FORMATION OF NANOSTRUCTURED SURFACE REGIONS UNDER A CONCENTRATED LOAD

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1. Introduction

The methods of concentrated loading (indenting, scratching) have been widely used for a long time to assess the mechanical properties of solids, and to study the mechanisms of deformation. For this reason, the deformation structure around indentations and scratches on different crystals have been studied [1-3]. However, the question of what happens in the material in the direct proximity of the contact with the tip of the indenter, where the maximum stresses (of the order of shear modulus) are generated, has not been well studied. A number of authors have made different suggestions concerning the state of the material under the indenter: from creation of an enormous density of dislocations, forming a strong stationary network [1,2], to the complete absence of dislocations [4] and phase transformations [5].

The investigations of the structure, created directly under the indenter tip have shown [6,7] that less than 10 % of the energy dissipation are used on dislocation and cracks formation, and more than 90 % evidently are consumed on the structural changes under indenter during deformation. Apparently, it is the inadequate understanding of the processes occurring directly at the point of contact of the indenter with the crystal that prevents the provision of an unequivocal physical meaning to the concept of microhardness [8]. The aim of this work is to investigate experimentally the character of structural changes taking place under the indenter tip, and also to describe the structural changes in terms of an orbifold model of deformation.

2. Results and Discussion

Single crystals of different structure and hardness have been investigated. Among these are refractory oxides, alkali halides, and semiconductors. The samples were deformed at room temperature using a Vickers diamond pyramid, sapphire spheres of different radii, and silicon whiskers. The materials were studied by scanning electron microscopy-cathodoluminescence (SEM-CL), X-ray microanalysis (XMA), X-ray-structural analyses, and X-ray photoelectron spectroscopy (XPS).

In our preceding works [9,10] we have shown that the relaxation of the high stresses under an indenter proceeds via the formation and displacement of point defects, and that this process results in a reconstruction of the structure with the formation of the nanocrystalline (NC) state. This reconstruction is accompanied by strong changes in physical properties of the material in regions with NaCl structure. SEM-CL investigation showed that:

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Firstly, the NC regions located in direct contact with the indenter of all of the crystals exhibit enhanced luminescence capability. Figure 1 displays a schematic diagram and a cathodoluminescence image of contact regions (light-colored in CL) on the surface and in the volume under a scratch in NaCl (the surface with a scratch and a perpendicular cleavage surface are visible). The size of this region depends on the load, and the radiation disperses diffusely at depths close in magnitude to the half-diameter of the scratch. The enhancement of the CL in this case is associated with the increase in the intensity of excitonic emission bands [10]. This indicates a relative improvement of the nanocrystalline structure, i.e. a decrease in the number of other defects, which form competing channels for dissipation of the energy of the electron beam.

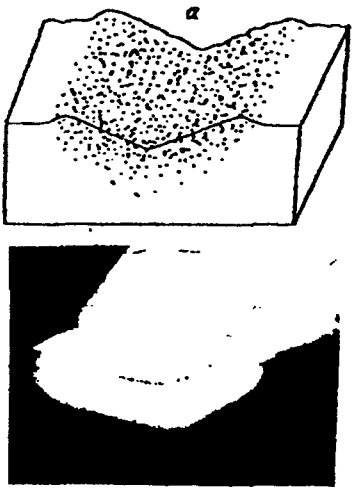

Fig.1. Schematic (a) and CL image of the scratch on a vertical cleavage plane of a NaCl single crystal. The scratch is 30μm wide.

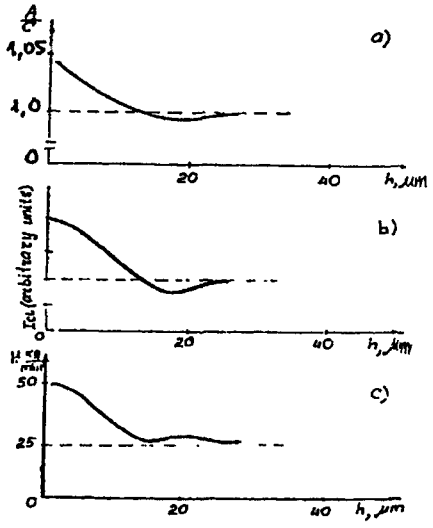

Fig.2. Changes in stoichiometry (a), CL intensity (b), and microhardness (c) with the depth under the imprint (NC regions).

It should be noted that the CL intensity at the imprint bottom may be higher or lower than that in the undeformed matrix. The increased luminescence in the contact zone between indenter and specimen is observed only at loads below the value P_{lim} typical for each crystal studied. Loads above this value cause luminescence quenching [11]. Studies of the degree of perfection of crystal structure using election channeling microscope [12] have confirmed the above suggestion that the CL quenching at $P > P_{lim}$ is connected with the distortion in crystal structure of imprint bottoms, and scratches up to the amorphous structure.

