THE EFFECT OF SURFACE PROCESSES ON THE FLOW STRESS OF DOPED NaCl CRYSTALS HEAT TREATED IN AIR*

J. SÁRKÖZI, A. TÓTH, K. ORBÁN, T. KESZTHELYI and P. KÁLMÁN

DEPARTMENT OF EXPERIMENTAL PHYSICS, INSTITUTE OF PHYSICS, TECHNICAL UNIVERSITY
1521 BUDAPEST, HUNGARY

The effect of surface processes due to heat treatment on the flow stress of NaCl crystals doped with different divalent impurities is investigated. The results show that in the surface layer of the crystals annealed in air some chemical reactions take place leading to substantial changes in surface conditions and thus in the flow stress of the crystals. The effect may dwarf the flow stress increment caused by dipole—dislocation interaction in the bulk, and may be the reason for some contradictory results in the literature.

Introduction

The flow stress of alkali halide crystals is mainly determined by divalent cation impurities [1]. When having individual impurity vacancy dipoles in crystals, the flow stress depends on the type of impurity ion forming the dipoles [2]. But in crystals even with low impurity concentration the dipoles tend to aggregate, and to investigate the role of individual dipoles one has to quench them in by annealing at higher temperature and subsequent cooling to room temperature. In spite of the fact that the importance of some surface treatments in plastic behaviour is well known (e.g. Joffe effect, Rebinder effect [3, 4]), there are several investigations [5, 6, 7], where the annealing of samples is carried out in air, and no attention is paid to the surface effects arising in this way. The aim of the present paper is to investigate the role the surface processes play in the flow stress in doped NaCl crystals heat treated in air.

In order to avoid any misleading effects we used specially grown, OH^--free NaCl: M^{2+} crystals at our disposal, which practically did not contain other impurities [8]. It is of primary importance because unwanted impurities, especially OH^-, can chemically react with the dopant during heat treatment and thus make its effect on flow stress inexplicable [9].

Experimental results

In our investigations the flow stress and microhardness of heat treated crystals were measured at room temperature. The microhardness measurements were to trace the hardening effect of the heat treatment in vacuum and air on crystal surfaces. In

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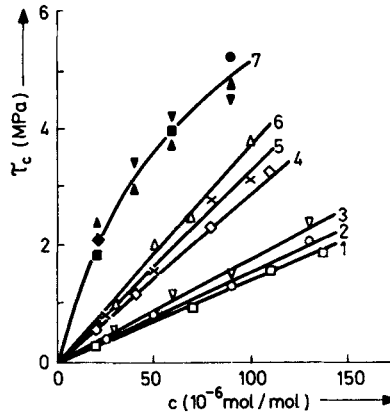* Dedicated to Prof. I. Tarján on his 70th birthday.

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Fig. 1. The dependence of resolved flow stress increment τ_c on the impurity concentration c in NaCl crystals. The dopants: 1 — Mg, 2 — Mn, 3 — Ca, 4 — Ba, 5 — Pb, 6 — Sr, 7 — different points correspond to different kinds of impurities mentioned above. Samples 1—6 were annealed and quenched in vacuum, samples 7 were annealed and quenched in air.

