Criteria of Activation of Powdery Materials by a Preliminary Mechanical Treatment

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Abstract

\( \gamma-\text{Fe}_2\text{O}_3 \) was vibration ball-milled with varying amplitude, \( a \), from 8 to 24 mm and grinding time. The enthalpy increase, \( \Delta H^* \), due to mechanical treatment was measured by a differential scanning calorimeter. Pretreated sample was subsequently heated at 693 K for 60 min, and the fractional transformation into \( \alpha \)-phase, \( a_1 \), was obtained. Both \( \Delta H^* \) and \( a_1 \) increased monotonically with grinding time with levelling off at longer milling time. The tendency of a level off was different, however, between \( \Delta H^* \) and \( a_1 \). \( \Delta H^* \) increased monotonically with increasing amplitude whereas \( a_1 \) showed a maximum at \( a = 10 \text{ mm} \). The correlation between \( a_1 \) and the lattice disturbance, the latter being obtained from the relative intensity of X-ray diffraction peaks, was not uniquely determined, but depended on the amplitude. This suggests that the same lattice disturbance does not always lead to the same degree of acceleration of the subsequent reaction. The reason was discussed on the basis of the content of \( \Delta H^* \) and the nuclei-growth mechanism of \( \gamma \to \alpha \) transformation of \( \text{Fe}_2\text{O}_3 \).

1. Introduction

A number of examples were found in the field of mechanochemical activation of finely divided solids in the last two decades\(^1,2\) Some of them are promising for the technological application. Until now, however, most of the industrial branches which have good possibilities to make use of mechanochemical activation techniques are reluctant to introduce them into an actual production line. One of the most serious objections for the application of such techniques is obviously the lack of quantitative data warranting the benefit of the technique.

Much effort has been made to quantify the mechanochemical effects through thermoanalytical and calorimetric studies\(^3\). Stored energy, \( \Delta H^* \) is most frequently used as a measure of activation. The increase in the enthalpy or the excess enthalpy is the thermodynamical definition of the measured stored energy. For the critical discussion, the change in the free energy is more desirable. However, we have to tolerate a substitute use of the enthalpy, letting the contribution of the entropy still open to the question\(^4\), for the time being, since a direct measurement of the free energy on powdery material is hardly possible.

The main purpose of the present study is to answer the question, if partly, whether and to what extent the stored energy can be used as a real criterion or a practical measure of mechanochemical activation. \( \gamma-\text{Fe}_2\text{O}_3 \) was used as a model substance, since the stored energy of mechanically treated \( \gamma-\text{Fe}_2\text{O}_3 \) is easily measured by DSC\(^5\). Different kinds of mechanical treatments were used and the correlation between \( \Delta H^* \) and the enhancement of the rate of transformation into \( \alpha-\text{Fe}_2\text{O}_3 \) on subsequent heating was compared.

2. Experimental

Pure \( \gamma-\text{Fe}_2\text{O}_3 \) for magnetic recording (Toda Kogyo, Hiroshima, Japan) was used as a starting material without any special treatment. Primary particles are acicular with an average...
length about 0.5μm. The material was mechanically treated in two ways, i.e., by grinding with a vibratory mill and by compressing in a die. Vibration ball-milling was carried out by using a laboratory-sized mill with a varying amplitude, α, from 8 to 24mm. The frequency was kept constant at 12Hz. 1.5g starting material was put into a cylindrical steel vessel of 50cm³, together with 100 pieces of 6mm steel balls and 30cm³ cyclohexane. Mechanical treatment was also carried out by compressing dry γ-Fe₂O₃ powder in a die cavity (0.05 - 0.5 GPa) or between a gap of a tapered anvil (1.0 - 2.0 GPa).

Stored energy, i.e., excess enthalpy, ΔH* was measured by using a differential scanning calorimeter (DSC, Thermoflex, High-Temperature type, Rigaku, Tokyo, Japan). The thermoanalysis was carried out at constant rate of heating, 10K min⁻¹, in air. An X-ray diffractometry was carried out in order to determine the extent of lattice disturbance and lattice distortion. The relative intensity of diffraction peaks from γ-Fe₂O₃ (220), (311) and (400) was determined by using CaF₂ as an internal standard.

γ-Fe₂O₃ with and without mechanical pre-treatment were subsequently heated in air. Fractional conversion into α-phase was determined by an X-ray diffractometry. Detailed analytical method was described elsewhere⁶).

3. Results and discussion

3.1 DSC profile

Typical DSC profiles of original, vibration ball-milled and compressed γ-Fe₂O₃ are shown in Fig. 1. For the original as-received material, only a single exothermic peak was observed at ca. 843K, which corresponds to the heat of transformation into α-phase⁵). A vibration ball-milled sample showed, on the other hand, an additional broad peak at lower temperatures. The latter is interpreted to be caused by the liberation of stored energy⁵), from which the enthalpy excess was calculated in a manner given elsewhere⁷). Compressed γ-Fe₂O₃ indicated little amount of energy storage, although the temperature of the transformation lowered significantly.

3.2 Variation of ΔH* with grinding time and amplitude

ΔH* increased monotonically with grinding time with a tendency of levelling off at longer grinding time, as shown in Fig. 2. Larger amplitude brought about higher excess enthalpy. These two observations are quite natural to be accepted, because the energy input or the work done increases linearly with time and parabolically with the amplitude⁸).

3.3 Variation of lattice disturbance with grinding time and amplitude

Relative intensity of X-ray diffraction peaks from γ-Fe₂O₃ (220), (311) and (400) were averaged. The mean value of the relative intensity was then divided by that of as-received sample to obtain the relative crystallinity, Iᵢ. I₁/Iᵢ is understood as a measure of the lattice
disturbance introduced during a preliminary mechanical treatment.

