Dislocations in Sodium-Chloride Crystals

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Distributions of dislocations in sodium chloride crystals, which were induced by heat treatment or working, were investigated, using a newly developed etchant.

The crystals, which were annealed above 300 °C, showed reduced dislocation densities and rearranged dislocation patterns. By raising the temperature to 600 °C or 700 °C many elongated subboundaries or subboundaries arranged in the ⟨110⟩-orientation were newly formed. The effect of annealing time on the dislocation rearrangement was small.

New dislocations were easily induced by stress. The samples, annealed at 600 °C after pressing, showed many enclosed subboundaries (polygonizations).

Various methods are available for the observation of dislocations in crystals, viz., etch pit technique, electron microscopy, X-ray micro-beam technique, and transmission infrared microscopy.

Especially, the etch pit method has much contributed to the observation of dislocations in ionic crystals, and many investigations have been performed on LiF [1–3]. Also studied was the NaCl crystal by MORAN [4], MENDELSON [5], and BARBER [6].

The writer [7] previously studied problems pertaining to dislocation etch pits in metallic crystalline zinc by segregating impurities onto dislocation sites. Dislocation etch pits in metallic crystals are in general not as clear as in ionic crystals.

In the present study, the etch pit technique has been used in order to examine the movement and distribution of dislocations in NaCl crystals influenced by heat treatment or working.

I. Principles

CABRERA [8] has theorized the mechanism by which an etch pit forms at a dislocation site.

The growth or dissolution of crystals may be considered as a series of monomolecular steps along the crystal surface [2]. The points at which such molecular layers terminate are named "kinks" (Fig. 1 a). The kinks are very active, and at these points formation or dissolution of molecular layers takes place easily. If a perfect crystal is exposed to a solvent, unit pits will form at irregular positions, and these unit pits will develope as shown in Fig. 1 a.

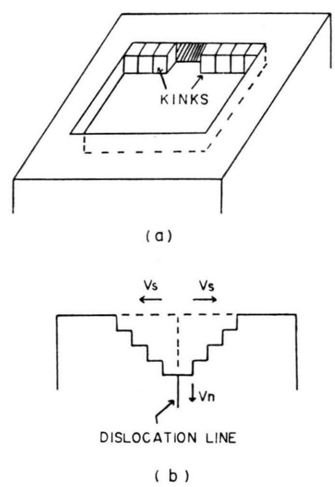

Fig. 1. Formation of etch pits: (a) enlarged unit pit of monomolecular depth, and (b) etch pit of a dislocation.

CABRERA insists that the dislocations are the preferential sites of unit pit formation. According to his theory visible etch pits will be formed only if the dissolution rates perpendicular (V_n) and parallel (V_s) to the crystal surface satisfy the condition

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1 J. J. GILMAN u. W. G. JOHNSTON, Dislocations and Mechanical Properties of Crystals, John Wiley, New York 1957, p. 116.

2 J. J. GILMAN, W. G. JOHNSTON, and G. W. SEARS, J. Appl. Phys. **29**, 747 [1958].

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$V_n/V_s \geqq 0.1$ (Fig. 1 b). V_n depends on the surface energy and the shear modulus of the crystal, and is not affected by the solvent. V_s, however, may be decreased by using a suitable inhibitor in the solvent. In other words, by increasing the ratio V_n/V_s it should be possible to obtain observable etch pits. In order to improve the dislocation etch pits in metallic crystals, impurities should be segregated at the dislocation sites (e. g., Ref. [7]). This increases V_n.

II. Results and Discussion

(a) Samples

Sodium chloride single crystals of optical grade were used. The samples were cleaved along the (100) face with razor blades. Cleavage along this surface can be easily done. As crystals are sensitive to stress, much care has to be taken.

(b) Etchants

The etchants for the observation of NaCl dislocation etch pits developed by MORAN [4], MENDELSON [5], and BARBER [6] were intercompared. MORAN's and BARBER's etchants did not produce satisfactorily clear pits, while MENDELSON's etchant showed clear etch pits.

The writer has developed a new etchant: 4 grams of mercuric chloride were used as inhibitor and dissolved in 1 liter of glacial acetic acid. Since $HgCl_2$ has a relatively small solubility in acetic acid and precipitates in supersaturated solutions, the solution should always be shaken before use to make it homogeneous.

