Oxidation Kinetics of Polycrystalline Zinc Sulfide Grains

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A porous solid reacting with a gas according to the reaction

$$A(\text{gas}) + bB(\text{solid}) \rightarrow \text{products}$$

is often taken as an assemblage of non-porous grains. The grain model (Szekely and Evans, 1970) assumes that the reaction of each grain having a uniform size follows shrinking core kinetics. In the regime of chemical reaction control, the conversion rate described by the model is proportional to the unconverted fraction of solid to the order of $2/3$. The grain model has been extended to the cases where the grains have size distributions (Kimura et al., 1981, 1983b). That is, the conversion rate of solid B is represented in general by the m-th order expression

$$\frac{dX_B}{dt} = \left(\frac{dX_B}{dt}\right)_{t=0} (1 - X_B)^m \tag{1}$$

where m varies in $2/3 \leqq m < 1.4$, as the standard deviation σ of the grain size distribution varies in $0 \leqq \sigma < 1$. Equation 1 has been verified by the data from oxidation of pelleted polycrystalline zinc sulfide powder having log-normal grain size distributions (Kimura et al., 1983a). However, the conversion rate data during the beginning stage of reaction showed the tendency to deviation from the model in accordance with the decrease in grain size. In this paper, the reaction of grainy porous solid is thereby investigated by using sample particles composed of very fine polycrystalline ZnS grains prepared with colloidal dispersions. We show that as grains become small in size, the size of crystallites relative to grain size becomes of great importance in forming the manner by which reaction proceeds, and the progress of reaction can no longer be described by the grain model.

Experimental

Spherical-colloidal dispersions of zinc sulfide having an average diameter in the range of 1–3 μm were prepared according to the procedures by Wilhelmy and Matijević (1984). Rinsed and dried ZnS powder was blended with a small amount of ethanol to make a thick paste so that grains cohered, followed by evaporation of the ethanol at room temperature. The cake of solid obtained was cut into particles of about 0.5 mm in size.

A differential flow reactor made of a quartz tube of 8 mm inner diameter was used for the oxidation. The ZnS sample particles were sandwiched between quartz wool in the reactor tube and heated to a prescribed reaction temperature in a stream of nitrogen. The sample was then contacted with reactant gas containing 1–3% of oxygen in inert nitrogen by switching the streamlines connected to the reactor. The flow rate of the reactant gas was kept identical to that of the nitrogen stream to avoid temperature changes. The oxidation was carried out at a temperature in the range of 988–1081 K. The temperature was measured by a thermocouple at the center of the reactor tube about 5 mm beneath the sample and controlled by a PID control unit. The progress of reaction was monitored by detecting SO_2 gas, produced by the reaction $2ZnS + 3O_2 \rightarrow 2SO_2 + 2ZnO$, using an IR SO_2 meter at the exit of the reactor. The detailed experimental procedures are described elsewhere (Kimura et al., 1983a).

It was confirmed that resistance to intraparticle diffusion through pores between grains is negligible for particles smaller than 1.0–1.2 mm in size. Also, gas film resistance and intraparticle temperature rise are negligible for a flow rate of reactant gas greater than 2.5×10^{-5} m^3/s, measured at room temperature. Hence, runs were made using particles of about 0.5 mm or less in size, at the flow rate of 3.33×10^{-5} m^3/s.

Sample particles were occasionally taken out of the reactor at several stages of reaction and quickly cooled down to room temperature in the nitrogen stream, then subjected to scanning electron microscope (SEM) inspections and X-ray diffraction (XRD) analyses.