Secondly, the microhardness of the NC regions (light areas in CL image of Fig.1) is tens of percent higher than that of the undeformed matrix and it diminishes with depth (Fig.2c). This fact was established by means of indentation of the bottom of the imprint produced by sapphire of comparatively large diameters (about 3 mm) and of a perpendicular cleavage faces.

Thirdly, it was found by backscattering electron modes in SEM [13] that the density variations in the deformed materials are less compared to that in the undeformed matrix. It is known [14] that the density of NC materials is much lower than that of poly-and single crystals due to the specific structure of the boundaries.

Fourthly, this region has a peculiar chemical composition. The studies carried out by XPS and XMA methods have shown the change of stoichiometry in the NC regions (Table 1), with the remarkable cation-deficiency.

Crystals	MgO	LiF	NaCl	KCl
C/A	0,91	0,95	0,96	0,98

TABLE 1. Ratio between numbers of cations (C) and anions (A) in the imprint bottom (NC regions) (the ratio for undeformed regions is 1).

Figure 2a demonstrates the stoichiometric changes with depth in NaCl. It is seen that near the surface the sodium-deficiency is the highest (up to 4%), whereas in the bulk there is a smaller deficiency. Near the boundary of the bright region (in Fig.1) the deficiency is not observed, and farther away an excess of sodium is detected. At great depths (beyond the regions with NC structure), the relation of sodium and chlorine quantity is similar to that in the undeformed single crystalline matrix.

It should be noted that in practically all crystals under investigation (especially the covalent crystals) XPS spectra show a displacement of the maximal energies of the photoelectrons in nanocrystalline regions relative to that in the single crystal matrix (Fig. 3). This indicates a change in the interatomic bonds that occur most likely at grain boundaries.

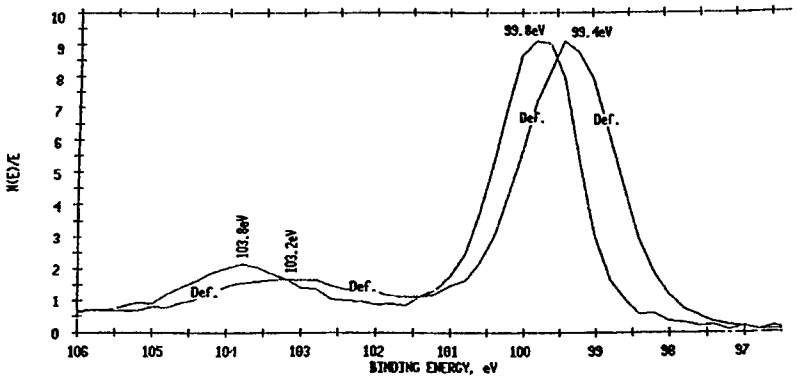

Fig.3. XPS ($2p_1$ and $2p_3$) spectra from the surface of single and nano (def) crystal of silicon.

We emphasize that nanocrystalline regions under the indenter are metastable. The storage of the deformed specimens (alkali halides) in air or the annealing causes the oriented grain growth. This is accompanied with recovery of the CL intensity, density and hardness of the material in these regions to the original ones, i.e. these regions lose the properties characteristic of the NC state. In the case of unsuccessful attempts to reveal the grains on the imprint bottom by SEM observation with a 10-nm resolution immediately after the indentation, one can resolve the recrystallized grains having size of several tens of nanometers. The analysis of the kinetics of the grain growth [15] and the extrapolation of the observed dependence of the grain size on annealing duration to zero time lead to the conclusion that the mean grain size (D) in alkali halides due to indentation is comprised of several nanometers (for NaCl, D≈10nm). In addition to the experimental data concerning the recrystallization process the energetic estimations of microimpressing will be made to evaluate the mean size of the grains formed. The work, W, done by indenter penetration can be measured quite exactly: W=Ph, where P is the load on indenter and h is the depth of recovered imprint. This energy (mainly above 90% of total) is expended largely on the formation of a region with NC structure. Let us assume that the total energy, W, is spent on the formation of the surfaces of grain boundaries in the volume with NC structure, i.e. W= δS, where δ is a specific surface energy and S is the total area of boundaries. Also, S=V/D, where D is the mean grain size and V is the volume of a region with NC structure. Thus, D=Vδ /W, where V is determined from the CL picture of the imprint profile (Fig.1), $V \approx d^3/4$, where d is an imprint diameter, W is measured, and δ is from 100 to 1000 erg/cm^2. Under the assumption that on formation of the NC structure 0.9W is consumed, the mean size of nanocrystallites, D, in alkali halides crystals should be several nanometers.