The sample is etched for 1.5 minutes by stirring it in the etchant, and it is then dried with hot air. The dislocation etch pits produced in this manner showed the same clearness as those obtained with MENDELSON's solution. All experiments, unless otherwise stated, were performed with the new etchant as described.

The effect of the quantity of $HgCl_2$ was as follows. Etch pits from 1, 2, and 4 gm of $HgCl_2$ per liter of glacial acetic acid displayed similar clearness. The pits in the case of 0.5 gm of $HgCl_2$ had no noticeable depth, and they appeared as widened. In the case of 9 gm of $HgCl_2$, the pits were similar in size as those from 4 gm of $HgCl_2$, but they were deeper and round-cornered or rhombic, one side being longer than the other, rather than of equal length.

The effect of the stirring was also examined. Without stirring, the pits were very small and round-cornered. With very slow stirring, the pits gave obscure figures. Upon vigorous stirring, the pits looked the most distinct. This is the same observation as made by MENDELSON [1] on NaCl, and by the GILMAN group [2] on LiF.

Fresh etchants have always been used. With etchants used several times, the pits grew, but became obscure. Dissolved NaCl must have reduced the etching rate. This has also been observed by the GILMAN group [2] on LiF.

Lowering the temperature decreased the magnitude of the pits, as did missing agitation.

When the dislocation density increased, the pits diminished in size, evidently because the pits interfered with each other.

(c) Correspondence between Etch Pits and Dislocations

It has been supported by many evidences, that one sees any dislocation existing in a crystal by means of etch pit technique. GILMAN and JOHNSTON [1], and MENDELSON [5] have enumerated these evidences. In the present experiments, the evidences listed by them have been confirmed. For instance Fig. 2 * displays the matched opposite faces of a crystal which was cleaved in two. The pits show the one-to-one correspondence. Each etch pit seems to be a counterpart to each dislocation. This sample was annealed three hours at 700 °C prior to etching.

In addition, edge and screw dislocations can be discerned by the etch pits made by this etchant. In Fig. 3, the symmetric pits indicate edge dislocations, and the asymmetric pits show screw dislocations.

The reason why in a rocksalt type crystal the edge dislocations result in symmetric pits and the screw dislocations in asymmetric ones has been thoroughly explained by AMERLINCKX [9], MENDELSON [5], and the GILMAN group [2]. The slip system of NaCl is given by $\{110\}$, $\langle 110 \rangle$ [10]. The screw and edge bands are shown in Fig. 4 a. Here the edge dislocation line comes out as symmetric pit because it is perpendicular to the plane (001) (vide Fig. 4 b), while the screw dislocation, since it is slanted by 45° from

* Fig. 2—12 see p. 302 a—c.

[9] S. AMERLINCKX, Phil. Mag. 1, 269 [1956].

[10] E. SCHMID and W. BOAS, Kristallplastizität, Springer-Verlag, Berlin 1935.

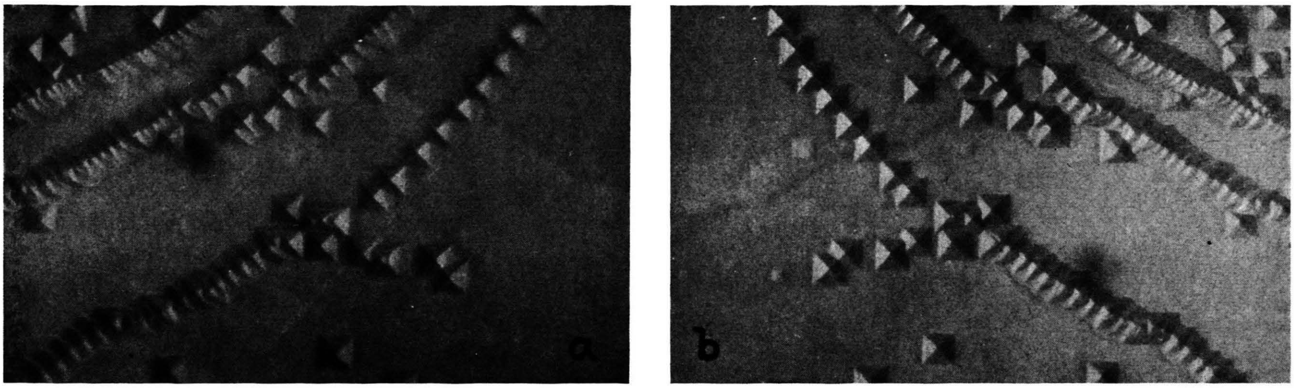

Fig. 2. Etch pits on matched opposite sides of a cleaved crystal. × 500.

