Review

The Evaluation of Activity and Reactivity of Mechanically Treated Fine Powdered Materials

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1. Introduction

Being the theme of an international symposium, and for the last two years also that of an international journal, the reactivity of solids is currently one of the most important issues in the research and development of materials.

Although remarkable progress has been made in the last two decades, the quantitative characterization of reactivity is still very limited. There are two reasons for this. The first one is the limited possibility of the direct measurement of the activity, either from a structural (crystallographical) or energetic (thermodynamic) point of view, in spite of the recent development of instrumental analyses. Another one is the diversity of the parameters and their cross terms included in the reactivity. These make the correlation between the specific parameters of activity and reactivity complicated and ambiguous.

In the first issue of this Journal, the present author made a contribution entitled, “Criteria for the Activation of Powdery Materials by Preliminary Mechanical Treatment,” where the factors affecting the rate of transformation of gamma ferric oxide were discussed.

As a result of several recent additional experiments obtained, some generalization now seems to be possible. Thus, a second contribution is being made here which concentrates on: (1) answering the question, what should an appropriate measure or a criteria for the activity of fine powders be; (2) designating the reactivity of finely divided solids; and (3) pointing out the problem of interconnecting the activity and the reactivity. Two important concepts, “effective surface area”, and “the availability of the stored energy” are introduced. Detailed and classified discussion will not be made here but only cited as reference material.

2. Excess enthalpy

Excess enthalpy, $\Delta H^*$, is understood as one of the standard measures of the activity of solids. Since $\Delta H^*$ is assessed from the difference in the heats of reaction between activated and intact materials, its determination is also well defined. Experimental methods for determining $\Delta H^*$ using dissolution calorimetry were explained elsewhere. Detailed techniques for partially dissolved material were also discussed.

Fig. 1 The relationship between excess enthalpies obtained from dissolution calorimetry, $\Delta H_f^*$, and thermoanalysis, $\Delta H_p^*$. 

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It is also possible to determine the excess enthalpy from decomposition or other heats of reaction, by using thermoanalytical techniques. An example was given where two excess enthalpies, one from the heat of dissolution and the other from the heat of decomposition, were compared. As shown in Fig. 1, they tallied fairly well. The problem of the temperature dependence of $\Delta H^*$ and related arguments on the role of the entropy term, however, continue to persist. As a case study, the correlation between $\Delta H^*$ and the rate of decomposition of mechanically activated PbCO$_3$ is given below.

Mechanically activated PbCO$_3$ of known excess enthalpy, $\Delta H^*$, is subjected to subsequent thermal decomposition. First-order kinetics was applied to the first stage of the isothermal decomposition, PbCO$_3$ $\rightarrow$ $(1/3)$(PbCO$_3$·PbO) + $(2/3)$CO$_2$, in an N$_2$ flow at temperatures between 523 and 573K. Correlation between the rate constant of decomposition, $k_p$, and $\Delta H^*$ was examined in Fig. 2. Grinding in cyclohexane or with a smaller amplitude brought about a comparable or even higher rate constant, compared at the same network done or the same relative noncrystallinity, in spite of smaller excess enthalpy.

3. Effective surface area

The equivocal correlation between the excess enthalpy and the rate constant of the reaction discussed above requires some additional parameters other than overall enthalpy, to predict the reactivity of active powdery materials. The concept of "effective surface area" is now introduced as one of typical extensive parameter, for "normalizing" the rate constant of the reaction. A case study is given next.

Decomposition and dissolution kinetics of vibro-milled Mg(OH)$_2$ were studied to elucidate the dominating factors in each reaction. The specific surface area measured either by air permeability, $S_p$, or by BET adsorption, $S_B$, decreased after vibro-milling, as shown in Fig. 3. Again, first-order kinetics was applied to the isothermal decomposition reaction in air at temperatures ranging from 583K to 643K. The rate constant of the decomposition, $k_p$, increased with increasing grinding time, as shown in Fig. 4. A similar analysis was carried out for
the reaction of dissolution into 0.1M EDTA, to which contract sphere model kinetics was applied. In contrast to the case of \( k_p \), the rate constant of the dissolution, \( k_d \), measured at temperatures between 283K and 313K, decreased with increasing grinding time, as also shown in Fig. 4.

The difference in the change of reactivity between decomposition and the dissolution reaction seems to be attributed mainly to the difference in the effective surface area of each reaction. Each rate constant divided by an appropriate surface area showed a steep increase with a quick levelling off or slow decrease as the time of activation increased, as shown in Fig. 5. This was similar to the change in the X-ray amorphous portion, \( 1-I_f \), as shown in Fig. 5. As shown above, dividing \( k_d \) by \( S_p \) normalized the rate constant. It seems therefore safe to assume that the specific surface area measured by the air permeability method, standing for the characteristics of highly aggregated particles is one of the dominant extensive parameters for the rate of the dissolution reaction. On the other hand, the hypothetical boundary surface of the crystallite seems to play an important role in the decomposition reaction.