addition to this, the change in crystal surface state was also followed by means of electron microscope. Gold decorating method was applied, which is based on the fact that decorating particles deposited on the surface of a sample map the places enriched in impurity. If a thin carbon layer is evaporated onto the gold decorated surface it will image the distribution of gold particles. On removing the carbon layer from the surface it can be put in electron microscope to make a picture of the impurity distribution. In the studied NaCl:Mg, NaCl:Mn, NaCl:Ca, NaCl:Sr, NaCl:Pb, NaCl:Ba crystals the impurity concentration ranged from 10 to 150 ppm whereas in the "pure" reference crystal it was less than 0,2 ppm. The heat treatment was carried out in an oven of low heat capacity. The size of the samples and quenching rate were chosen so that thermal stress and plastic deformation could be avoided. Each sample was annealed at 600 °C for 2 h and quenched at a rate of 10 °C/min. The flow stress of samples quenched in vacuum and air vs impurity concentration is presented in Fig. 1. The curves show that the dependence of flow stress on the type and concentration of contamination is fundamentally determined by the kind of heat treatment applied. The impurity dependent flow stress increment ($\tau_c = \tau - \tau_0$ where τ and τ_0 denote the flow stress of doped and pure crystals, respectively) of samples annealed in vacuum varies linearly with impurity concentration depending on its type (curves 1—6). It is of particular interest that impurity ions replacing Na^+ ions, with ionic radius smaller than or equal to that of the Na^+ ion (curves 1, 2, 3 for Mg^{2+}, Mn^{2+}, Ca^{2+}) have a weaker flow stress increasing effect than those having larger ionic radius (curves 4, 5, 6 for Sr^{2+}, Pb^{2+}, Ba^{2+}). As a result of annealing in air, however, the flow stress no longer depends on the type of impurity (curve 7) and at the same time τ_c becomes proportional to $\sqrt{c}$ instead of c.
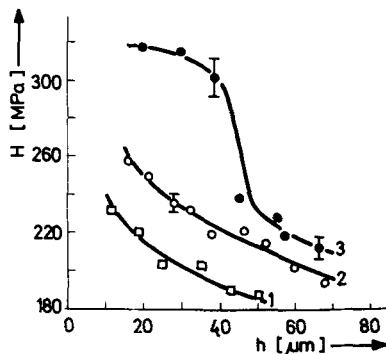
Fig. 2. The dependence of microhardness *H* on the depth of indentation *h* in NaCl crystals: 1 — pure NaCl, 2 — NaCl doped with Pb and annealed in vacuum, 3 — NaCl doped with Pb and annealed in air

