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LOW-TEMPERATURE STATIC RECRYSTALLIZATION IN STRONTIUM DOPED POTASSIUM CHLORIDE

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Introduction

It is well known that under deformation in compression at strain levels in the range of 60–80% and at temperatures below $0.57T_m$ (where $T_m = 1033K$ is the melting point), alkali halide single crystals (AHC) become polycrystalline with a grain size of about $10\mu m$ (1). Such a deformed structure has a higher mechanical strength than the single crystal, but this improvement in strength progressively relaxes with time, in particular at room temperature (RT), due to the processes of polygonization and recrystallization.

In the present investigation the processes of recrystallization after deformation in Sr doped KCl were studied. A new and efficient mechanism for grain growth at room temperature was observed in deformed doped AHC, specifically twin growth during the first stage of static recrystallization. In the doped crystals, the volume fraction of recrystallized grains is considerably smaller than in pure AHC. The process of aging at RT, as examined by X-ray methods and light microscopy, was found to be the main reason for grain growth inhibition in Sr doped KCl crystals.

Experimental

The single crystals were grown by the Czochralski method. The dopant $SrCl_2$ was mixed with the KCl powder before melting. The composition of the crystals was analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) method. Three types of samples were investigated: pure KCl and KCl containing 0.02 and 0.06 wt% of Sr. Specimens of dimensions $3 \times 3 \times 7$mm and with $\{100\}<001>$ orientation were cleaved from a single crystal bar. Before deformation all specimens were annealed at 873K and furnace-cooled. The specimens were deformed in compression up to 70% of the initial length. The compression axis was parallel to the $<100>$ crystallographic direction, the strain rate was $2 * 10^{-4}\ s^{-1}$ and the deformation temperature was 523 75 ($\cong 0.5T_m$).

Pole figures (PF) were used to plot the orientations of the crystals in the initial and deformed conditions, which allowed following further changes in the texture and grain orientation during storage at RT. The description of these methods can be found elsewhere (2). X-ray diffractometry (3) was applied for the phase analysis. To reveal grain boundaries, the specimens were etched in a 50:50 mixture of ethyl alcohol with KCl saturated water solution.

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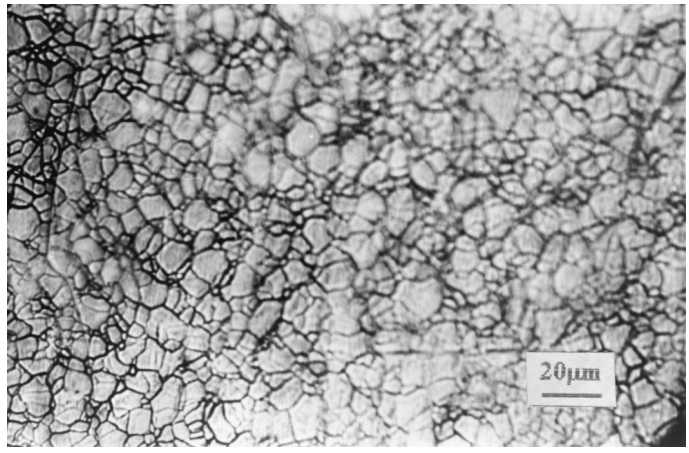

Figure 1. Microstructure of a KCl specimen as deformed up to 70% in compression along the <100> direction.

