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Generation of Dislocations by Hydrostatic Pressure in NaCl Monocrystals Containing Na_2SO_4 Particles

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Single crystals of NaCl, of known surface dislocation substructures and containing precipitate particles of Na_2SO_4 approximately 10 μm in diameter, were subjected to hydrostatic pressures in the range 1 to 10 kbars and subsequently re-etched at atmsopheric pressure. Rearrangement and nucleation of dislocations in the vicinities of the precipitates was observed to result from pressurisation treatments above 3 kbars. After pressurisation at 8 and 10 kbars the dislocation groups were in general complex; linear arrays on $\langle 110 \rangle$ $\{110\}$ and "rosettes" were, however, observed. The observations are discussed in terms of recent theories (developed for metal matrices) of generation of dislocations at misfitting particles and are in fair agreement with the model of Ashby and Johnson.

1. Introduction

For some impure cubic metals e.g. iron [1], chromium [2, 3] and copper [4], there is evidence that dislocations are generated at matrix/precipitate interfaces when the material is subjected to a hydrostatic pressure of the order of 10 kbars. When a cubic crystal containing second phase particles (with different elastic constants) is subjected to a *hydrostatic* pressure, *shear* stresses exist in the matrix. If the theoretical shear strength is exceeded, fresh dislocations are generated; at lower stresses rearrangement of existing dislocations may take place if these are not strongly locked.

The generation of dislocations by pressurisation is thought to take place in a similar manner to that by quenching – in the latter case the "misfit" between the particle and the matrix is due to difference in the coefficients of thermal expansion. Theoretical calculations of the maximum shear stress, τ_{max} (reached at the particle/matrix interface) when the material is subjected to a pressure P have been made, following the method of Mott and Nabarro [5], or Sokolnikoff [6], by Das and Radcliffe [7], and by Ashby, Gelles, and Tanner [4]. For the case of an elastic inclusion of bulk modulus, K_P, in a matrix of bulk modulus, K_M, and shear modulus, G_M, these calculations yield:

$$\tau_{max} = \left| \frac{3G_M P}{K_M} \left(\frac{K_M - K_P}{3K_P + 4G_M} \right) \right| \qquad (1)$$

The shear stress varies as the inverse cube of the distance from the interface [5] and τ_{max} is independent of particle size.

Results of investigations of metals containing inclusions differ from the predictions of this simple model on two important points, namely [4, 7]: dislocations were observed to have been nucleated at critical hydrostatic pressures dependent on the particle size, and these pressures resulted in maximum shear stresses (calculated using equation 1) only of the order of 10^{-2} G_M, i.e. much less than the theoretical strength of crystalline solids. These considerations have recently led Ashby and Johnson [8] to present a more complex treatment of the phenomenon.

The observations on metals have been made primarily by transmission electron microscopy [1-4, 7] and accordingly the comparison of unpressurised and pressurised volumes of the material has not been made. The preceding considerations should apply to non-metallic cubic crystals; we have therefore investigated doped sodium chloride for which etch pitting techniques are well established. The first system studied contained particles of sodium sulphate, thenardite.

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2. Experimental Procedure

The specimens, of approximate dimensions $10 \times 2 \times 2$ mm, were cleaved on $\{100\}$ planes from a single crystal grown by the Czochralski method from AnalaR NaCl melt containing 3500 ppm of Na_2SO_4. The samples were annealed at 600° C to remove internal stresses produced by cleavage and then slowly cooled to room temperature. The crystals were subsequently polished in a 1 : 1 mixture of methyl and ethyl alcohols and etched in a 1 : 2 mixture of methyl alcohol and glacial acetic acid. The specimens were then examined by transmission and reflection optical microscopy and photographs were taken before pressurisation. These treatments were carried out for ~5 min in iso-pentane at 8 or 10 kbars in a piston-cylinder apparatus. Following pressurisation the specimens were immediately rinsed in ether and dried before further etching and polishing operations. Several treatments were also carried out at other pressures, ranging from 1 to 5 kbars.

3. Results

Examination of the cleavage surface of unpressurised crystals by extraction replica electron microscopy revealed approximately spherical particles which were identified as Na_2SO_4 by selected area diffraction. These particles were randomly distributed and their spacing was generally much larger than their diameters; figs. 1 to 4 show examples of these precipitates observed by reflection and transmission optical microscopy. The diameters of the particles were between ~2 and ~20 μm; the majority being ~10 μm in diameter.