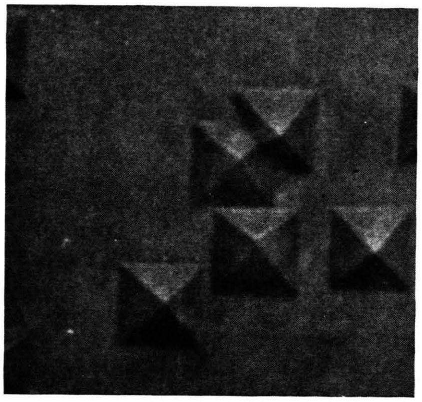

Fig. 3. Etch pits at edge and screw dislocations. Lower left pit is at edge dislocation, others are at screw dislocations. × 1,000.

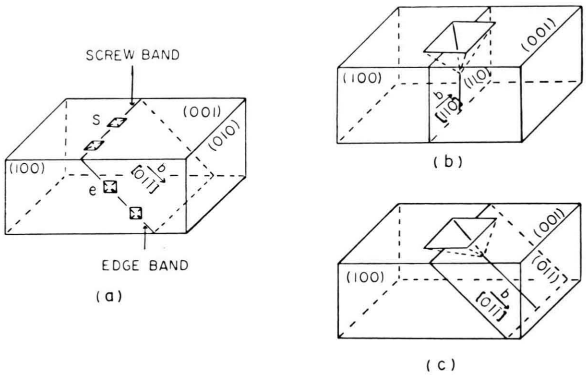

Fig. 4. Schematic comparison of edge and screw dislocations. (a) In the glide plane are shown the edge dislocations "e" and screw dislocations "s". (b) Symmetric pyramid pit at edge dislocation. (c) Asymmetric pyramid pit at screw dislocation.

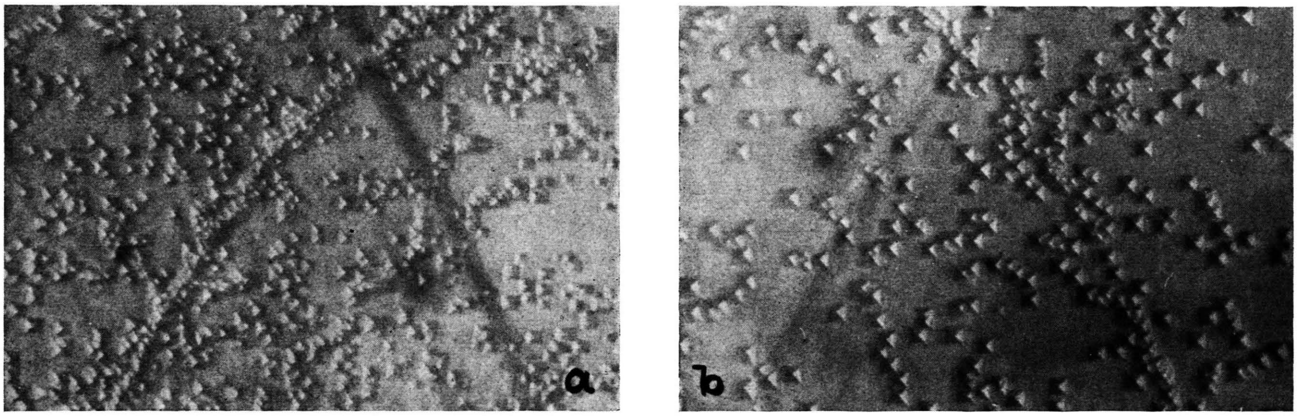

Fig. 5. Effect of heat treatment on the distribution of dislocations. A sample was cleaved in two. (a) One piece which was not heat treated. (b) Matching crystal face of second piece which was annealed at 600 °C for 3 hours. × 500.

