

## The Role of Stress in Nucleus Development during Dehydration of Certain Alums

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**Summary** Microscopic examination of dehydration nuclei developed on cleaved faces {111} of potassium alum and a mixed K(Al, Cr) alum revealed a characteristic progressive sequence of surface textural changes and crack propagation before and during the initiation and growth of the product phase; these surface modifications are interpreted as evidence that local stresses may be a more important contributory factor in nucleation than has hitherto been recognized.

KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O and of KAl<sub>0.49</sub>Cr<sub>0.51</sub>(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O. A Reichert Zetopan optical microscope was used, equipped with interference contrast and interferometer after Nomarski. Crystal surfaces of satisfactory perfection were examined and features of interest photographed in air before and after appropriate periods (5 min—20 h) of evacuation (< 10<sup>-2</sup> Torr) at known temperatures (± 1 K) between 288 and 300 K. Nucleation was a rate process, continuing to completion of surface reaction. The reactivities of different cleaved surfaces, even between crystals from the same preparation, showed appreciable variations but were invariably less than those of external boundaries of solution-grown crystals.

Thermal decomposition reactions of many crystalline solids proceed by nucleation and growth processes; these are characterized by the restriction that the controlling chemical transformation occurs only within the immediate vicinity of a reactant-product contact interface. Kinetic expressions obeyed by such reactions are derived from consideration of the systematic variations in geometry which arise during interface advance. Each of the various<sup>1</sup> rate equations which have been applied to such systems represents quantitatively the kinetic consequences of an appropriate combination of a law of nucleus generation and a law of growth. The constituent expressions, used in the formulations of such rate equations, were originally developed from microscopic measurements of the onset of reactions at the surfaces of a range of solid reactants. We have re-examined specific features of one of the processes which was the subject of early interest, the dehydration of alums.<sup>2</sup> Exploiting recent improvements in microscopic technique, we have identified a characteristic pattern of local variations in surface texture which culminated in the production of a stable nucleus. These surface distortions are indicative of the presence of stress in the boundary region of the reactant, probably extending to a depth of several microns. This is positive evidence that the nucleation step is less localized than has been indicated in previous theoretical treatments of nucleation, which have proposed, for example,<sup>3</sup> that growth nuclei appear after the occurrence of a small number of unimolecular or bimolecular chemical steps at a reaction site (each site presumably having dimensions comparable with that of a lattice unit cell). Our microscopic observations demonstrate that, for the systems studied here, there was strain involving the co-operative displacements of large numbers of ions immediately before and during the generation of each nucleus. The conclusions presented below are intended to initiate discussion as to whether the onset of reaction is a direct consequence of the development of insupportable stress, within microscopically visible volumes of reactant, or, if the alternative theory, that the onset of reaction follows a small number of distinct and individual *chemical steps*, provides the more acceptable representation of nucleation phenomena. This topic is important since nucleation kinetics constitute a fundamental feature of the formulation of rate equations.

From comparative and critical examinations of the cleaved surfaces of numerous crystals, the following stages in the development of dehydration nuclei were distinguished. (There was, however, some overlap between the divisions indicated).

1. Surfaces freshly exposed on cleavage included planar areas in which there were no recognizable features; the present report is concerned with reaction initiation within these zones of relative perfection. (Damaged and imperfect areas, although also present, are not considered further here).
2. After a short period of evacuation, planar surfaces became distorted through the development of a characteristic structure comprised of irregular mounds and depressions (the texture resembling the outer surface of orange-peel). This deformation increased somewhat with time of evacuation and widely spaced, star-shaped zones of relatively more intense local distortion were noticed. Within such zones of maximum deformation a single crystal appeared; this is identified as the first step in nucleation.
3. Initial growth of each newly generated nucleus (believed to be a single crystal) was outwards, normal to the surface, and each developed an associated circular zone, having a well defined outer boundary, within which there was extensive irregular deformation, attributable to considerable local strain.
4. The central single (?) crystal of each nucleus subsequently underwent reorganization, being replaced by an assemblage of irregularly disposed small crystallites. The outer boundary of the associated circular zone of surface distortion often developed as a crack and connected with similar cracks radiating from the original centre of the nucleation site.
5. Cleavage of partially reacted crystals through established hemispherical nuclei revealed the presence of cracks across the advancing interfacial zone, which apparently propagated from the product into the bulk of undecomposed reactant.

The above observations clearly demonstrate that, for these alums, both the nucleation and the growth processes are closely associated with stress deformation and cracking of the reactant. The volume changes consequent upon the elimination of water from the lattice results in rapid initial

Our studies were particularly concerned with the structures of dehydration nuclei<sup>2</sup> formed on fresh {111} surfaces exposed by cleavage of large solution-growth crystals of

distortion of all surfaces (yielding the 'orange-peel' texture) and similar forces cause the characteristic textural modification apparent at surfaces some distance in front of advancing established reaction interfaces. Also, within the crystal bulk, insupportable forces are developed in association with the reactant-product contact, since the presence of cracks could be detected microscopically. We conclude, therefore, that, although external crystal surfaces undergo rapid textural modification on evacuation, there is no indication that this leads to recrystallization which, in contrast, is a characteristic feature of established nuclei. Since it has long been accepted that available water may promote lattice reorganization (*e.g.* in explanations<sup>2</sup> of Smith-Topley behaviour), it is reasonable to suppose that the very existence of nuclei is a direct consequence of a temporary retention of water within the narrow channels, cracks, and pores of a disorganized product phase, the recrystallization of which is thereby promoted. On such a model the interface is represented as being incoherent and diffuse, since water loss is envisaged as occurring at the surfaces of disintegrating crystals within a reaction zone of appreciable thickness which constitutes the boundary of each hemispherical nucleus. Concurrently, reactant within this active zone is undergoing breakdown through crack

propagation and water-facilitated reorganization to yield crystalline product. Outer crystal surfaces lose some water but lattice reorganization does not occur under strongly dehydrating conditions.

We therefore identify stress as exerting an important control over the initiation of reaction. For these alums nucleation cannot be regarded as solely arising from a sequence of a small number of essentially localized bond redistribution steps, but also involves stress deformation within volumes of salt that are sufficiently large to be visible microscopically. The implications of these observations will be discussed in greater detail in a later paper. A general consequence of such a model is that the significance of measured Arrhenius parameters must be interpreted with due regard for the several contributory processes involved since the observed chemical changes are the cumulative consequences of water elimination coupled with control through such factors as stress deformation, recrystallization, crack propagation, *etc.*

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