The mean dislocation densities in as-cooled crystals were in the range 1 to 5×10^6 cm^{-2}. The distribution of dislocations appeared to be random; only infrequently was there evidence of

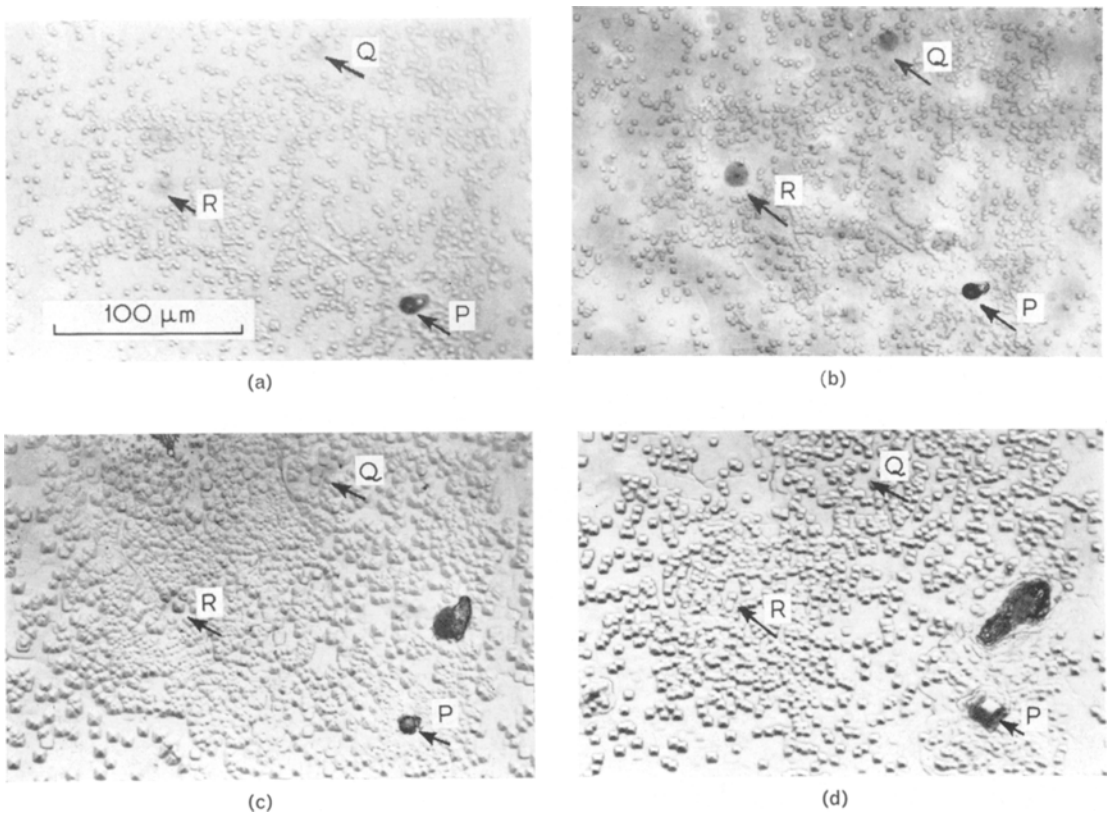


Figure 1 (a) An area of a $\{100\}$ face of Na_2SO_4 doped NaCl crystal before pressurisation at 10 kbars, reflection micrograph; (b) transmission photograph of the 2 mm thick crystal showing that precipitates are located at P, Q and R; (c) same as (a) following pressurisation, surface re-etched; (d) same as (a) and (c), but after polishing to remove 40 μm from the surface, re-etched. Note the increased dislocation densities around the precipitates following the pressurisation (c).

generation of dislocations at particle/matrix interfaces (e.g. by P in fig. 1a and b) during cooling from 600° C, or on cleaving. Following pressurisations at 10 (or 8) kbars the density and arrangement of surface dislocations changed considerably and fig. 1c shows an example of generation of dislocations by three precipitates, which were located approximately 50 μm below the surface. As the surface layers were polished off, the details of the etch pit patterns changed (fig. 1d).

