Thermal Recrystallization of Precipitated Zinc Sulfide

Abstract. *Changes in morphology during thermal recrystallization of zinc sulfide precipitate were observed under an electron microscope. Intra-aggregate coalescence of precipitate grains proceeds with unexpected rapidity until the limiting identity of aggregate and grain is attained.*

Zinc sulfide is of basic interest in luminescence research. Properly activated by certain impurities in controlled amounts, it is extremely efficient in transforming primary energy into visible radiation. Also unique is its versatility in accepting primary energy in any of the usual forms: ultraviolet radiation, x-rays, cathode rays, and electric field; no other phosphor responds strongly to all these stimuli. Research-grade zinc sulfide is generally prepared in an acidic aqueous medium: hydrogen sulfide is passed into moderate ($\sim 1M$) zinc sulfate solution, and precipitation proceeds to virtual depletion of zinc ion in the aqueous phase.

A necessary step in development of the luminescent characteristics of activated zinc sulfide is thermal recrystallization of the precipitate. Thermal treatments take place in the region of stability of the hexagonal modification (~ 1200°C) or at temperatures promoting the cubic variety (below 1024°C) (*1*). Sometimes an inorganic salt such as sodium chloride is added to increase the rates of the various transport processes that effect the recrystallization; even in these optimal cases the thermal treatments are usually 1 hour or more in duration. Average particle size, as indicated by measurements of sedimentation rates in air, increases slowly from about 7 to 27 μ in 2 hours at 1200°C; for this reason little attention has been paid to the events that may take place during the first few minutes of the thermal recrystallization.

Our studies with the aid of the electron microscope reveal interesting and dynamic morphologic activity that contrasts with the expected slow changes. The surface of a particle of precipitated zinc sulfide consists of an aggregation of grains (Fig. 1*A*). While the exact mechanism of nucleation during precipitation is unknown, once nuclei form, accretion is made extremely rapid by the combination of relatively high concentrations of reactants and slight

