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Microstructures, thermal diffusion and decomposition studies in the two phase solution grown mixed crystals of NaCl and KCl

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Abstract. Mixed NaCl-KCl crystals are grown from water solution. Thermal diffusion, decomposition and microstructures studies by employing the etching technique are reported. It is shown that microstructures consisting of alternate lamellae of NaCl and KCl arranged in ⟨100⟩ and ⟨110⟩ directions in the two-phase mixed NaCl-KCl crystals observed at room temperature get converted to the one consisting of random mixture of both the phases on finer scale on heating at 300°C for 30 hr. The dissociated matrix on heating at 600°C for 15 hr regains almost all the characteristics of a single crystal transforming the material into single-phase mixed (NaK) Cl crystals. The temperature dependence of the thermal diffusion is discussed.

Keywords. Microstructures ; etching ; dislocation pits ; non-dislocation pits.

1. Introduction

X-ray, optical and etching studies on the solution grown two-phase mixed NaCl-KCl crystals (Ingle and Ghadekar 1978, 1979, 1980) have clearly revealed vast structural differences between these solution-grown mixed NaCl-KCl and the melt-grown mixed (NaK) Cl crystals. The melt-grown mixed crystals have been extensively studied (Burgers and Tichelaar 1953; Wolfson *et al* 1966; Scheil and Stadelmair 1952 ; Elistratove and Zvinchuk 1960). Some interesting studies on thermal diffusion, decomposition and microstructures are now reported. The two phase NaCl-KCl crystals (NaCl 61·5% by wt. and KCl 38·5% by wt.) were grown from solution as reported earlier (Ingle and Ghadekar 1978).

2. Result and discussion

In the mixed crystal, owing to the identical crystal structures of the NaCl and the KCl and nearly the same ionic radii, the interphase diffusion substituting Na^+ ions by K^+ ions and *vice versa* is expected. Figure 1 shows the {001} face of the mixed NaCl-KCl crystal etched in ethanol (99%) + $PbCl_2$ till saturation for 1 min. (The

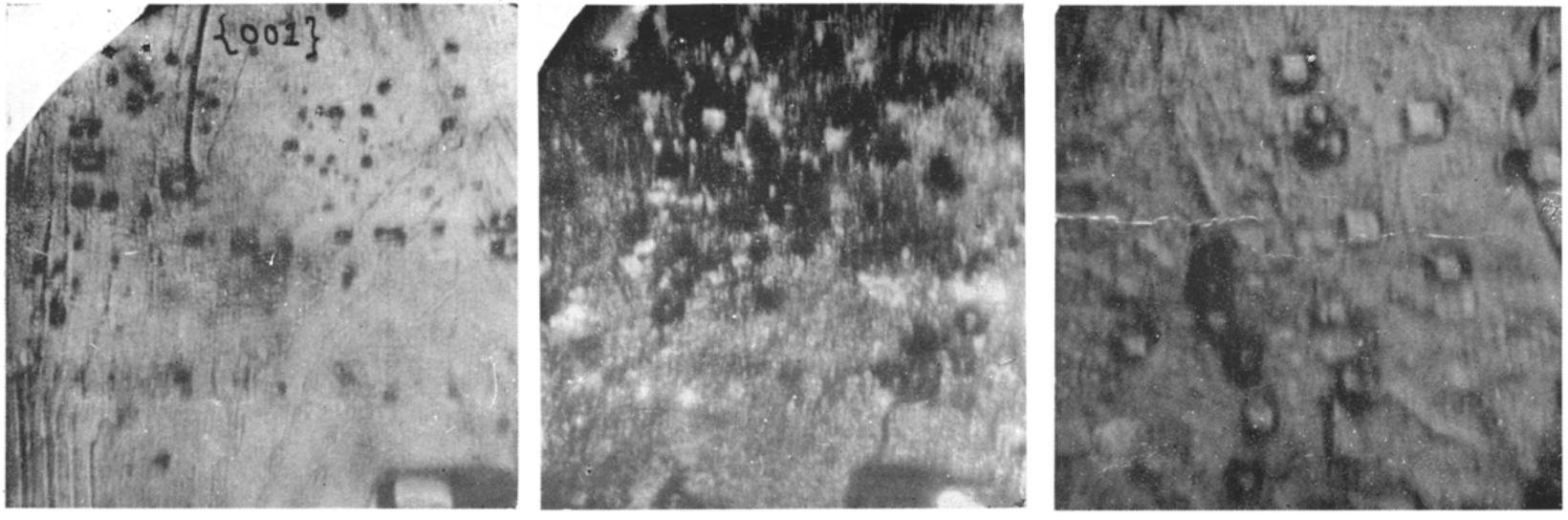
specificity of this etchant to sense the impurity sites of Na^+ ions has already been established by Ingle and Ghadekar (1980). The figure shows impurity pits of Na^+ ions at the non-dislocation sites. On heating the crystal at 300°C for 7·30 hr or for 22·6 hr at the same temperature, the density of theimpurity pits is found to increase correspondingly. This suggests that the diffusion of Na^+ ions in the lattice is temperature-dependent. On continuous heating for more than 22·6 hr the decomposition centres are found to nucleate on {001} surface in the regions with high defect density implying that the lattice defects facilitate decomposition. Figure 2 shows the microphotograph of the {001} face of the crystal obtained after heating for 30 hr and subsequently etched in ethanol + $PbCl_2$ for 1 min as usual. This etchant in this case produces no pitting on the surface but the normal dissolution rate of this etchant is found suitable to attack KCl regions efficiently; however the etchant produces no dissolution on the NaCl regions enabling identification of the participating phases. Thus, the regions deeply etched (dark) mark the KCl phase and the lightly etched (whitish) regions mark the NaCl phase. If such {001} face is etched in glacial acetic acid (99%) for 3 min (Ingle and Ghadekar 1978), no dislocation pits characteristic of single crystal nature are produced. This clearly indicates that the crystal has lost the single crystal nature, the crystal matrix being dissociated with loss in coherency of the phases. In contrast, on heating the crystal at 300°C for not more than 22·6 hr the matrix remains undissociated and the constituent phases remain in tact.