The dislocation arrangements, in general, were complex, indicative of complex stress fields present in the vicinities of the precipitate particles. Fig. 2b shows two curved dislocation arrays, AB and CD, emergent on the {100} plane, which appeared to be associated with particles P, Q and R and were produced by pressurisation at 10 kbars. As the surface was progressively removed and only traces of particles remained (fig. 2d) the distribution AB disappeared completely and the etch pit density in CD was considerably reduced.

Among the many dislocation structures which resulted from pressurisation we would like to draw particular attention to two relatively simple types. The first is the linear array on ⟨110⟩ {110} e.g. PA on fig. 3, apparently generated by the particle P. The second characteristic type, the "rosette", is illustrated in fig. 4. The micrograph of fig. 4 was taken when ~55 μm of the surface had been removed; the general features of the

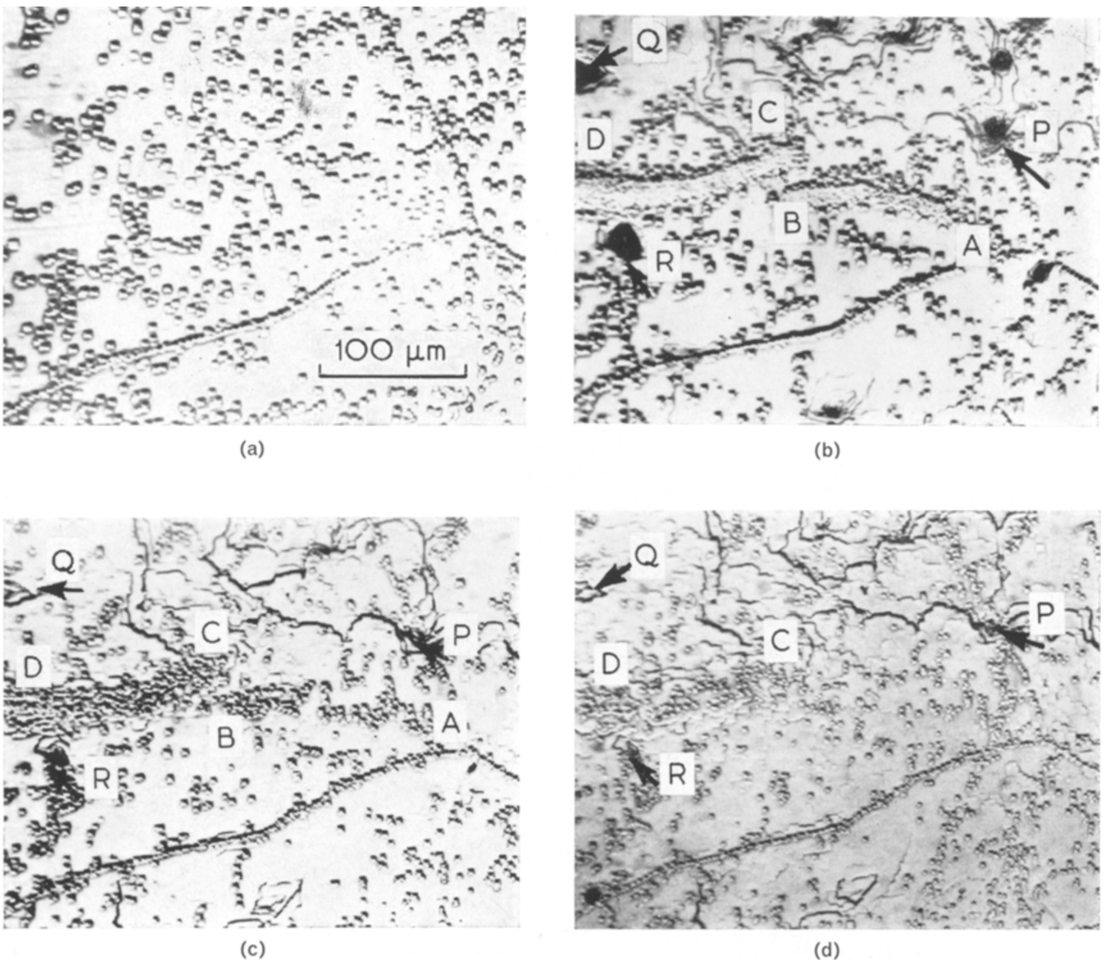


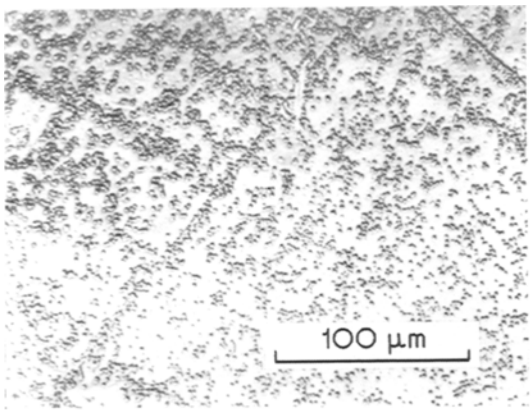
Figure 2 A sequence of micrographs of the {100} surface of NaCl single crystal containing Na_2SO_4 precipitates at P, Q and R (a) before pressurisation and (b), (c) and (d) following pressurisation at 8 kbars and removal of 15, 30 and 45 μm respectively, from the surface. Note the complex dislocation arrays AB and CD in the vicinities of the precipitates and that they extend over a distance of ~ 100 μm.

rosette were discernible at a distance of at least 15 μm above and below this depth.

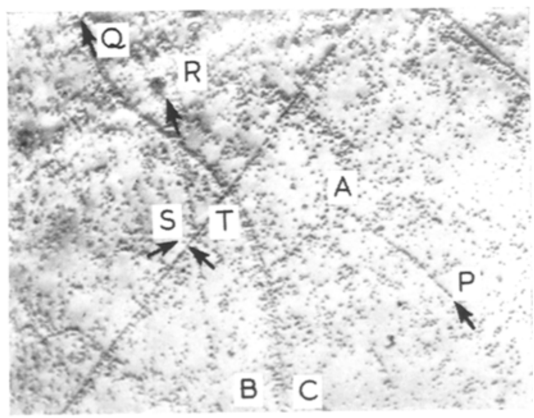
4. Discussion