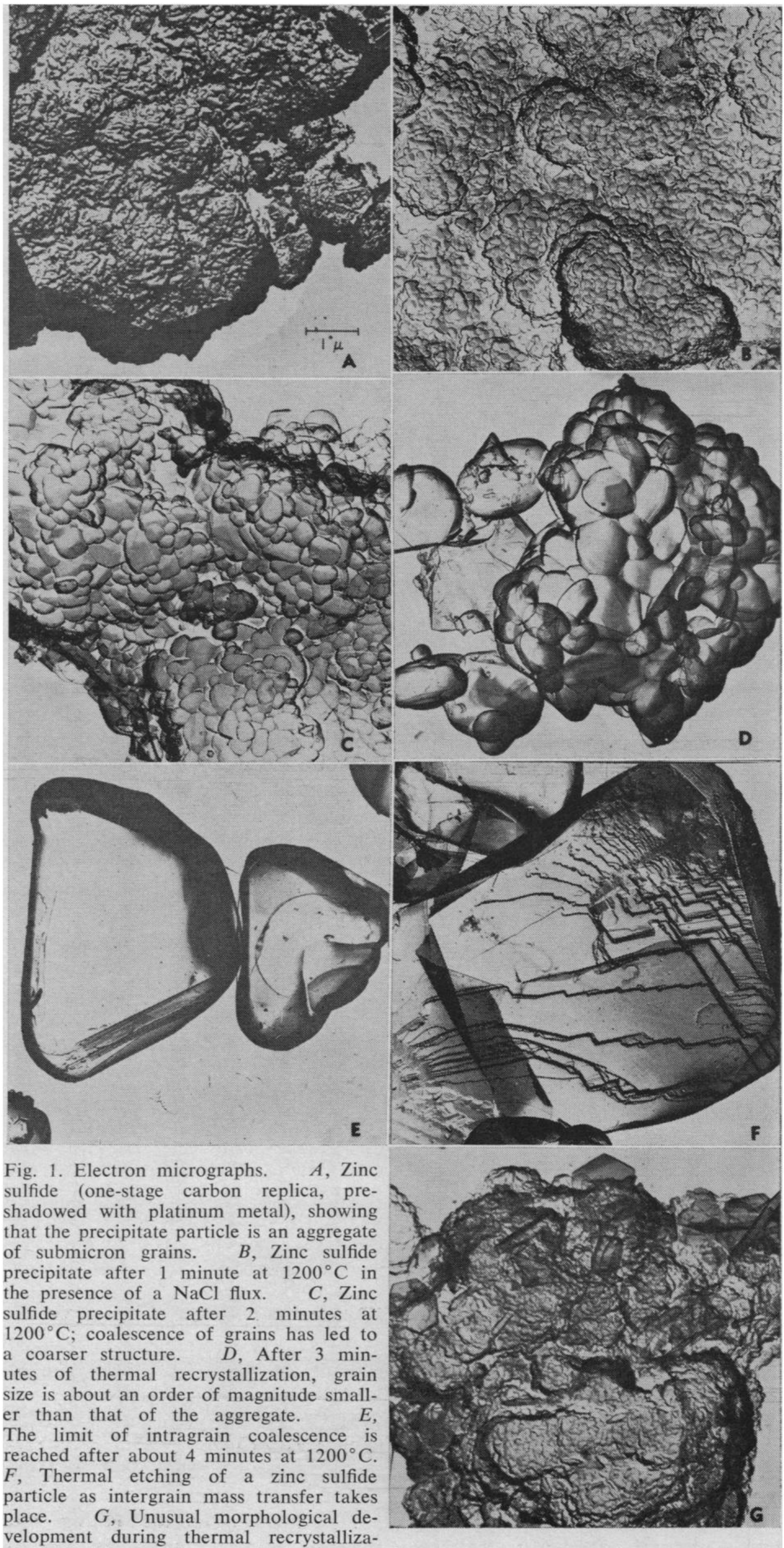

Fig. 1. Electron micrographs. *A*, Zinc sulfide (one-stage carbon replica, preshadowed with platinum metal), showing that the precipitate particle is an aggregate of submicron grains. *B*, Zinc sulfide precipitate after 1 minute at 1200°C in the presence of a NaCl flux. *C*, Zinc sulfide precipitate after 2 minutes at 1200°C; coalescence of grains has led to a coarser structure. *D*, After 3 minutes of thermal recrystallization, grain size is about an order of magnitude smaller than that of the aggregate. *E*, The limit of intragrain coalescence is reached after about 4 minutes at 1200°C. *F*, Thermal etching of a zinc sulfide particle as intergrain mass transfer takes place. *G*, Unusual morphological development during thermal recrystallization: Well-formed hexagonal platelets can be seen growing from the aggregate; This is in marked contrast with the usual development of larger but asymmetric grains.

solubility of the product. Under these conditions one may expect that the crystal-growth process is somewhat unorganized and produces large vacancy and defect populations; moreover, crystallite size is expected to be small, as observed, and aggregation probably results from surface charges on the grains. Measurements of gas adsorption of the zinc sulfide precipitate reveal extremely high porosity of the aggregate (2) and suggest that almost the entire surfaces (including the inner) of the constituent grains are active in adsorption.

After 1 minute at 1200°C in the presence of a NaCl flux constituting 2 percent of the total weight, some coalescence of adjacent grains has taken place (Fig. 1*B*). After 2 minutes, total surface area is sharply reduced, although average aggregate diameters, as determined by measurement of air sedimentation rates, are unchanged (Fig. 1*C*); rapid intra-aggregate growth is clearly indicated, although interaggregate mass transport has not occurred to a measurable extent. The coalescence process is considerably advanced after 3 minutes (Fig. 1*D*); individual grains are of the order of 1 μ in size, while average aggregate diameters are approximately 6.5 μ and relatively unchanged from diameters at time zero.

After 4 minutes, the coalescence process is essentially complete and the limiting identity of grain and aggregate has been attained (Fig. 1*E*). Because of obvious problems of heat transfer, clearly the exact stage of coalescence for a given sample depends on sample size and geometry. In our experiments, sample sizes were of the order of 5 g and the thermal treatment was carried out in covered silica crucibles.