The microstructures of figure 2 show that the participating phases are distributed randomly on finer scale. These microstructures are remarkably distinguished from the type generally observed at RT consisting of the patterns of alternate lamellae of NaCl and KCl very much similar to the eutectic one (Ingle and Ghadekar 1978). Thus microstructures with lameller patterns heated as above get converted to the type with random mixture of the phases.

On heating the mixed solid at temperature above the miscibility gap such as 600°C for 14 or 15 hrs, the randomly distributed phases start reorientations transforming the material into a single phase solid solution (NaK)Cl. This is clearly seen in figure 3 which is the microphotograph of the {001} surface of figure 2 obtained after heating as explained above. The surface comparatively becomes smoother and thermal pits are produced because of evaporation at atomic steps. Such a surface if etched in the etchants (Ingle and Ghadekar 1978) such as glacial acetic acid (99%) or ethanol + $PbCl_2$, produces square dislocation pits on {001} face characteristic of a single crystal nature.

3. Conclusion

The lamellar microstructures consisting of alternate lamellae of NaCl and KCl arranged in ⟨100⟩ and ⟨110⟩ directions are found to transform on heating at 300°C for more than 22·6 hr to the type consisting of random mixture of both the phases on finer scale. The dissociated matrix on heating at 600°C for 15 hr get converted to a regular matrix, the matrix of a single phase mixed (NaK) Cl single crystal.



(1) (2) (3)

Figures 1-3. 1 {001} face of the mixed crystal when etched with ethanol + $PbCl_2$ at room temperature for one min. Figure shows the impurity pits of Na^+ ions [× 300] **2.** Same face of figure 1 when heated at 300°C for 30 hr and etched in ethanol + $PbCl_2$ for 1 min. The lightly etched (white) phase is NaCl and the deeply etched phase [dark] is KCl. The phases are dispersed on finer scale. Mark the inhomogeneity of the phases with roughness [× 300]. **3.** Same face as figure 2 when heated at 600°C for 15 hr. The crystal forms a solid solution and the surface is smoother, producing complete homogeneity of the phases. Thermal pits are also seen (× 300).

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