CRACKING IN SURFACE-ADJACENT LAYERS OF KDP SINGLE CRYSTALS: EFFECT OF LOCAL STRESS CONCENTRATION REGIONS

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ABSTRACT

The effect of the composition and structural state of impurities on the formation of microcracks in KH_2PO_4 single crystal grown under different conditions is cosidered. It is shown that local internal stresses on dispersed solid- and liquid-phase inclusions are one of the sources of cracking. Revealed are the impurities which decrease the value of mechanical strength and intensify the tendency of the crystal surface to stress corrosion in the presence of atmospheric moisture.

KEYWORDS

Single crystal, mechanical treatment, inclusions, microstructure, cracking, mechanical properties.

Crack formation is a frequently occuring microstructure defect for single crystals grown from aqueuos solutions. In most cases it is related to absorption phenomenon taking place on the surface of the growing face and resulting in the appearance of local stresses in the volume of the material (Petrov et al, 1983). For KH_2PO_4 crystals such stresses may originate, e.g. in the impurities present in the raw material or specially introduced for the purposeful modification of the crystals' properties. The said crystals possess noticeable brittleness in a wide range of temperatures including the room temperature (Atroshchenko, 1987a), therefore the local stresses which arise during the crystal growth process must lead to cracking. The latter phenomenon is a result of the brittle deformation of the material, so it essentially depends on the value of the local stresses and their distribution in the volume of the crystal.

Considered in the framework of the present research is the effect of the impurity composition and the solubility limit for impurities in the crystal lattice matrix of KH_2PO_4 on cracking which accompanies the growth of these crystals. KH_2PO_4 single crystals with different dopants are grown along the direction [001] on prismatic seeds by the method of solvent recirculation from the raw material of the same purity degree, the growth rate being 0.5 mm/24 hrs. As shown by the investigations of their microstructure, phase mechanical characteristics, all the considered impurities are to be divided into three groups in accordance with their influence on the "embrittlement" of KH_2PO_4 crystals.

Belonging to the first group are the so-called structural impurities which form limited substitutional or interstitial solid solutions with the matrix of the crystal under consideration when their concentration reaches some definite value. Structural impurities give rise to changes in crystal lattice parameters. Lead is an example of such substances. Based on the data of microscopic investigations as well as on the measurements of the crystals' microhardness and elementary cell parameters we have shown that this impurity, if having a concentration reaching $1.9 \cdot 10^{3}$ mass %, forms limited solid solutions with KH_2PO_4 (Atroshchenko and Kolodyazhnyi, 1990). Within the monophase solid solutions region the value of the brittle strength σ_s exceeds that of the undoped crystals by 60 % (for the latter σ = 13.0 kgs/mm²). Microscopic investigations performed on Pb-doped KH_2PO_4 single crystals have revealed the absence of microcracks initiated by the impurity playing the role of a local stress concentration region in the crystal growth process.This is explained by the fact that lead having the said concentration completely enters the crystal lattice of KH_2PO_4 and does not form the second phase inclusions.

The second group of impurities comprises the substances which are contained in the solution for the crystal growth, but practically do not enter the crystal lattice. For example, we have made an attempt to dope KH_2PO_4 crystals with bromine and iodine. The chemical analysis of the grown crystals shows that the concentration of these elements in both the upper and the lower parts of all the crystals is below the sensitivity threshold for the method of their determination ($<10^{-3}$ mass %), though the content of the impurities in the solution has varied from 10^{-3} to 10^{-2} mass %. Thus, the said dopants are not captured by the growing crystals and do not enter its lattice; therefore they do not affect the crystal's mechanical properties and cracking resistance.

The third group of impurities consists of the so-called nonstructural ones. These substances enter the crystal, but practically do not form substitutional or interstitial solid solution with the crystal matrix. The said impurities precipitate in the crystal in the form of a dispersed phase. As shown, e.g. for synthetic quartz, sodium, lithium and potassium impurities which enter the lattice in the form of discrete submicroscopic aggregates give rise to optical inhomogeneity and microscopic cracks in the regions containing such dopants (Khadzhi, 1962). We have found that for KH_2PO_4 single crystals nonstructural impurities are the ions of rare earth elements, in particular, holmium. In our experiments the concentrations of Ho ions in the solution for the crystal growth has varied from 10^{-4} to 10^{-2} mass %. The morphology of Ho-doped KH_2PO_4 crystals is similar to that of the undoped crystals, no tapering of the natural growth faces being revealed.

For the crystals doped with holmium the calculated value of brittle strength σ_s equals 7.3 kgs/mm² i.e.it is approximately a half of this magnitude for the undoped crystal. Moreover, we have found that for the former crystals stress corrosion is by far more intensive in the presence of atmospheric moisture, aqueous solution and other surface-active substances. In particular, this fact manifests itself in the 50 % elongation of cracks around the microhardness indentation on the face (001) along the directions [100] and [010] (according to Atroshchenko (1987b) these are directions of the easiest dissolution for KH_2PO_4 crystals in the presence of surface-active substances). We have also revealed that the mechanically polished surfaces of the doped crystals kept in air degrade, this process being accompanied by the formation of local regions with corrosion damage and cracks.