Results and Discussion

Fig. 1 shows the structure of a KCl crystal deformed up to 70%. The structures of the deformed pure and doped KCl crystals were similar, except for the average size of the deformed subgrains. The latter was 10μm in pure KCl and 4μm in KCl:0.06wt%Sr. The textures of both the pure and doped deformed crystals were of almost the same ideal orientation, {100}<001>, with a slightly higher scatter in the doped samples. Nevertheless, further textural and structural evolution of the doped materials was different from the one found in the pure crystals. As illustrated by Fig. 2-a and -b, the processes of grain growth at room temperature differ in the pure and doped crystals. In the pure crystals the subgrain boundaries spread out, polygonization took place and, as a result, new perfect subgrains were formed. The main texture of the polygonized crystals remained unaltered. In the deformed crystals of $SrCl_2$ doped KCl, the processes of grain growth were essentially distinct from those described above. After a couple of days (about 50 hours) of storage at RT, a few triangular or rectangular grains appeared on a face parallel to {100}. According to the PF data these grains were twins with respect to {100}<001> (2). It is quite uncommon to find twins adjacent to the deformed matrix. Twins are more often observed at later stages of recrystallization when new grains comprise the majority of the volume. In the KCl crystals with largest KCl concentration, grain growth saturated after two months of storage at RT. In this case the volume fraction of recrystallized grains did not exceed 10%. The kinetics of twin growth was the same for the 0.02wt% and 0.06wt%Sr doped crystals. However, one important difference should be mentioned. In the crystals with higher dopant concentration, recrystallization stopped with the saturation of twin growth, whereas in the less doped ones it kept going on due to migration of non-special grain boundaries.

Fig. 3a, b shows diffractograms of the initial samples as well as of the specimens aged after deformation. It is obvious that the new phase KCl $*$ $2SrCl_2$ (39–1136, JCPDS) manifests itself instead of the cubic $SrCl_2$ phase (06–0537, JCPDS), which was observed in the initial state. No less than three different lines were observed for each phase. So it seems justified to ascribe the presently observed lines to phases mentioned in the JCPDS list as being detected in the KCl-$SrCl_2$ system. To determine whether a line definitely belonged to one of these phases, only the lines corresponding to considerably different interplanar distances were taken into account. The solubility limit of Sr in the metastable system of $SrCl_2$ doped KCl scarcely reaches 0.01 mol per cent at 400°C (4). As to the stable phase diagram (5), Sr is known to be absolutely insoluble in KCl. Therefore, it is not surprising that free $SrCl_2$ appears in

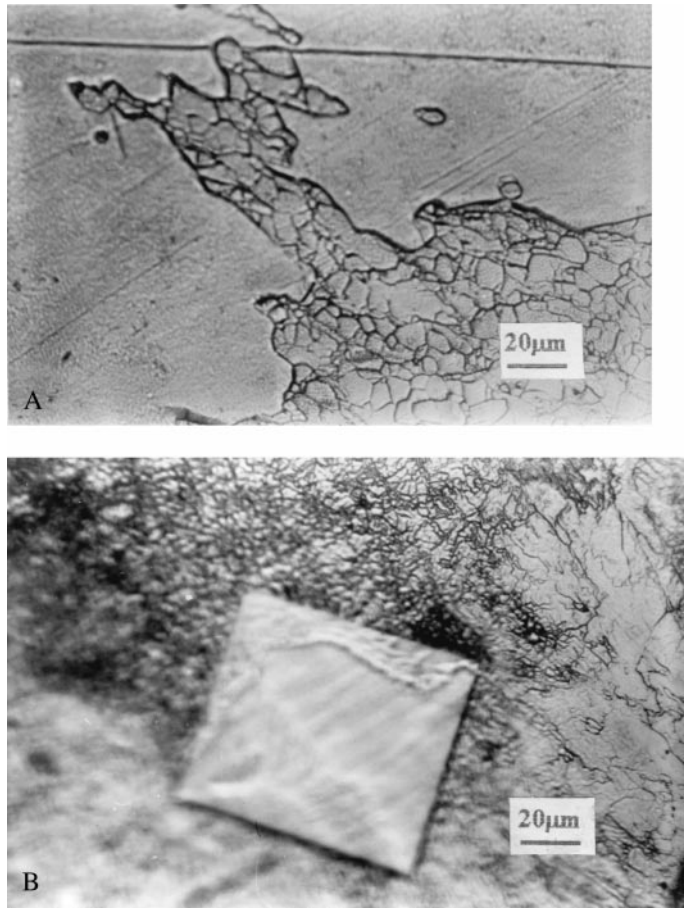

Figure 2. Microstructure of KCl crystals after deformation up to 70% and subsequent storage for 5 months at RT (a) pure KCl, (b) KCl:0.06wt%Sr.