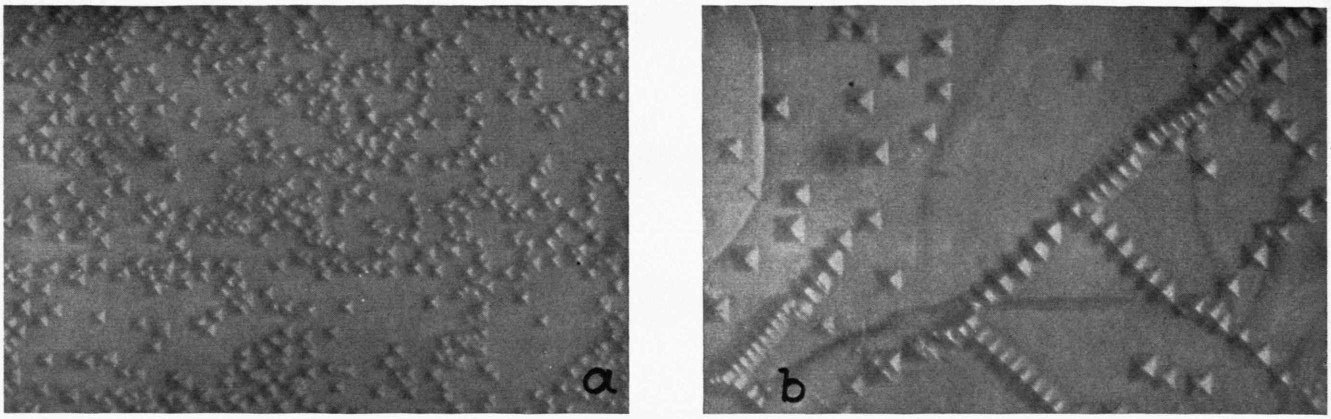

Fig. 6. Effect of annealing temperature on the dislocation structure of NaCl. A sample was cleaved in two. (a) One piece which was annealed at 400 °C for 3 hours. (b) Matched opposite face of second piece which was annealed at 700 °C for 3 hours. × 500.

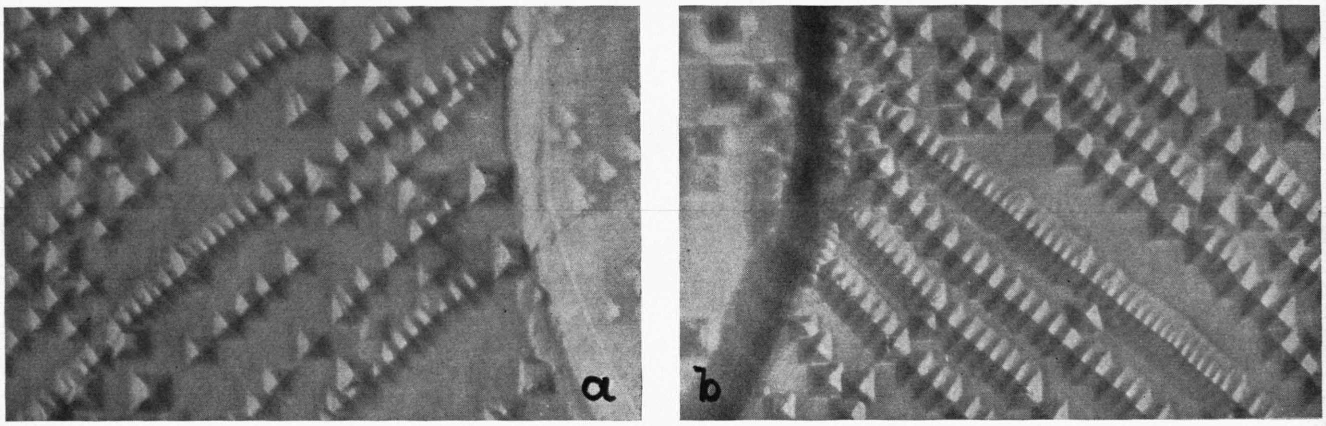

Fig. 7. Effect of annealing time on the distribution of dislocations. A sample was cleaved in two. (a) One piece which was annealed 3 hours at 600 °C. (b) Matched opposite side which was annealed at 600 °C for 6 hours. × 500.

