In nanomaterials plastic microsliding occurs at considerably less loadings than in compact materials which is due to the additional concentration of AQPs in nanoparticles but it is interesting to explain why the microsliding of one of its parts in relation to another one along a certain plane and not plasticity of the whole material is observed. The microsliding in nanomaterials is easily explained by the new mechanism of change of atoms location in materials offered by us in the following way. In nanomaterials nanoparticles composing them are located chaotically in terms of their crystallographic directions. Crystallographic directions of nanoparticles composing nanomaterial mainly don't coincide, i.e. these directions are located chaotically. On application of the loading to nanomaterial the direction of the pressure and crystallographic directions will have different angles. At definite angles the approach of bonding and antibonding levels will take place. This will increase the AQP concentration and correspondingly, the mobility of atoms, especially in sub-surface range of nanoparticle. In those directions of the nanomaterial where the amount of such nanoparticles is more, the microsliding will occur (Fig.5).

არაორგანული ქიმია

ქიმიური ბმები ნანომასალების სისაღის ცვლილებაში

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დატვირთვის ქვეშ მყოფი ნანონაწილაკებისაგან შემდგარი ნანომასალები იქცევიან სრულიად განსხვავებულად იმავე ნივთიერების ჩვეულებრივი მასალებისაგან: დატვირთვით გამოწვეული თვისებების ცვლილების სიდიდე და ზოგჯერ მიმართულებაც დამოკიდებულია შემადგენელი ნანონაწილაკების ზომებზე. მიუხედავად მრავალი ცდისა ამ ფენომენის ახსნა ჯერ არ არსებობდა. მოცემულ ნაშრომში შემოთავაზებულია ამ ფენომენის ახალი მექანიზმი. ეს მექანიზმი დაფუძნებულია ატომის ადგილმონაცვლეობის ახალ წარმოდგენებზე, რომელიც განიხილავს ატომის ქიმიურ ბმებში მონაწილე ელექტრონების კვანტურ მდგომარეობის ცვლილებას. ეს ცვლილება შეიძლება გამოწვეული იყოს სხადასხვა საშუალებით: ტემპერატურით, სინათლით, წნევით, ელექტრული და მაგნიტური ველებით, ნანონაწილაკების ზომების შემცირებით. შემოთავაზებული მექანიზმი თვისებრივად ხსნის ნანომასალების დატვირთვისთან დაკავშირებულ ყველა ექსპერიმენტულ ფაქტს.

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