the annealed crystals before deformation. The observation of the KCl ∗ $2SrCl_2$ seems a bit surprising in slightly Sr doped KCl crystals since this compound normally exists in the region of $SrCl_2$ concentration from 33 to 65 mol per cent (5). It is well known that the so-called Suzuki phase can form in the earth-alkali doped alkali halide crystals (6). Suzuki observed a metastable phase $CdCl_2$ ∗ 6NaCl and a stable phase $CdCl_2$ ∗ 2NaCl in $CdCl_2$-doped NaCl, in the domain of dopant concentration from 2 to 20 mol per cent. In the present study two series of lines belonging either to the stable phase $SrCl_2$ or to the stable phase KCl ∗ $2SrCl_2$, were observed in the diffractograms of the $SrCl_2$-doped KCl crystals. Three phases containing Sr are known to have been detected by x-ray diffractometry in the KCl-$SrCl_2$ system, namely, cubic $SrCl_2$, orthorombic $SrCl_2$ and KCl ∗ $2SrCl_2$. This is the reason why it seems justified to identify the two observed sets of lines (Fig. 3a, b) to the two phases $SrCl_2$ and KCl ∗ $2SrCl_2$. Undoubtedly, there must be definite orientation relationships, which enabled revealing the small volume fractions of the phases reported below: some lines, belonging to one of these phases manifested in diffractograms at definite orientations of a crystal (with respect to diffraction vector). These lines disappeared and other ones would sometimes appear, as orientation of a sample changed. Lines, irrelevant to pure KCl, were not recorded at diffractometry of powders, made of Sr-doped single crystals. However, it has not been possible as yet to determine these relationships.

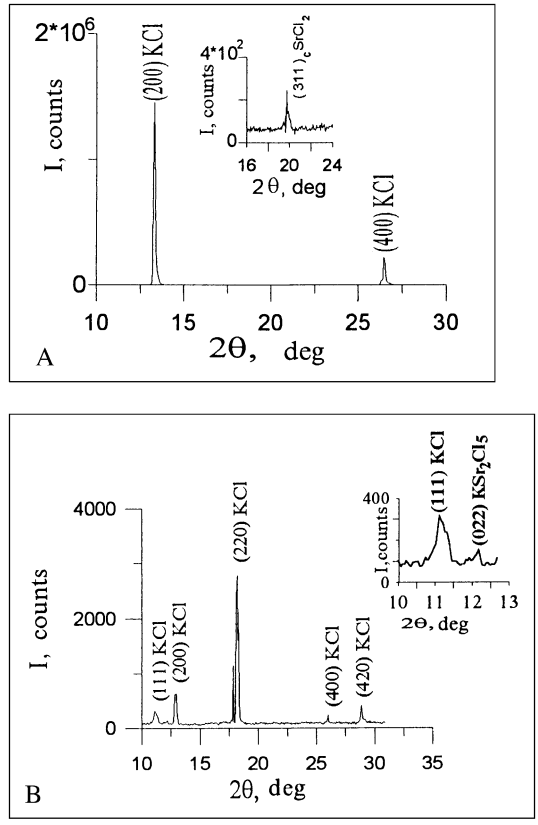

Figure 3. Diffractograms of KCl:0.06wt%Sr specimens (a) in the initial state, (b) after 70% strain and further aging for a fortnight at RT.