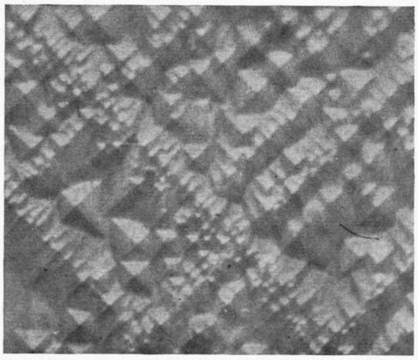

Fig. 8. Subboundaries rearranged in the slip system. The sample was annealed at 600 °C for 3 hours. × 500.

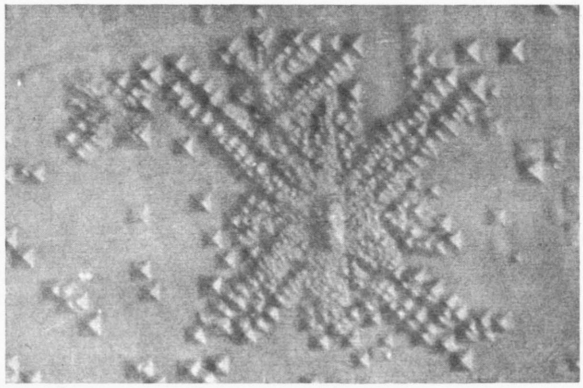

Fig. 9. "Rosettes" produced by falling 80-mesh carborundum. × 500.

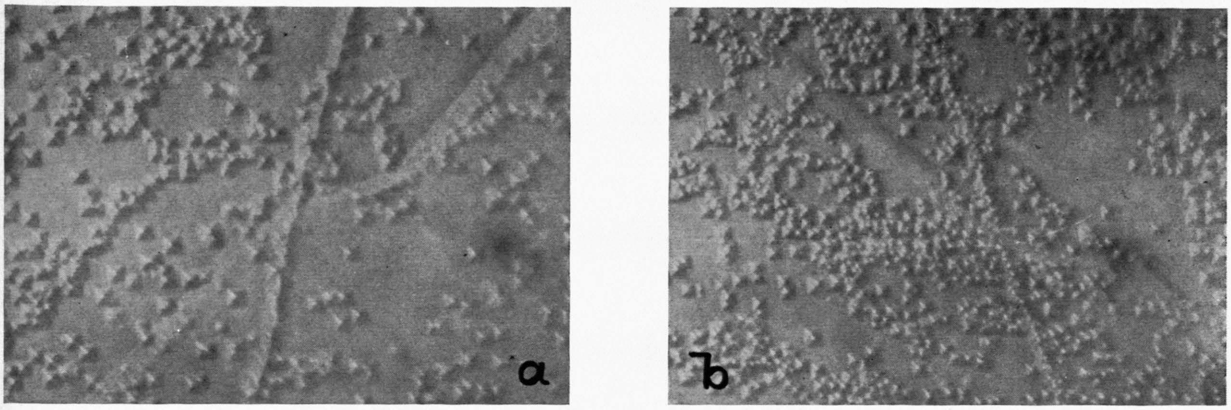

Fig. 10. Effect of working on the dislocation structure of NaCl. A sample was cleaved in two. (a) A piece which was not worked. (b) Matched opposite face of second piece, viewed after pressing (1.25 kg/mm^2) on its face. $\times 500$.

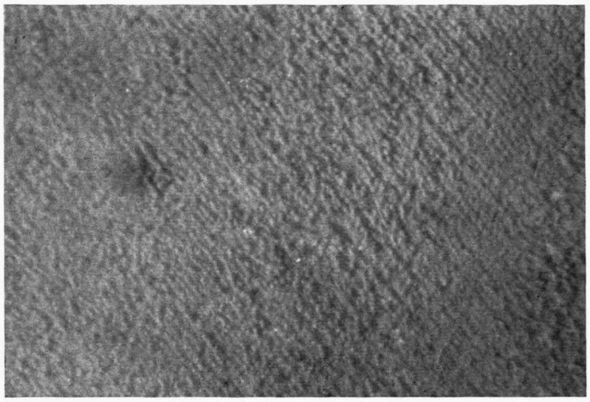

Fig. 11. Dislocation etch pits after pressing on its face. Slip directions are observable. $\times 500$.