The shear yield stress of the sodium sulphate doped rocksalt crystals is $\sim$10 bars, i.e. only slightly greater than that of pure NaCl monocrystals [9]. This latter stress is generally considered to be a lattice friction stress [10], for the large precipitate particles would not be expected to strengthen the material. The effect of even relatively small stress fields, therefore, should be to rearrange the existing free dislocations. The magnitude and extent of the shear stress fields (according to the simple model described in the Introduction) around spherical particles 5, 10 and 20 μm in diameter under a hydrostatic pressure of 10 kbar, has been calculated taking the values of G_{M} [11], K_{M} [12] and K_{P} [13] to be 0.13, 0.27 and 0.47 Mbars, respectively. The results are presented in fig. 5 and it is seen that a shear stress of 10 bars still exists 45 and 85 μm away from the surfaces of the 10 and 20 μm particles, respectively. Examination of the micrographs presented, and of others, shows that the majority of the dislocation activity was in fact restricted to regions within $\sim$100 μm of the precipitate particles. The stress at the particle/matrix interface, $\tau_{\max}$, evaluates to $\sim$1.5 kbars, i.e. $\sim 1.1 \times 10^{-2}\, G_{\mathrm{M}}$, which is thought to be much smaller than the theoretical shear strength of a crystal.

Studies of metals containing hard particles have yielded similar values of $\tau_{\max}$ (as fractions of G_{M}) at which dislocation arrays were first

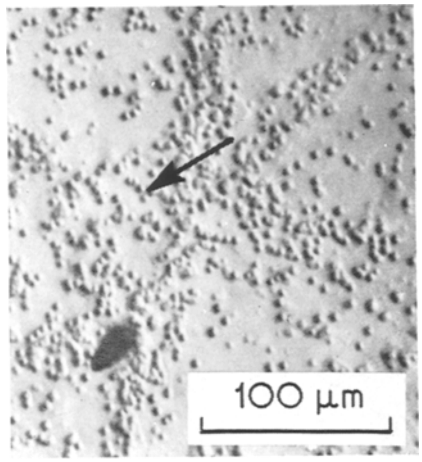


(a)

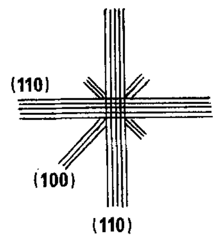


(b)

Figure 3 (a) An area of a {100} face of NaCl monocrystal containing Na_2SO_4 precipitates. The positions of some of the particles near the surface: P, Q, R, S and T are indicated in (b) which show the same area as in (a) following pressurisation at 10 kbars and removal of 15 μm from the surface. Note the simple linear ⟨110⟩ {110} dislocation array PA and that the others; QC, RSTB are complex.