4. Availability of stored energy

As mentioned in Section 2, the increase in the reactivity due to mechanical activation cannot always be correlated uniquely with the calorimetric parameter. Although the effective area, mentioned above, serves as a "hidden parameter", which could further explain the correlation between activity and reactivity, it is insufficient.

For mechanically activated materials, one of the main factors in enhanced reactivity is the higher availability of excess free energy for subsequent chemical reactions. The concept of availability includes the feasibility and efficiency of utilizing excess free energy. Factors dominating availability are related to the kinds as well as the distribution of structural imperfections. To quantify and elucidate the above-mentioned availability is one of the most important tasks for better understanding and for the application of mechanical activation.
Fig. 6 The variation in the rate constant of decomposition, $k_p$ for activated (filled symbols) and non-activated lead carbonate with a concentration of doped Sr$^{2+}$.

A third case study given below deals again with the thermal decomposition of PbCO$_3$ doped with 0.1 $\sim$ 10 mol % Sr, with and without mechanical activation by vibro-milling$^{13}$. Excess enthalpy, $\Delta H^*$, imparted to the activated materials, remained almost constant, irrespective of Sr concentration. The first-order rate constant of isothermal decomposition, $k_{p0}$, of the doped materials without mechanical activation decreased only slightly with the increase in the concentration of Sr. For the mechanically activated materials, however, $k_p$ significantly decreased with the increase in the concentration of Sr, as shown in Fig. 6.

A quasi-linear relationship was found to exist between the apparent activation energy, $E_a$, and the logarithm of the pre-exponential factor, $\ln A$, of the decomposition, as shown in Fig. 7. This enables the determination of the characteristic temperature, $T_x$, at which the Arrhenius plots cross each other, for each group of samples with different Sr concentrations. At $T = T_x$, the excess free energy was assumed to become null$^9$. The relationship between $T_x$ and the decomposition temperature, $T_D$, determined from the DSC profile is shown in Fig. 8. The extent of excess free energy dissipated during the decomposition reaction was suspected to decrease due to Sr doping, since it is

Fig. 7 The relationship between $\ln A$ and $E_a$ for the decomposition of Sr-doped lead carbonate$^{12}$, where $A$ and $E_a$ denote the frequency factor and the activation energy.

Fig. 8 The relationship between $T_x$ and $T_D$ for Sr-doped lead carbonate. Open and filled symbols denote the non-activated and activated materials, respectively.
expected from Fig. 8 that the utility of the stored energy decreases with increasing amounts of doped Sr. The structural imperfection of the decomposed products is one evidence of the above idea. This is an example of the change in availability due to foreign materials.

5. Topochemical aspects of mechanical activation

One of the factors closely related to availability is the topochemical distribution of active centers. An attempt was also made to obtain experimental information about the topochemical distribution of active sites on and in mechanically activated PbCO₃. Vibro-milled PbCO₃ was dissolved into dilute aqueous solutions of acetic acid. For a series of partially dissolved samples, particle size, shape, surface structure and morphology were observed by an SEM.

Finer primary particles on the surface of aggregates preferentially dissolved and disappeared. With an increase in the extent of partial dissolution, X, activity parameters, ΔH°, decreased monotonically and approached the values of as-received PbCO₃, as shown in Fig. 9. This is obviously attributed to the preferential dissolution of finer and more active particles during acid leaching.

When the same amount of the net mechanical work done was applied to the materials in a vibro-mill with different amplitudes, a difference in the distribution of the active center arose. When the total network done was kept constant, a larger number of smaller impacts were applied to the material when ground at a smaller amplitude. Conversely, the mechanical effect could reach deeper into the interior of the particle when ground at a larger amplitude, the number of hits being smaller. This kind of difference was discussed in conjunction with the effects of different grinding machines. The former inevitably causes a more even distribution of active centers near the surface of the particle.

6. Summary

Excess enthalpy, which will eventually be substituted for excess free energy, is experimentally determined from conventional calorimetry or thermal analysis. In spite of being a good and appropriate measure or the activity, a terminology distinct from the definition in thermodynamics, the increase in the rate constants of thermal decomposition of dissolution due to mechanical activation, cannot be correlated uniquely with the excess enthalpy. This is attributed to its dependence on the effective surface area, and to the difference in its availability.

A simple positive correlation between the surface area and the degree of mechanical activation cannot always be expected either, particularly in cases where significant agglomeration takes place due to severe mechanical treatment. The introduction of the concept of effective surface area and its specification serves to better elucidate mechanical activation.

For further elucidation, discussion from a microscopic point of view, as well as detailed analysis of real structure, particularly in the region finer than the limit of X-ray diffractometry, seem to be of the utmost importance.
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