The great difference between the effects of annealing in air and vacuum calls attention to the question of the surface conditions of crystals. Plastic behaviour of the surface was studied by measuring microhardness in dependence on indentation depth. This dependence for NaCl:Pb as an example is demonstrated in Fig. 2. Curve 1 belongs to pure crystals and serves as a reference curve, which is in agreement with expectation [10]. Curve 2 that shows the microhardness of doped samples after annealing in vacuum against indentation depth is the same as curve 1 if displaced in parallel. Consequently, the hardness increment caused by impurity is independent of the indentation depth. The indentation depth dependence of microhardness for NaCl:Pb annealed in air (curve 3) is essentially different from what is described by curves 1 and 2. According to curve 3 hardness drops at $h \approx 40$ μm and beyond ≈ 50 μm it runs parallel to curve 2. All this means that there must be an approximately 40 μm thick, rather hard layer on the surface of the samples quenched in air. This layer presumably develops by chemical interaction between the atmosphere and impurity diffused to the surface during heat treatment. In order to prove this assumption we have taken decorated pictures about the surface of pure NaCl and NaCl:M^{2+} crystals annealed in vacuum and air. Here too, similarly to the presentation of hardness vs indentation depth, we show pictures of NaCl:Pb^{2+} crystal as an example, because all the other impurities look the same. Information on the surface conditions of extremely pure crystals quenched from high temperature in vacuum and air is given in Figs 3a and 3b, respectively. The two ways of heat treatment do not have essentially different effects, the only difference appears in the arrangement of thermally etched steps. Figs 3c and 3d show the surface of Pb doped crystals annealed in vacuum and air, respectively. Contamination in doped samples diffuses to the surface during tempering in vacuum [11] and the thermal etching maps the enriched areas. As it can be seen in Fig. 3c the surface roughens through formation of small square pits. The effect of annealing in air is shown in picture 3d which was taken after a mere half hour of
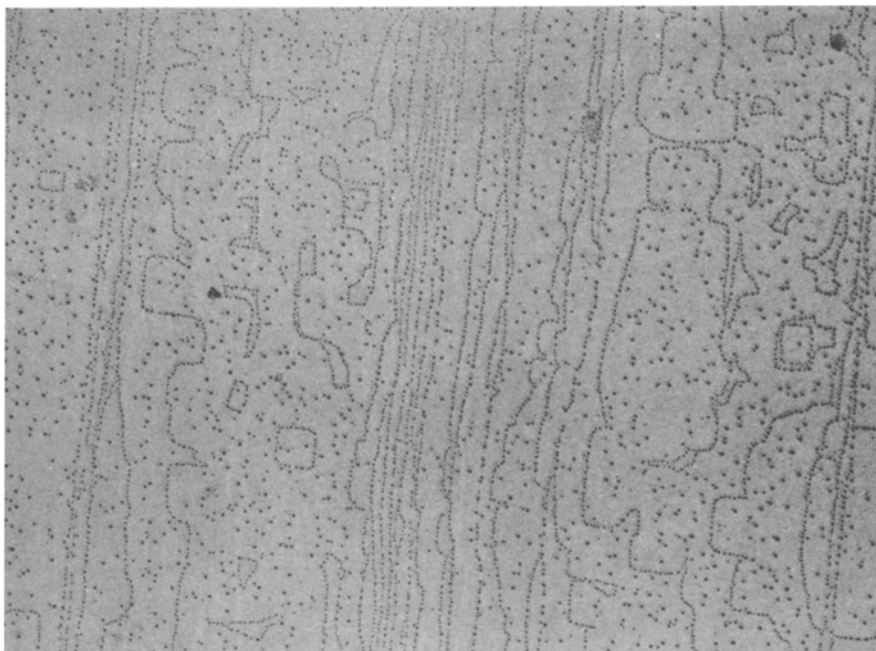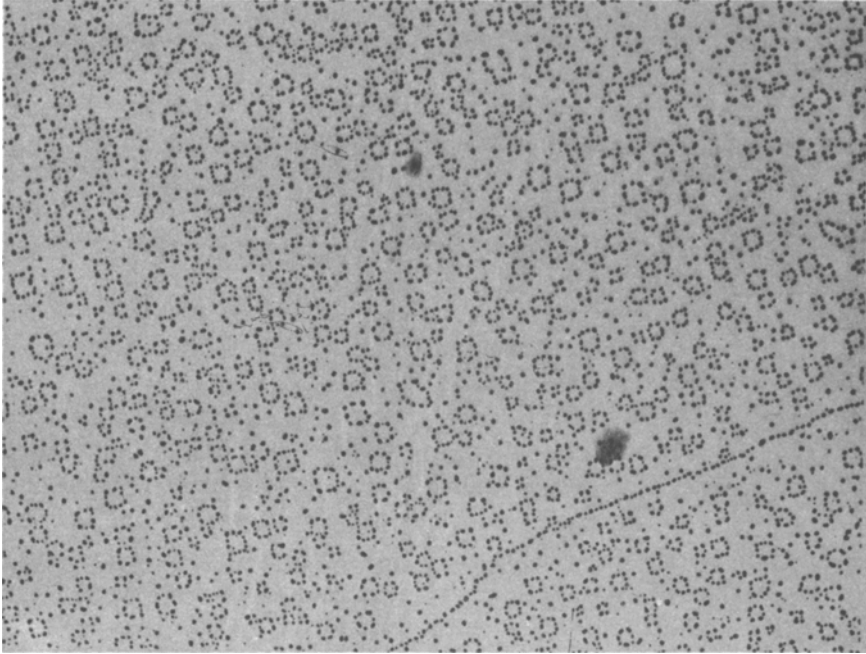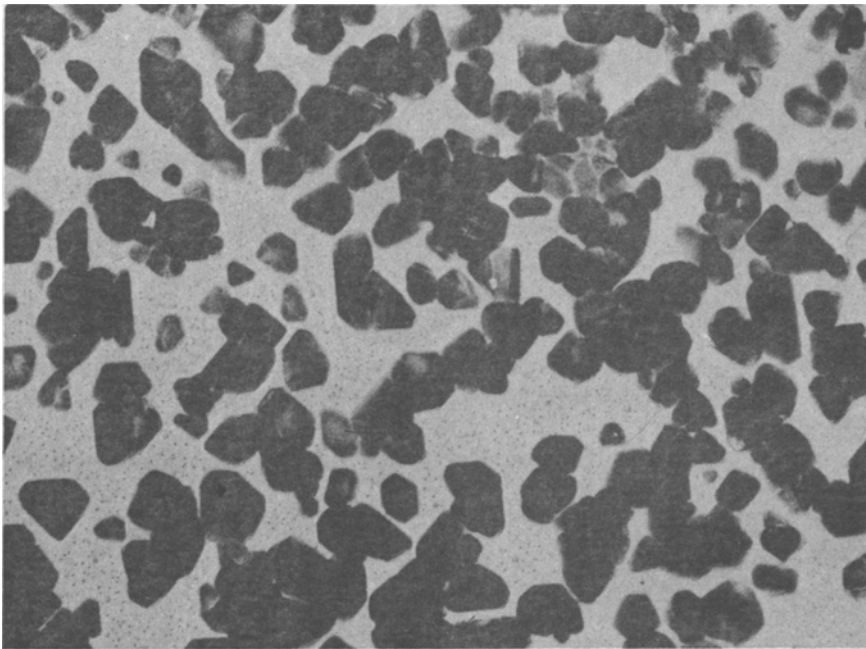
a)
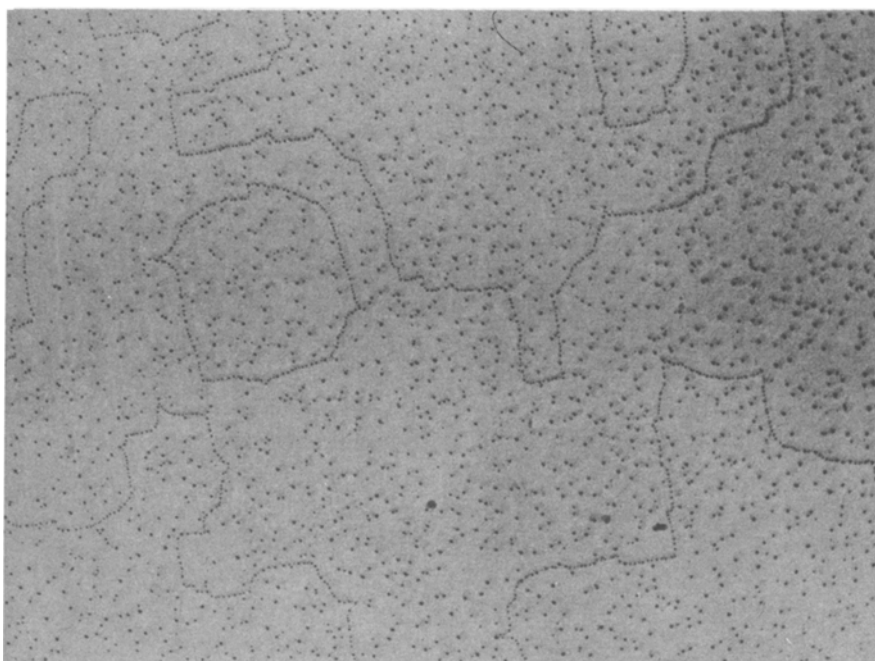
b)