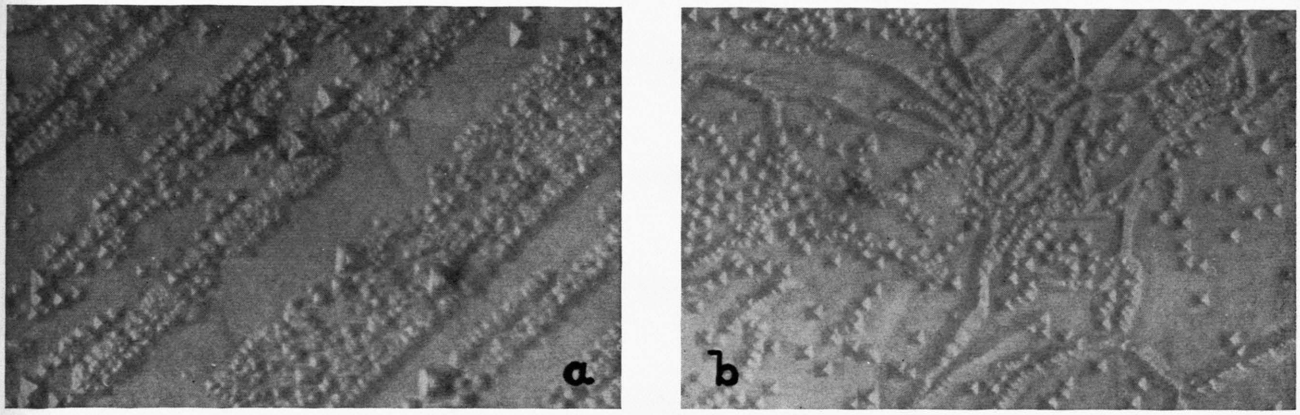

Fig. 12. Effect of working and heat treatment. A sample was cleaved in two. (a) Only heat treated piece (600 °C; 3 hours). (b) Matched opposite face which was annealed (600 °C; 3 hours) after pressing (0.95 kg/mm^2). $\times 500$.

the plane, turns up as an asymmetric pit (vide Fig. 4 c). We can, of course, find also etch pits of intermediate character between edge dislocations and screw dislocations.

(d) Effect of Heat Treatment

Samples were cleaved in two pieces. One of them was heat-treated, the other not. Then the etch pits of the two pieces were compared.

Fig. 5 a and 5 b represent matched opposite faces. We can see that the dislocation density decreases and is re-distributed by annealing at 600 °C. This is attributed to the fact that with the aid of thermal energy the dislocations of opposite sign recombine and are rearranged into a stable energy state.

After annealing at 300 °C for three hours – the heat-treated piece showed only a small reduction of dislocation density and a small shift of the dislocations.

A piece of cleaved crystal and its opposite matched side were annealed at 400 °C and 700 °C, respectively. It was difficult to locate the matching position. Typical etch pits are shown in Fig. 6. It shows that the influence of temperature is very strong, and the annealing at 700 °C contributs much to the annihilation of dislocation density and to the formation of subboundaries.

In the next case, one side of the cleaved crystal was annealed at 600 °C for three hours, and its matched opposite side for 6 hours at the same temperature (Fig. 7). The effect of lengthening the annealing time was only a small increase in the formation of subboundaries.

Many subboundaries, formed by heat treatment, are of elongated form (Fig. 7), and occasionally their dislocations are oriented in the ⟨110⟩-direction (e. g., Fig. 8).

(e) Effect of Stress

NaCl crystals show a very high sensitivity to stress (working). New dislocations are easily formed. When carborundum of 80-mesh fell from a height of 2 or 3 mm on the crystal surface, which was annealed previously at 700 °C for three hours, rosettes appeared as shown in Fig. 9.

In Fig. 10 one piece of the cleaved crystal was stressed, and the other not. The stress was produced by an Instron Testing Machine perpendicularly to the observed surface with a pressure of 1.25 kg·wt /mm^2. Faces parallel with the stress show pit distributions similar to Fig. 10.

In Fig. 11, dislocations are arranged in the ⟨110⟩-direction, a big stress being applied. It represents the NaCl slip system {110}, ⟨110⟩; which, however, does not appear frequently even under stress.

In Fig. 12, the stressed, as well as the not stressed piece of the cleaved crystal were annealed at 600 °C for three hours.

The result is, that the stressed crystal constructs polygonization under the influence of annealing over 600 °C, while the unstressed one easily forms elongated subboundaries or substructures arrayed on {110} plane.

Acknowledgment

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