Results and Discussion

In Figure 1, (a) shows an SEM photograph of sample ZnS grains. It is seen that grains are spherical, and nonuniform in size. It was confirmed by a statistical test that the sample ZnS grains have log-normal size distributions. Grains used for com-

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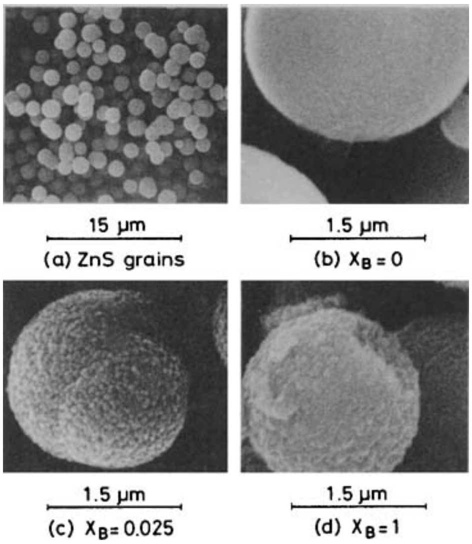

(a), ZnS grains prepared with colloidal dispersions; (b)–(d), change in the feature of grains with the progress of conversion.

Figure 1. Scanning electron microscope photographs of ZnS grains and reacted ones.

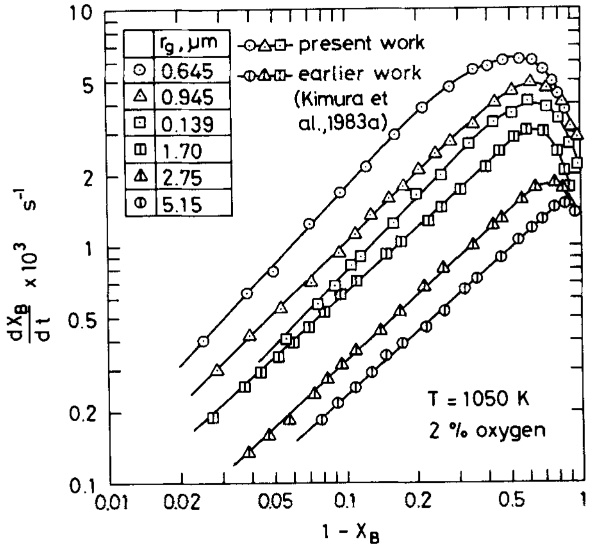

Figure 2. Change in conversion rate with the progress of conversion, showing the shift of peaks toward the middle stage of reaction.

posing sample particles have mean radius $\bar{r}_g$ and standard deviation σ of the size distribution as shown in Table 1.

Figure 2 illustrates the change in conversion rate of sample particles, evaluated by graphical differentiation of conversion X_B vs. time t curves, with the progress of reaction in terms of dX_B/dt plotted against $1 - X_B$ in log-log scale. In Figure 2 the results of our earlier work (Kimura et al., 1983a) are also shown, which were obtained by sample particles composed of rather large nonporous polycrystalline grains, 99.9% reagent ZnS (Mitsuwa Pure Chemicals), and having mean radii in 1.7–5.2 μm. When the size of grains is large, the data (Kimura et al., 1983a) indicate that the peak of conversion rate appears at the very initial stage of reaction. Then, a linear relationship holds between the two during the rest of the course of the reaction. Thus, the progress of the reaction is described by the m-th order kinetics as given by Eq. 1 except at the very beginning of reaction. As the grain size becomes smaller, the conversion rate becomes greater; the extent of conversion where the conversion rate becomes maximum shifts toward the middle stage of reaction around $X_B = 0.5$. The linear relationship holds merely during the end stage of reaction, that is, when $X_B > 0.7$–0.8.

It has been shown by particles composed of rather large grains (Kimura et al., 1983a) that the initial conversion rate, evaluated by extrapolating the linear relationship toward $X_B = 0$, follows the relation

$$\left(\frac{dX_B}{dt}\right)_{t=0} = 3bk'C_A^n v_B \frac{\exp(\sigma^2/2)}{\bar{r}_g} \qquad (2)$$

Equation 2 suggests that the initial conversion rate is proportional to the external surface area of grains represented by the term $\exp(\sigma^2/2)/\bar{r}_g$. Applying the same procedures, the apparent initial conversion rate may be evaluated for particles composed of the smaller grains by extrapolating the linear relationship, held during the end stage of reaction, toward $X_B = 0$. The results, obtained with temperature and oxygen concentration kept constant, are shown in Figure 3 in terms of $\exp(\sigma^2/2)/\bar{r}_g$.

