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Formation of voids by precipitation of vacancies in Au-doped sodium chloride

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Attempts to decorate dislocations in sodium chloride with gold precipitates by the method proposed by Barber *et al.* [1] have led to the very reproducible observation of voids associated with the gold precipitates.

1. Experimental technique

Very pure NaCl single crystals, purchased from Harshaw Chemie, were cleaved along {100} planes into 10 mm × 10 mm × 2 mm samples and annealed for 15 h at 760°C together with a piece of gold wire (length: 10 cm, diameter 70 μm) in a quartz tube filled with Cl_2 gas at a pressure of 460 mm Hg (at room temperature). After slow cooling (1°C min^{-1}) they were observed by means of a Reichert metallographic microscope. Being transparent, the crystals could be examined in depth by focusing inside the samples.

2. Observations

After the annealing treatment, the samples were of a light blue colour, due to the presence of gold precipitates, although these were too coarse to decorate the dislocations properly. However, most of the bigger precipitates were associated with voids. Three distinct configurations of voids could be observed.

(a) *Isolated voids in the bulk of the crystal.* The voids were cubical or nearly cubical, about 20 μm on edge, with faces along {100} planes (Fig. 1). Roughly spheroidal gold precipitates, about 2 μm diameter were located at the angles of the cubes. The void density was typically 10^4 to 10^5 voids cm^{-3}.

(b) *Voids on subgrain boundaries* (Fig. 2). These voids have the shape of elongated rods or thin platelets, they are also associated with precipitates and are located over the whole area of the subgrain boundary. Some voids of irregular shape evidently result from the coalescence of neighbouring voids. Some platelet-like voids show bright uniform interference colours.

(c) *Voids in a planar array beneath the free surfaces* (Figs. 3 and 4). There is a planar array of voids about 10 μm beneath each of the free surfaces of the sample. The voids have the shape of thin platelets whose angles are often rounded. Some of them show interference colours. Coalescence has frequently occurred. The gold precipitates are smaller and located along the edges of the voids. Stringers of fine precipitates often entirely surround the voids. The planar density of voids is about 10^5 voids cm^{-2}.

3. Discussion

The mechanism of the voids formation is still being investigated, however, a tentative explanation of their existence can be proposed.

At high temperature, the gold wire reacts with gaseous chlorine to give the compound $AuCl_3$. Au therefore, very likely diffuses into the NaCl lattice in the form of trivalent Au^{3+} ions. The electrical neutrality of the crystal must be preserved by the formation of negatively charged cationic vacancies, whose concentration is equal to twice the concentration of trivalent gold ions in solution. Below a certain temperature as the sample is cooled down, metallic gold precipitates by capturing electrons by a mechanism which may be analogous to the one operating during the precipitation of metallic colloids in alkali halides with an excess of cations. The extrinsic vacancies, no longer necessary to the electrical neutrality, are in supersaturation and may cluster and form voids, possibly containing chlorine. The planar array of voids below the surfaces may be related to the existence of a space charge in these regions.