The smooth, rounded particles of Fig. 1*E* are typical of those observed in many electron micrographs corresponding to thermal treatments of long duration. Also observed in the longer-term samples are many particles exhibiting sharp step characteristics (Fig. 1*F*). The difference in the morphologies is readily appreciable in the light of two facts: First, such mesa patterns are never observed in particles during the period of intra-aggregate coalescence; secondly, particle growth, after coalescence is completed, must proceed by intergrain attrition. The grain in Fig. 1*F* has clearly been etched thermally, and just before quenching of the sample it was in the process of supplying nutrient to other grains. Interesting is the extent to which single-crystal properties are suggested by the edges and discontinuities revealed in Fig. 1*E*; prominent topographical features can generally be traced backward linearly to the point of origin of the defect. X-ray studies with single grains of recrystallized zinc sulfide powder also indicate that each grain is a single crystal (see *3*).

Figure 1*G* illustrates a rare event in the process of recrystallization of precipitated zinc sulfide. The large central grain exhibits crystal-growth characteristics that have not been observed in hundreds of other electron micrographs of zinc sulfide particles. A number of platelets of hexagonal symmetry are observed in the process of developing from the precipitate grains, in contrast with the usual process of coalescence into grains without well-defined geometries. What the later development of such an aggregate would be is not suggested by any of our observations of numerous particle surfaces. The partially coalesced sample to the side of the aggregate in question shows that not all intra-aggregate processes in a given sample proceed identically; this is because of the variation of rate of heating with particle position within the sample. The micrographs in Fig. 1, *A–E*, represent an average state of development for small samples.

Recrystallization of precipitate at 1000°C proceeds with morphological changes identical with those observed at 1200°C, except that the process is somewhat slower. The inclusion of copper at 1000°C, which is known to favor additionally the cubic modification, also fails to affect the coalescence process although the degree of polytypism is reduced.

In summation, the electron microscope was used to demonstrate intra-aggregate grain coalescence during thermal recrystallization of zinc sulfide precipitate. It was clearly shown that the first few minutes of the thermal treatment are a time of dynamic activity, contrary to projections based on the slow rates of increase of particle diameters. The electron micrographs also explain the differences in morphologies of crystallite types that are observed in samples in which interparticle growth has occurred.

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References and Notes

1. Although the literature reports the transition temperature as 1024°C, the small energy difference between the crystalline modifications allows polytypism on both sides of that temperature. Impurities also may strongly influence the degree of transformation.
2. Details of particle-size measurements, luminescence development, and x-ray crystallography corresponding to the short-term morphological effects described in this report have been published: L. Bodi, "Some aspects of the thermal recrystallization of precipitated zinc sulfide," in *Proc. Intern. Conf. Luminescence Budapest 1966*, in press.
3. G. Gashurov, General Telephone and Electronics Labs., Bayside, N.Y., private communication.

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Undersea Air Supply

Abstract. *The interior air of a simulated underwater habitation was continuously washed or scrubbed with sea water by means of a gas exchanger of the venturi type. The sole method for supplying oxygen and removing carbon dioxide was the scrubbing process. A microburner placed inside the experimental habitation chamber continued to burn until it was intentionally extinguished. Two rats maintained in the chamber for 8 hours suffered no discernible ill effects.*

The gases dissolved in sea water are a potential source of air for men to breathe underseas. Similarly, the carbon dioxide–absorbing capacity of sea water is a potential means for disposing of respiratory wastes. These potentialities were partially verified in experi-

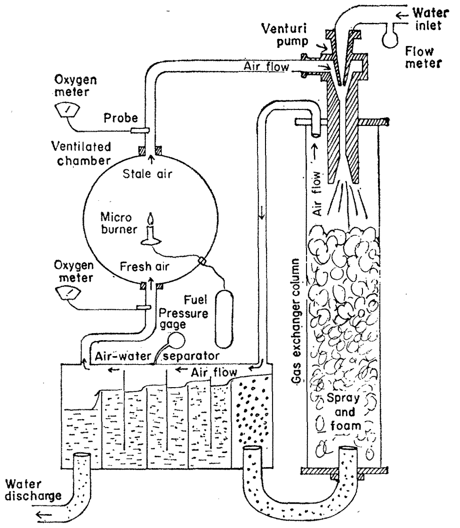

Fig. 1. Apparatus for scrubbing interior atmosphere of metabolic combustion chamber with sea water, thereby replenishing the chamber with oxygen and freeing it of carbon dioxide.