Fig. 3. Electron micrographs showing the surface structure of heat treated NaCl crystals. *a* — pure crystal annealed in vacuum, *b* — pure crystal annealed in air, *c* — Pb doped crystal annealed in vacuum (next page), *d* — Pb doped crystal annealed in air (next page). (Magnification: 1 000 X)

c)

d)

annealing instead of several hours as usual. This picture shows small separate crystalline grains which in the course of a longer heat treatment multiply to such an extent that they grow into a continuous layer. The survey of its chemical composition (probably some sort of lead oxide) would require further investigation — here we confine ourselves to proving its presence.

Discussion

As mentioned in the introduction heat treatment for the purpose of experimental investigation of flow stress increment due to impurity in alkali halides is often carried out in air. According to our experiments this way of heat treatment is rather unsuited for clearing up the role the impurity-vacancy dipoles play in increasing the flow stress. The layer developing on the surface of samples quenched in air adds to the flow stress so much that it dwarfs the increment caused by dipole—dislocation interactions. In association with it the direct proportionality of flow stress increment to impurity concentration in crystals quenched in vacuum is replaced by its variation with $\sqrt{c}$. This square root-like dependence is usually explained by Fleischer's theory for rigid, tetragonal point defects (dipoles) [12]. In our opinion, for the description of the interaction between dislocations and tetragonal point defects the linear dependence ($\tau_c \sim c$) obtained after quenching in vacuum is acceptable. Such a dependence can be explained by assuming that the dipoles are not rigid but can rotate and it is through the Snoek effect that they hinder the moving dislocations [13]. It is worth special mentioning that only good quality crystals annealed in vacuum can show the explicit difference between flow stress increments caused by different impurities. This dependence is blotted out by annealing in air.

Acknowledgement

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