(a)



(b)

Figure 4 (a) The "rosette" pattern 55 μm below the surface of a Na_2SO_4 doped NaCl monocrystal pressurised at 10 kbars, sketch in (b). The position of the precipitate (determined by transmission microscopy) is indicated by the arrow.

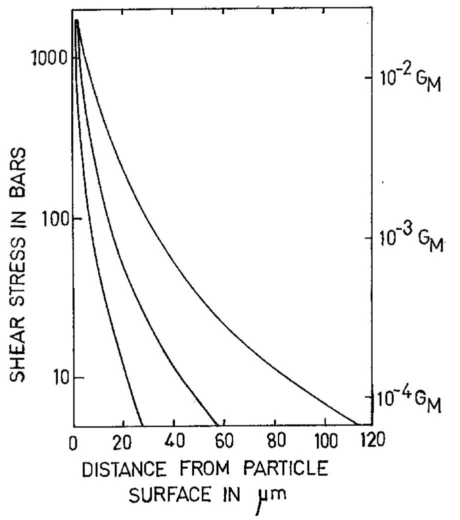


Figure 5 The shear stresses in the NaCl matrix subjected to a hydrostatic pressure of 10 kbars in the vicinities of Na_2SO_4 particles 5, 10 and 20 μm in diameter, calculated according to the model of Mott and Nabarro [5].

formed. Das and Radcliffe [7], who observed dislocation generation in a tungsten matrix at $G_M/300$, have suggested that real particles contain sharp steps or angularities at their surfaces which act as stress raisers. They point out that for the case of a small indentor [14] a contact pressure of 10^{-3} G_M is sufficient to punch out dislocation loops. It is pertinent to draw attention, in this context, to some of our dislocation distributions which resemble the "rosettes" produced by sharp indentors. In the analysis of such patterns, however, the friction stress [15] and not the dislocation nucleation stress has usually been considered.

In discussing similar results on the Cu-SiO_2 system Ashby *et al* [4] considered energy criteria in addition to the simple stress criterion of Weatherly [16] (which overestimates the critical misfit required to nucleate dislocations and fails to predict a dependence on particle size). They took note of a size dependent lower bound of the critical misfit which Brown, Woolhouse, and Valdré derived [17] by calculating the condition for the energy of the system to decrease when a single prismatic dislocation loop surrounds the particle. This approach ignores the problem of nucleation of the first loop and Ashby *et al* in fact found that their measurements were well above this bound [4]. Ashby and Johnson [8], however, went on to consider a model similar to that of Brown *et al* but in which a shear loop is nucleated at a particle and then transforms, by cross-slip, into a prismatic loop. The criterion for the lower limit is again strongly size dependent and above that of Brown *et al* [17], but agrees quite well with the results of Ashby *et al* [4] and of other investigations [8]. Ashby and Johnson [8] concluded that dislocations were generated when a misfit approximating to the lower bound was reached at incoherent particles, probably because the interfaces contain line defects which can bulge from the interface.

The Na_2SO_4/NaCl interface is incoherent; for particle diameters of 20, 10 and 5 μm this lower bound evaluates to 3.3×10^{-4} G_M, 6.9×10^{-4} G_M and 1.2×10^{-3} G_M respectively – well below the stress of 1.1×10^{-2} G_M calculated to be present at the interface at 10 kbars. On this model, pressurisation at 0.3, 0.6 and 1.1 kbars would be sufficient to generate dislocations in NaCl containing particles of Na_2SO_4 20, 10 and 5 μm in diameter, respectively. Specimens were accordingly treated at lower pressures: 1, 2, 3, 4 and 5 kbars. In the experiments carried out so far in the pressure range 1 to 5 kbars, definite dislocation activity was found to have taken place in only one specimen, pressurised at 3 kbars.

The agreement between the model of Ashby and Johnson [8] (developed for a metal matrix) and our results is considered to be fair and encouraging. However, an alternative means of generation of a prismatic dislocation loop during pressurisation, not previously referred to, is through the interaction of a glide dislocation with a precipitate particle. The possibility of such a mechanism operating has been suggested by Hirsch [18] and, although a detailed theory has not yet been worked out for NaCl, its operation in a matrix containing relatively free dislocations must be considered.

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