EVOLUTION OF DEFECT STRUCTURE AND EXPLOSIVE DECOMPOSITION OF NACL UNDER ELECTRON IRRADIATION

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INTRODUCTION

Since the 1950s, scientists had pointed to salt as one of the most promising geological media for a radioactive waste repository, and the world's only certified deep radwaste repository (Waste Isolation Pilot Plant) is in deep salt beds in New Mexico [1]. Laid down in evaporating seas long ago, salt is rock-solid and essentially impermeable. However, it can store the energy of ionizing radiation emitted by HLW in the form of radiolytic products, i.e. colloidal sodium and molecular chlorine. Accumulation of stored energy under irradiation was the subject of numerous investigations [2, 5-8], some of them concluded that a saturation of radiation damage with increasing irradiation dose occurs well within the acceptable range for repository safety [2, 5]. On the other hand, our previous work has shown that natural rock salt from the Netherlands and Germany (Asse) does not behave as pure NaCl. Systematic experiments on many heavily irradiated samples have shown that with increasing dose the stored energy value increases without any sign of saturation [6]. What is more, very large and unstable voids are produced at relatively low irradiation doses, and explosions have been observed in many irradiated natural rock salt samples, indicating that voids are important ingredients for the explosive processes [7, 8]. Subsequently, a theory of radiation damage in NaCl has been proposed [9, 10] based on a new mechanism of dislocation climb, which is described in the present paper. The mechanism involves the production of V_F centers (self-trapped hole neighboring a cation vacancy) as a result of the absorption of excess *H* centers (halide interstitial ion with a trapped hole). Voids are shown to arise and grow rapidly due to the reaction between V_F centers and *F* centers (vacancy in the halide sub-lattice with a trapped electron) at the surface of halogen bubbles.

2. EVOLUTION OF DEFECT STRUCTURE UNDER IRRADIATION

In the alkali halides, the principal radiation damage consists of *bubbles of fluid halogen* formed by agglomeration of *H* centers and of the complementary inclusions of alkali metal *(«colloids»)* formed by agglomeration of *F* centers. According to the conventional Jain and Lidiard model [11], *the dislocation bias* for *H* centers is the driving force for the colloid growth in alkali halides exactly in the same way as for the *void growth in metals* under irradiation. However, the mechanism of dislocation climb [12] used in the Jain and Lidiard model, requires two *H* centers and leaves behind a molecular center, i. e. halogen molecule in a simple vacancy pair. Thus, only dispersed molecular centers and metal colloids can be formed according to the Jain and Lidiard model, which can not explain the void formation observed in our experiments.

According to our model, halogen bubbles and voids are formed instead of dispersed molecular centers. When an *H* center approaches a dislocation, it is assumed to displace a lattice cation and form with this ion a stoichiometric interstitial pair (needed for the dislocation climb) *leaving behind a hole trapped next to a cation vacancy.* The latter is known as the V_F center, which is a mobile «antimorph» of the *F* center (electron trapped in an anion vacancy), so that their mutual recombination would result in production of a stoichiometric vacancy pair in both anion and cation sub-lattices. Such a recombination is expected to take place first of all at halogen bubble surfaces since coherent colloids are assumed to be transparent for V_F centers and do not trap them. An important consideration is that the production of V_F centers by dislocations requires excess of incoming *H* centers over *F* centers, since the latter induce a back reaction. Similarly, the production of vacancy pairs at the bubble surface requires an excess of incoming *F* centers over *H* centers. This means that all reactions involved in the production and absorption of V_F centers at extended defects are controlled by the biases for absorption of *H* centers or *F* centers.

An edge dislocation is biased towards absorption of *H* centers due to stronger elastic interaction with them as compared to *F* centers. So dislocations are a potential source of extra *F* centers and V_F centers under irradiation. Agglomeration of *F* centers gives rise to formation of metallic colloids, which are expected to be coherent with the host matrix as long as they are small.

When several *H* centers meet each other they combine to form a halogen bubble which «digs its own hole» in the lattice by punching out a perfect self-interstitial loop (SIA-loop). This process is exactly analogous to the loop punching from helium bubbles in metals [13].

The threshold pressure for the loop punching is inversely proportional to the bubble radius and can be very high for small bubbles. High pressure induces a large positive addition to the bubble bias [10] so that a small halogen bubble has a higher bias for *H* centers than the mean bias. It means that bubbles initially can absorb surplus *H* centers and grow via SIA-loop punching, which is an *additional driving force* for the separation of the *H* and *F* centers into bubbles and metal colloids.

At later stages of radioanalyses, surplus F centers start to arrive at the bubble surface and recombine with V_F centers producing stoichiometric vacancy pairs that would increase the bubble size and so decrease the pressure below the threshold level for loop punching. After that, the bubble pressure is determined both by the number of halogen molecules and the number of vacancy pairs in it via the equation of state. Accordingly, the bubble evolution takes place in the

two-dimensional phase space [10] of the number of halogen molecules, n_{Gas}, and the number of vacancy pairs in it, n_{Vac}, as it is schematically shown in Fig. 1.