Similar voids have been observed in neutron

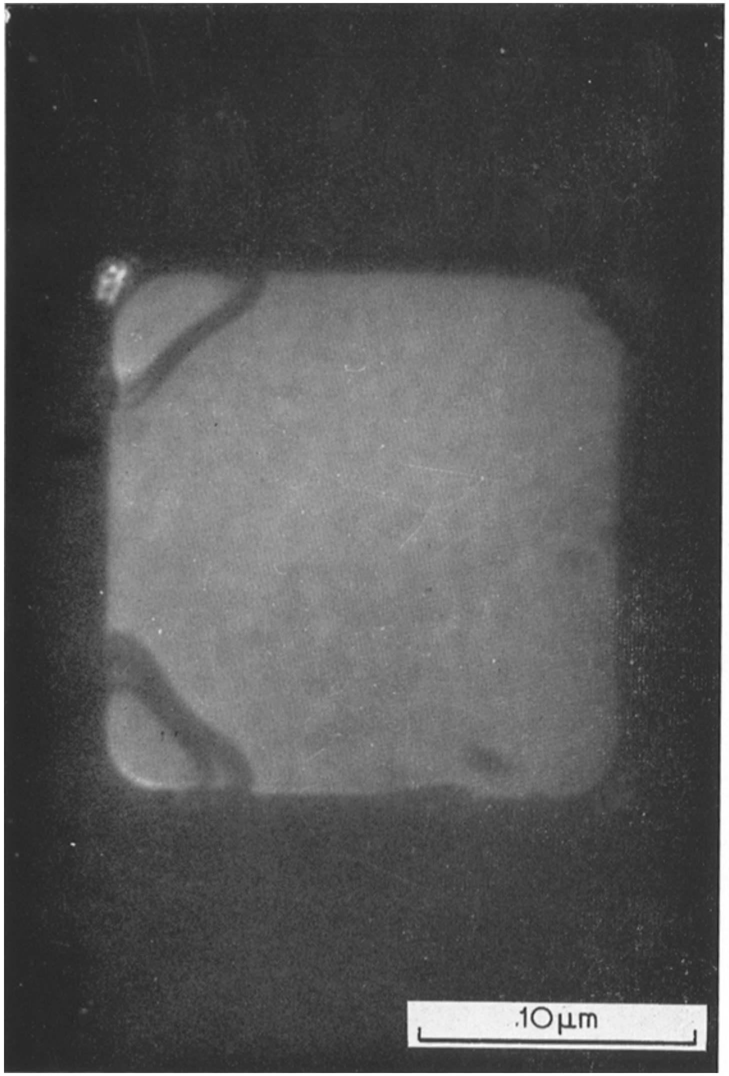

Figure 1 Isolated void in bulk. Observe the steps at the truncated angles and the gold precipitates at the angles.

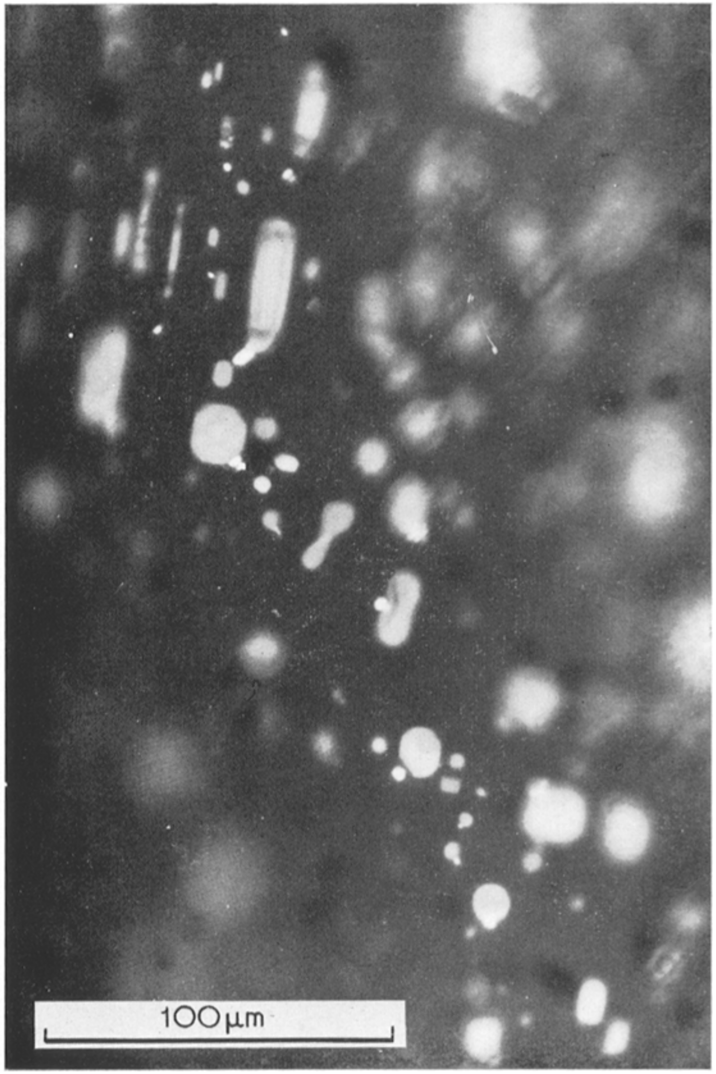

Figure 2 Voids on a subgrain boundary. The voids are in focus only in the central region of the sloping boundary. The white specks close to the voids are bright gold precipitates.