Table 1. Properties of Mono-dispersed Colloidal ZnS Grains

Sample No.	Mean Grain Radius, $\bar{r}_g$(μm)	St. Dev., σ	Mean Crystal. Size, δ (nm)
1	0.645	0.186	—
2	0.840	0.320	—
3	0.855	0.192	—
4	0.945	0.303	5.66
5	0.960	0.356	—
6	1.03	0.262	—
7	1.20	0.364	—
8	1.27	0.461	—
9	1.33	0.448	4.97
10	1.39	0.443	5.22

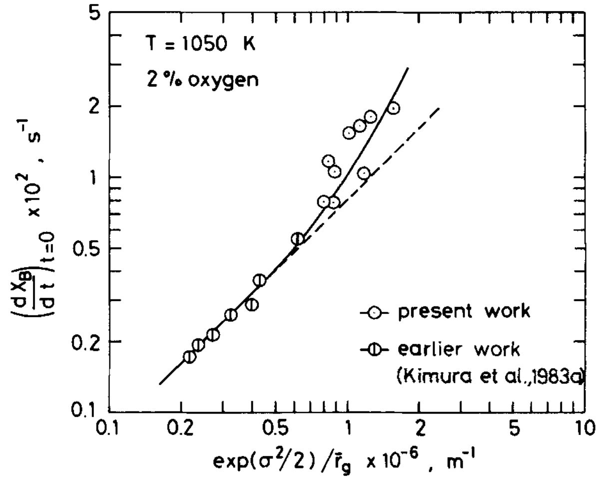

Figure 3. Initial conversion rate becomes greater than that provided by the external surface area of grains as grains become smaller in size.

As the grain size becomes smaller, that is, as the magnitude of exp $(\sigma^2/2)/\bar{r}_g$ becomes greater, the initial conversion rate deviates from the line, representing the proportionality obtained on the basis of particles composed of the larger grains. The deviation from the line implies that the reacting area becomes greater than that provided by the external surface area of grains.

The apparent activation energy, obtained by the temperature dependency of the initial conversion rate of the present system, yielded 230 kJ/mol. This value is very close to 244 kJ/mol for the larger grains (Kimura et al., 1983a). Thus, there is no significant difference of reactivity between the two systems. The observed difference in the progress of reaction of the different grain sizes is considered to be attributed to the difference in grain morphology.

XRD analyses revealed that the ZnS grains prepared by the procedures used in this system are also polycrystalline (Williams et al., 1985). Figure 4 shows the change in the size of crystallites resulting from the heat treatment and reaction. The colloidal ZnS grains are composed of crystallites having an average size of 5–6 nm. The crystallites grow to 20–25 nm in size due to aggregation of crystallites during the process of heating to reaction temperature. The higher the temperature, the greater the crystallite size.

Since the molar volume decreases by about 40% due to the conversion from ZnS to ZnO, it is expected that the crystallites shrink in size by about 16% when each crystallite reacts independently of the others. However, the crystallites after the conversion to ZnO are slightly greater in size than that of unreacted ZnS and do not change much in size with temperature in the range investigated. The reason for this is unclear yet. It should be mentioned that the average size of grains was reduced by about 10% due to reaction.

In Figure 1, (b), (c) and (d) compare the features of grains, prepared with colloidal dispersions, changing with the progress of conversion. Grains keep their spherical shape even after the complete conversion. However, their exterior surfaces show that they change remarkably in solid structure. The surface of grains is rather smooth and nonporous before the reaction, while after the onset of reaction each grain is converted into an assemblage of small clusters and becomes very porous. The same feature was also observed for the larger reagent grains.

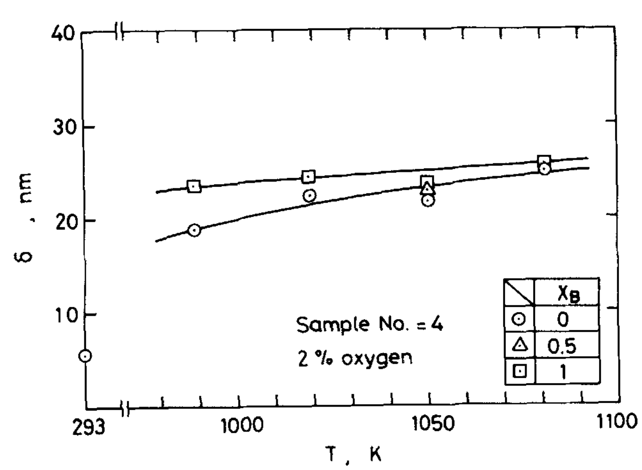

Figure 4. Change in crystallite size due to heating treatment and reaction.