When $I_f$ is plotted against grinding time, an almost monotonically decrease with levelling off at longer grinding time was observed as shown in Fig. 3. This corresponds seemingly well to the monotonic increase in ${\Delta}H^*$ shown in Fig. 2. It is noteworthy, however, that, whereas the effect of increasing amplitude is profound in the case of ${\Delta}H^*$, two curves of Fig. 3 for different amplitudes run almost the same track, indicating little effect of increasing amplitude on $I_f$. On the other hand, variation of $I_f$ with the amplitude is somehow peculiar as shown in Fig. 4.

3.4 Reactivity increase

When mechanically pretreated $\gamma$-Fe$_2$O$_3$ is heated at 673-713K, a part of the sample transformed into $\alpha$-phase very rapidly, followed by a much slower second step$^7$. As reported previously, as-received $\gamma$-Fe$_2$O$_3$ never transformed into $\alpha$-phase when heated at 713K even for 9hr. Therefore the fraction transformed, $a_1$, after heating at 693K for 60 min in air was chosen as a measure of the increased reactivity.

Relation between $a_1$ and the grinding time is shown in Fig. 5. $a_1$ increased with grinding time. However, the tendency of levelling off was much more significant than in the case of ${\Delta}H^*$. With $\alpha = 24$mm, $a_1$ even decreased when ground for 300 min. Furthermore, samples ground with smaller amplitude showed higher reactivity.

3.5 Relation between $\Delta H^*$ and $a_1$

As expected from Figs. 2 and 5, the correlation between $\Delta H^*$ and $a_1$ is by no means straightforward. Both quantities are plotted in Fig. 6 against the amplitude of the vibration mill. In the amplitude range smaller than 10mm, both $\Delta H^*$ and $a_1$ increased, the correlation therebetween being positive. $\Delta H^*$ further increased with increasing amplitude. Since $a_1$ little increased with increasing amplitude between $\alpha = 10$mm and 14mm, the correlation between $\Delta H^*$ and $a_1$ is not so clear as with smaller amplitudes. With the amplitude larger
than 14 mm, the correlation between $\Delta H^*$ and $a_1$ is even negative.

3.6 Relation between $I_f$ and $a_1$

The relation between $I_f$ and $a_1$ are shown for varying grinding time in Fig. 7, and varying amplitude in Fig. 8. Figs. 7 and 8 suggest that the same lattice disturbance does not always lead to the same degree of acceleration for the subsequent reaction. Lattice imperfection introduced at early stages of grinding with larger amplitude contribute quite significantly to $I_f$, as shown in Fig. 7, but not very much for the acceleration of the transformation. When $I_f$ is plotted against $a_1$ for serial data of varying amplitude as in Fig. 8, the curve falls on between the two curves of Fig. 7. The correlation between $I_f$ and $a_1$ is rather simple and straightforward.

3.7 Contents of $\Delta H^*$

The excess enthalpy of mechanically pre-treated $\gamma$-Fe$_2$O$_3$ is attributed partly to the lattice disturbance. As shown just above, the same extent of lattice disturbance does not always correspond to the same increase in the enthalpy, e.g., when the amplitude is different. The tendency is much more striking when we compare the results of vibration ball-milling and compressing experiments. Since the lattice disturbance was also observed for compressed samples where no significant energy storage was detected, the lattice disturbance solely cannot be the reason of the energy storage. Disordering
of the structural vacancy and/or the site exchange of the vacancy could also share a part of energy storage\(^9\). The present experimental results point out that not all of the stored energy can contribute to the enhancement of the transformation.

### 3.8 Enhancement of phase transformation

Transformation of \(\gamma\)-Fe\(_2\)O\(_3\) into \(\alpha\)-Fe\(_2\)O\(_3\) is initiated by the nucleation of hematite in the matrix of the spinel structure of maghemite. In the case of mechanical pretreatment, a part of the fcc stacking of oxygen (111) plane in the spinel is supposed to be faulted, resulting in the local hexagonal stacking. This stacking fault can serve as an embryo of hematite\(^5\). The embryo can become easily a nucleus of hematite with a slight displacement of Fe\(^{3+}\) ions\(^{10}\).

The enhancement of the transformation is achieved mainly through the enhanced nucleation rate, as inferred from the kinetic analysis\(^{11}\). The same is true for the isomorphous transformation of \(\gamma\)-Al\(_2\)O\(_3\) into \(\alpha\)-Al\(_2\)O\(_3\)\(^{12}\). It is therefore to be expected, that only a part of the lattice imperfection which directly serves as an embryo, viz., the stacking fault of oxygen layers, contribute significantly to the enhancement of the transformation.

When the nature and the distribution of the crystal imperfection generated during mechanical treatment favors the nucleation, the ratio \(a_1/\Delta H^*\) is larger, as in the case of vibration ball-milling with \(a = 10\) mm. The ratio \(a_2/\Delta H^*\) may be even much larger in the case of compressed material, since \(\Delta H^*\) is much smaller or even null for the compressed material. Details of press experiments will be reported elsewhere.

### 4. Concluding remarks

The present experiment suggests that the nature and the distribution of the crystal imperfection is largely different, depending on the method of mechanical pretreatment and accordingly on the distribution of the applied external stress. The overall relationships among the crystallographical, thermal and chemical properties are therefore often ambiguous. Topological studies with regard to the mechanical activation are of urgent importance for the further elucidation of the usefulness of the mechanochemical activation. Enlightening investigations are now in the course of their development in some institutions\(^{13, 14}\).

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