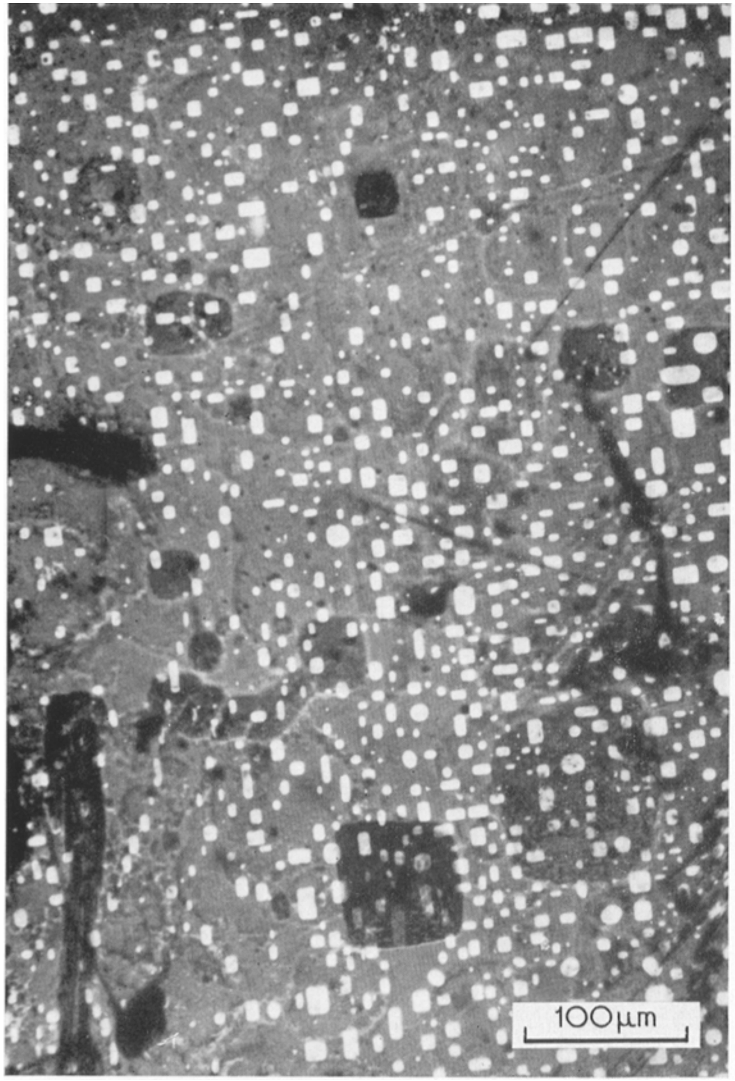

Figure 3 Planar array of voids 10 μm below the surface. The sloping line on the left hand corner is the trace of a subgrain boundary.

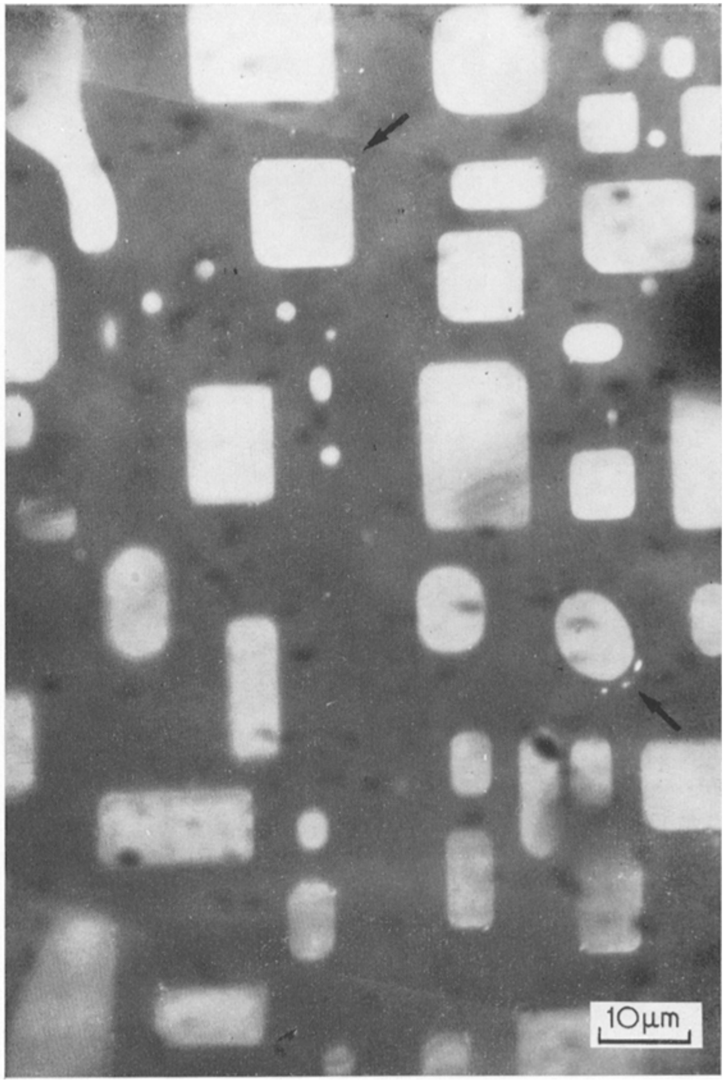

Figure 4 Planar array of voids 10 μm below the surface (detail). Notice the very fine stringers of precipitates around some voids (arrows).

irradiated lithium fluoride crystals [2, 3] but it is not clear whether all vacancies are produced by irradiation displacement cascades or by escape of fluorine ions during irradiation or anneal, leaving an excess of cations.

Investigation of the simpler case of NaCl doped with gold could be helpful in better understanding void formation in irradiated ionic ceramics. It may be that void formation is general in ionic crystals doped with aliovalent ions that can precipitate in metallic form. This could be of practical importance for the fabrication of sintered ceramic materials since the presence or absence of porosity in the sintered product often depends on which dopant has been used to achieve a successful sintering.

Acknowledgement

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