The clusters grow in size as the extent of conversion becomes high, possibly due to the aggregation of clusters. Figure 5 illustrates this in terms of the average size (d_c) of clusters observed on the exterior surface, vs. the extent of overall conversion (X_B). It should be noted in Figure 5 that the size of clusters at the onset of reaction is equal to that of ZnS crystallites, shown by a dark circle on the ordinate. Thus, the clusters are supposed to originate from the crystallites of ZnS.

Diffusion of ions and defects in the solid phase through the boundaries between crystallites, is often much greater than that through the bulk of crystal lattice structure (Kingery et al., 1976). Hence, the reaction along the crystallite boundaries proceeds much faster than in the crystallites, and cleavages are supposed to be formed along the boundaries, resulting from the decrease in molar volume due to reaction. Crystallites, surrounded by the cleavages, then react gradually. The increase in reacting surface area due to the progress of cleavage may result in the appearance of a maximum value in conversion rate and the shift of its location toward the middle stage of reaction. These particular phenomena can not be described by the grain model.

There are several models (Adschiri et al., 1987; Avrami, 1940; Bhatia and Perlmutter, 1980; Gavalas, 1980; Park and Levenspiel, 1975) which predict that the conversion rate reaches maximum value during the course of reaction. Phenomenologically, the progress of reaction may apparently meet the description by the crackling core model (Park and Levenspiel, 1975). It assumes that the nonporous particles first crackle from the exterior inward, leaving behind a grainy porous structure and that each grain reacts according to the shrinking core kinetics. However, the extent of conversion at which the conversion rate becomes maximum does not exceed 0.38 in the model, whereas it even slightly exceeds 0.5 in the present data. Hence, the progress of reaction of each crystallite is supposed to be different from the shrinking core kinetics. When the size of grains is large enough compared to that of crystallites or clusters of crystallites behaving as reacting units, the progress of reaction may be described by the shrinking core model except for the very initial stage of reaction, which is predicted by the crackling core model (Park and Levenspiel, 1975). However, as the grain size

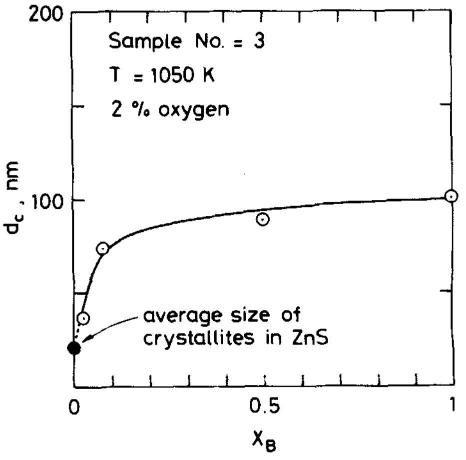

Figure 5. Change with the progress of reaction in the average size of clusters observed on the exterior surface of grains.

decreases and becomes insignificant compared to the crystallite size, the reaction is unable to be described by either the shrinking core model or the crackling core model. Development of a new model, capable of predicting both situations, is required.

Acknowledgment

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Notation

b = stoichiometric coefficient
C_A = gaseous reactant concentration, mol/m^3
d_c = average size of clusters formed resulting from reaction, nm
k = surface rate constant, $(m/s)(m^3/mol)^{n-1}$
m = reaction order with respect to solid reactant B
n = reaction order with respect to gaseous reactant A
$\bar{r}_g$ = mean radius of grains, m
t = reaction time, s
v_B = molar volume of solid reactant B, m^3/mol
X_B = fractional conversion of solid reactant B
δ = average size of crystallites, nm
σ = standard deviation of grain size distribution

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