Using polarized light in an transmission optical microscope, particles of an optically anisotropic phase (of about 5μm in diameter) were observed in the 0.06%wt Sr doped KCl and further stored at RT (3). The volume fraction of this phase was found to be $0.06 \pm 0.01\%$. A simple estimate shows that the dopant concentration in a specimen containing 0.06%Sr is sufficient to provide the experimentally observed amount of this phase. In contrast to the cubic Suzuki phase, the observed phase is optically anisotropic. These results allow us not only to identify the observed particles with the monoclinic $KCl * 2SrCl_2$ compound, but also to assume that this compound has formed from $SrCl_2$, due to defects stored during the RT aging of the deformed crystals. These particles grow on the grain boundaries of the recrystallized grains of twin orientation (3). This proved to be one of the reasons why the formation of new grains was inhibited. The ratio of the particle size d to the grain size D and the volume fraction of recrystallized grains α obeys Zener's criterion for grain growth inhibition (7):

$$d/D \leq 1.5\alpha \tag{1}$$

Indeed, $d/D = 5\mu m/300\mu m = 0.017$ whereas $1.5\alpha = 1.5 * 0.06 = 0.09$

Huang diffuse x-ray scattering (DXS) experiments were performed on the deformed samples during aging at RT, close to the {220} reflection. In this case the intensity of the DXS is much higher than that for the initial single crystals. Moreover, the DXS of the deformed crystals has its own three-fold symmetry axis, which does not coincide with the symmetry of the corresponding single crystal. In

parallel, the line {111}KCl, which is normally weak (less than 1%) for KCl (41–1476, JCPDS) owing to the practically identical scattering factors for K and Cl ions, distinctly shows up in the diffractograms (see Fig 3-b). The fact that line {111}KCl is visible only when Huang scattering of the same order of symmetry is recorded and vice versa, make us reckon that in highly anisotropic medium, which we are dealing with, a reconstruction of structural defects takes place. Though we do not know much about the nature of the defects, we assume that they might affect the recrystallization processes.

A similar mechanism of nucleation and growth of twin grains during the first stage of recrystallization was observed at room temperature after pressure induced reversible polymorphic transition B1⇔UB2 in pure KCl (8). However, in that case, recrystallization was not inhibited by dopants, so recrystallized grains gradually occupied the whole volume due to non-special grain boundary migration following the twin growth. Thus, further investigations of the nature of the defects and their interactions with dopants, which might be responsible for the high or low mobility of the twin grain boundaries during RT recrystallization in AHC, are of interest.

Conclusions

KCl single crystals of {100}<001> orientation, both pure and doped with small amounts (0.02 and 0.06wt%) of Sr, were deformed in compression up to 70% at 250°C ($0.5T_m$).

Microstructure and X-ray examinations bear evidence of recrystallization in the doped crystals taking place at room temperature. New grains, which proved to be twins with respect to the {100}<001> single crystals, were observed during further the RT storage of the samples. Twin growth was found to be an important mechanism of room-temperature recrystallization in AHC. It has been shown that on reaching a concentration of 0.06wt%Sr, recrystallization was confined within the first stage (twin growth). In this case the total recrystallized volume fraction did not exceeded 10% after at least two years. It is suggested that grain growth is inhibited in the doped and deformed crystals due to aging at room temperature. Two processes are thought of being important in this respect. First, the new phase $KCl * 2SrCl_2$, whose particles inhibit grain growth, forms during the RT storage. It seems reasonable to assume that, in spite of the very small concentration of Sr in KCl, the process of precipitation starts with the formation of Sr-enriched phases and not with a kind of Suzuki compound which would have a composition like $SrCl_2 * 6KCl$, as yet unknown for Sr doped KCl. The experimental results lead to the assumption that the phase transition from $SrCl_2$ to $KCl * 2SrCl_2$ particles can then take place. Next, being sensitive to single defects and clusters (9), the high intensity recorded by Huang diffuse scattering leads to the assumption that the interaction between structural defects in the matrix and the dopant also occurs at RT.

These results show up the low-temperature mechanism of recrystallization in AHC and illustrate the role of aging in this process.

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