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Abstract

Full Text

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PHYSICAL CHEMISTRY

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ON THE ROLE OF DISLOCATIONS IN THE PROCESS OF THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE CRYSTALS

(Presented by Academician N. N. Semenov, 3 VIII 1964)

In work (1) it was shown that the reaction of thermal decomposition of NH_4ClO_4 begins at individual centers at different points of the crystal and develops anisotropically, forming a cloud of moving nuclei that merge toward the middle of the center. It was also suggested there that this character of the development of the reaction is due to the presence and motion of dislocations in ammonium perchlorate crystals. The present work is devoted to a more detailed study of the behavior of dislocations in ammonium perchlorate crystals and to clarifying their role in the process of its thermal decomposition.

Ammonium perchlorate crystals were grown by evaporation of an aqueous solution of twice-recrystallized NH_4ClO_4 at 0° . Dislocations were detected by etching the surface of the crystals in 95.5% ethyl alcohol. The etching process was continuously observed under a microscope (the process was carried out in a transparent chamber). When high magnifications were used, the etchant itself served as the immersion liquid.

Figure 1 shows a photograph of etch figures formed on the rhombohedral face of a single crystal. In most cases the etch pits were elongated in chains along the main diagonal of the rhombohedron (010), in the same direction in which the maximum rate of development of the decomposition reaction was observed. However, there were cases in which the etch pits were arranged disorderly (Figs. 1, 2, 3, 4; see insert to p. 1135).

To prove that the etch figures were not associated with surface defects, the crystals were etched to a considerable depth. As a result it was found that the etching pattern either remained unchanged or the number of etch pits increased, probably owing to the presence of dislocation loops in the crystal.

Etching of the lateral (rectangular) faces also showed the presence of dislocation outcrops. In this connection, attempts were made to detect a three-dimensional dislocation network. Figure 2 shows the etching pattern of the fracture surface of a crystal, on which a network of interacting dislocations is clearly visible. In addition, on many crystals it was shown that dislocations are grouped near growth defects (Fig. 3a), as well as near mechanical damage (Fig. 3b).

Direct experiments showed that the greatest density of dislocations arises at the point where a load is applied to the crystal during its plastic deformation. Upon annealing deformed ammonium perchlorate crystals, polygonization was observed, which, as is known, is a consequence of the formation of groups of edge dislocations during their motion in the crystal.

Annealing experiments on undeformed crystals were carried out as follows: first the crystal was etched and photographed—

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Fig. 1. Etch figures on the rhombohedral face of the crystal, 600×

Fig. 2. Network of interacting dislocations, 350×

Fig. 3. Grouping of dislocations near growth defects, 400× (a); the same near mechanical damage, 300× (b)

Fig. 4. Polygonization on the rhombohedral face, 750×

surface was revealed, crystals with a disordered arrangement of etch pits were selected, and then the single crystals were heated in air for four hours at 130°. (Under these conditions the decomposition reaction is not yet manifested.) Subsequent etching gave a distinct picture of polygonization (Fig. 4).

We carried out experiments on etching crystals that had already been preliminarily heated to the decomposition temperature. They showed that near the nucleus the dislocation density is increased. This indicates that the catalytic effect on the rate of the reaction product may be connected with the appearance, caused by it, of an additional number of dislocations in the layer of the initial substance bordering on the product.

The average dislocation density on the rhombohedral face (as judged by the number of etch pits) is $\sim 10^6$ per cm^2 . However, the density varies strongly from crystal to crystal. In addition, it may be nonconstant even on one and the same face because of the nonuniform distribution of dislocations. The dislocation density in NH_4ClO_4 is extremely sensitive even to weak mechanical actions and tends to accumulate during prolonged work with the crystal.

The observed pronounced similarity in the anisotropy of the arrangement of dislocations and the anisotropy of the development of the decomposition reaction of NH_4ClO_4 , as well as the localization of nuclei near the points where dislocations emerge on the surface of ammonium perchlorate, which was observed in our experiments, indicates the important role that dislocations, as structural defects,

may play in the process of thermal decomposition of ammonium perchlorate.

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1. A. V. Raevskii, G. B. Manelis, DAN, **151**, 886 (1963).

Note: Figure translations are in progress. See original paper for figures.

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