To explain the observed decrease of the mechanical strength, the rising tendency of the Ho-doped crystals to cracking and the reduction of their corrosion resistance in comparison with the nominally pure material, a detailed examination of the crystals has been performed. The microstructure of the samples has been investigated in transmitted light. The surface of the face (001) has been examined after etching in a solution which reveals dislocations. As shown by the repeated sequential chemical polishing and etching of the surface, it is in the volume, but not on the surface of the crystals that the structural changes emerge. The obtained results are easily reproducible in the process of layer- by-layer analysis. The largest manifestations of the optical microscope allow to observe hardly noticeable point precipitations of the second phase. Their concentration rises with the increase of the content of Ho. In some crystals the distribution of the impurity is zonal-sectional. Revealed on the face (001) of Ho-doped KH_2PO_4 crystal are various etch patterns. Along with regular tetrahedral single etch pits unambiguously corresponding to growth dislocations, we have observed lens-like etch patterns stretched along one of the two directions [110] on the plane (001). As shown by Atroshchenco et al (1988) they are conditioned by the local decrease of the crystal symmetry and a partial breakdown of hydrogen bonds. Other types of the observed etch patterns are T-shaped ones having "rays" along the directions [100] and [010] as well as dendrite-like grooves extended along the same directions. Some inclusions are surrounded by network crack patterns along the directions [100] and [010], this testifying to the existence of local stresses around the precipitations of the dispersed impurity phase (Fig.1.). Repeated chemical polishing and etching lead to the formation of cracks on the entire surface of the face (001).

Based on the obtained results as well as on analogy with other investigations (e.g. the study of cracking in quartz doped with nonstructural impurities) we draw the following conclusion. In Ho-doped KH_2PO_4 single crystals there exist dispersed inclusions of the impurity phase which is hardly revealed by means of optical microscopy method due to its small size; however, this phase noticeably influences the mechanical properties of the considered crystals, in particular, crack formation. The nonstructural impurity may be adsorbed on various active centers of the growth surface: on the points

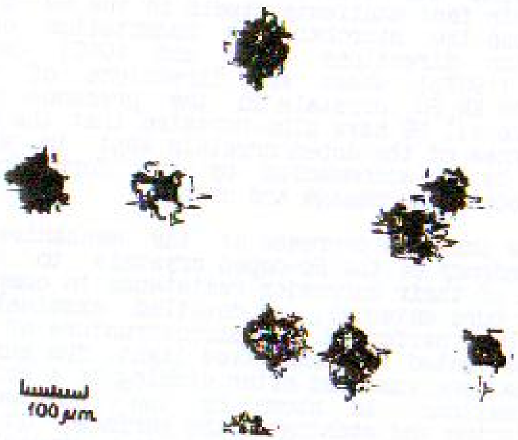

Fig.1. Precipitations of dispersed impurity phase with cracks.

where dislocations reach the surface, on the joints of growth sectors and zones, etc. Naturally, the finely-dispersed particles of the impurity are surrounded by local stress regions. The differences in the morphology and extension of cracks in separate parts of the crystal indirectly testify to the variations of the dispersity degree for the impurity phase and the local stress initiated by this phase. The variety of the etch patterns and different degree of their distortion show that the crystals are optically inhomogeneous and have rather low structural perfection.

The mechanical treatment of the crystals which contain finely-dispersed second phase inclusions is accompanied by substantial difficulties. Emerging inside the surface-adjacent layer of the crystal subjected to cutting, grinding and polishing is a layer with a large number of cracks caused by the presence of essential local stresses on impurity inclusions. The depth of this layer exceeds that of the damaged layer of undoped KH_2PO_4 crystals by several times. In this case it is practically impossible to obtain polished crystal surfaces without cracks.

A special investigation has been performed on the crystals grown along the directions [010] and [100] at a rate exceeding the conventional ones used for the growth of KH_2PO_4 crystals along the direction [001]. It has been found that the crystals obtained by the high-rate method may entrap liquid-gaseous-liquid-phase inclusions (Fig.2.) and the impurities which are

the sources of stresses. As a rule, the mechanically treated surface-adjacent layers of such crystals are characterized by typical crack pattern (Fig.3.) observed along the directions [100] and [010] on the faces (001), and this essentially hampers the process of obtaining high-quality surfaces.

Isothermal annealing performed on the majority of the crystals containing the above-mentioned microstructure defects favours

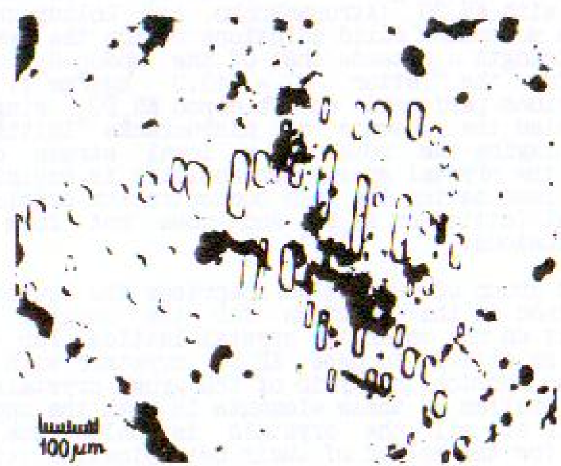

Fig.2. Liquid-phase inclusions.

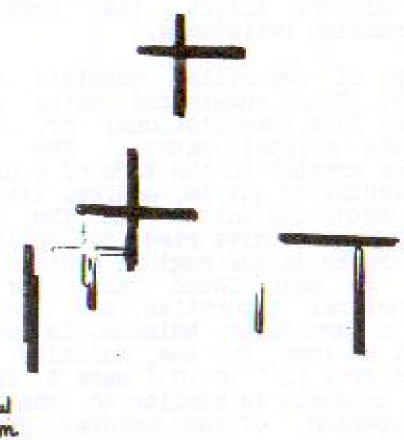

Fig.3. Cracks in single crystals grown at high rates.

the decrease of their tendency to cracking. This testifies to the reduction of the level of residual total and local (present on various inclusions) stresses. Nowadays this effect is being successfully used in practice for the improvement of the mechanical properties of articles based on KH_2PO_4 single crystals.

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