Besides the empirical estimations, a theoretical evaluation of the mean size of the nanocrystals formed by indentation is given based on energy assessments of micropressing: $D=K(\delta/H)$, where H is the microhardness and K is the coefficient depending on binding energy and shape of the indenter. Similar dependence can be obtained from the influence of nanocrystal size on CL intensity, density and stoichiometry of NC materials.

In view of the complexity of the concept of hardness, its physical meaning depends on the testing methods employed [8]. In accordance with our investigations it seems natural to return to the definition given by P.A. Rehbinder in 1936 [16]. According to which, the hardness is equal to the work required to form a unit area of a new surface of the solid. Thus, the experiment shows, that the deformation of a material under the indenter tip causes the formation of nanocrystalline structure. It seems that theoretically this process can be connected with so-called orbifold model of deformation of crystals.

3. Orbifold Model of the Deformation of Crystals

The peculiarities of NC materials are in accordance with their defect structures. However, they can be explained also from the point of view of an ideal crystal. The ideal crystal is a community of atoms of the definite Fedorov symmetry group. In the Eucleadean space an ideal crystal is infinite. As distinct from an ideal crystal the real one has the finite dimension and contains the volume defects. Any ideal crystal consists of cells that can be considered as independent ranges of the corresponding Fedorov group. The independent range of such Fedorov group is a part of the space without equivalent atoms according to this group. The equivalent atoms can be in the boundaries of independent range. The authentic view of the independent ranges of Fedorov group lies in the fact that the equivalent points in the boundaries are identified. In such a manner the compact local Eucleadean ranges (orbifolds) appear in topology [17]. In the case of two-dimensional space the orbifolds have a shape of the tore (Fedorov group Pb), Klein's bottle (Fedorov group Pg), Meubius ribbon (Fedorov group Cm) etc. Consequently, for every Fedorov group of any dimensionality there is its own orbifold [18].

At present the orbifold concept of crystal growth starts its advancement [19,20]. According to this concept the growth entities can be not only separate atoms but also atomic groups consisting of definite number of atoms present in the independent range of the correspondent Fedorov group. As a result of small dimensions these groups may shrink on themselves the free chemical bounds and become the quasineutral particle. The topology of this particle corresponds to the volume of an ideal crystal. When considering the deformation process of the crystals as opposite to the growth, the relaxation of enormous stresses causing the stability loss can be due to the break up of crystal structure into orbifolds. This permits the consideration of the orbifolds as a mathematical model of nanocrystal - a finite ideal crystal having the compensated bonds. However, in reality it is very difficult to obtain the total bond compensation on account of identifying orbifold. So, one can assume the compensation of only the strongest bonds.

According to the orbifold model the nanocrystals should have the following properties: 1. The nanocrystal is quasineutral, the closed bonds being relatively easy to break. 2. The volume of nanocrystal is a multiple of the integral number of the volumes of elementary cells. 3. The shape of nanocrystals is not rigid and it can be changed. 4. The nanocrystal can break up and unite into any combination of the whole elementary cells. 5. The smaller the nanocrystal size the stronger it compensates its unsaturated bonds, and hence weaker interactions with neighbors. 6. The nanocrystal has a perfect internal structure, the structural defects can only be in the boundaries, which have a fractal character making its contribution to the crystal properties.

These properties of the nanocrystals suggest the following model of crystal deformation. Initially at small stresses the usual dislocation mechanisms are operating. At high stresses and deformations (the action of a concentrated load, explosion deformation, rolling, etc.) the decomposition of blocks (orbifolds) to the smaller ones originates. The result of this should be the increase of the hardness of a material, which depends on particle dimension, i.e. on dispersion work according to A.P. Rehbinder [16]. The rise in hardness will be analogous with the Petch-Hall effect until the strongest bonds in each orbifold is compensated. Under these conditions each structure has an orbifold of definite size, its shape is determined mainly by the deformation conditions. After further reducing orbifold size the hardness will tend to decrease (anomaly of Petch-Hall effect) as a consequence of a continued compensation of the weakening of bonds between orbifolds. This facilitates the intergrain sliding. In the limiting case after the total compensation of the bonds inside the orbifolds the superplasticity should be revealed. Thus, the specific

properties of the materials are determined mainly by the orbifold dimensions (nanocrystals), which influence the boundary properties.

4. Conclusion

The high stresses arising under an indenter relax via the formation and migration of interstitial atoms, which result in the structural rearrangement with the formation of the NC state. The orbifold model of the crystal deformation based on new aspects of the peculiarity of the structure and properties of nanocrystalline materials is presented.

5. Reference

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