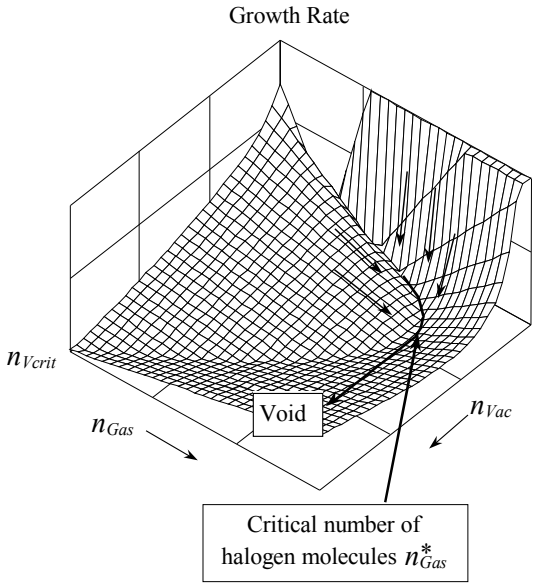

Fig. 1. The evolution path of bubbles resulting in their conversion to voids [10]. Below the critical number of halogen molecules, n^*_{Gas}, the bubbles move slowly along the valley, which provide the only stable path towards the point where the critical number of halogen molecules is reached. After the point is reached, the number of vacancies starts to increase, while the number of gas molecules stays constant. n_{Vcrit} is the critical number of vacancies required for growth of an empty void ($n_{Gas} = 0$).

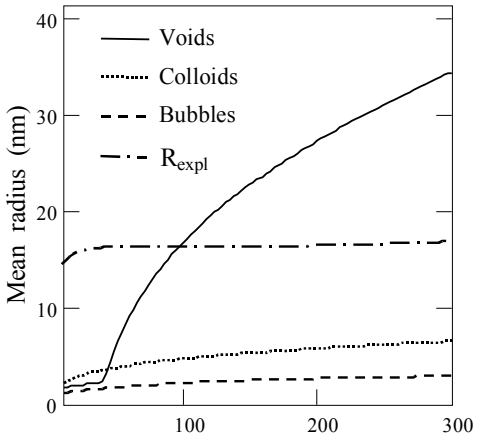

Fig. 2. Calculated dose dependence of the mean radii of extended defects in NaCl, according to ref. [10]. R_{expl}, is the mean distance between colloids. At $R_V > R_{expl}$, colloids start to be captured by growing voids, which would bring the halogen gas and metal to a back reaction inside the voids.

Below some critical number of halogen molecules, a bubble is forced to occupy a stable position along the curve in the «valley» where both components of the bubble growth rate are zero. A gradual decrease of the mean bias, which is due to the colloid growth, makes the bubbles move adiabatically along the curve until they reach a critical point, beyond which n_{Vac} would increase inexorably at n_{Gas} remaining constant. Thus a conversion of bubbles to voids would take place after some threshold irradiation dose of about 40 Grad, as it is shown in Fig. 2. It can be seen that there is no saturation of colloid growth, although voids can grow much faster than colloids since they have no misfit bias.

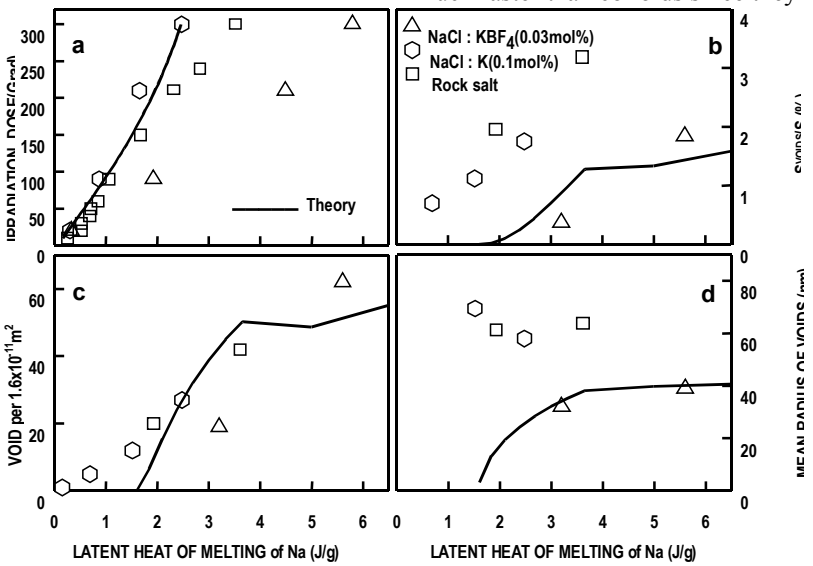

Fig. 3. Comparison between the experiment and the theory.
(a) Measured and calculated dependence of LHM of metallic Na, which is proportional to the colloid fraction, on irradiation dose at K = 240 Mrad/h and T = 100 ^{0}C.
(b-d) Void mean parameters (volume fraction (b), number density (c) and mean radius (d)) against LHM after irradiation up to 300 Grad for different dopants and temperatures (from 60 0C to 130 0C). Symbols correspond to experimental data, and curves are calculations based on the model [10].

Fig. 3 shows the calculated and measured dose dependencies of the sodium latent heat of melting (LHM) at 100 ^{O}C. LHM is proportional to the colloid volume fraction. The experimental data confirm that

there is no saturation of colloid growth. The void dimensions can exceed the mean distance between colloids and bubbles (R_{expl} in Fig. 2), which would eventually lead to their collisions with voids. Collisions with bubbles fill the voids with gas, and subsequent collisions with colloids (during further irradiation or heating) bring the halogen gas and metal to a back reaction inside the voids. Such a sudden release of stored energy can be shown to result in a temperature spike (above 10^4 K) and instantaneous gas pressure rise up to 1 GPa within the voids, which may transform voids into penny-shaped cracks along the cleavage planes of the matrix. A subsequent growth of the cracks results in the explosion driven fracture of the material. Such a sudden release of stored energy can cause cracks in the matrix resulting in the material destruction, which has been observed in some of our samples.

We would like to conclude that the amount of radiation damage in alkali halides should be evaluated with account of vacancy void formation, which strongly affects the radiation stability of material.

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