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# POLYMORPHIC TRANSFORMATION OF $\gamma$-$Fe_2O_3$ BY ISOTHERMAL BALL-MILLING AND VACUUM HOT-PRESSING

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# POLYMORPHIC TRANSFORMATION OF $\gamma$-$Fe_2O_3$ BY ISOTHERMAL BALL-MILLING AND VACUUM HOT-PRESSING

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## ABSTRACT

Matastable phase of iron (III) oxide, $\gamma$-$Fe_2O_3$, transforms to the stable phase, $\alpha$-$Fe_2O_3$, by either isothermal wet ball-milling or vacuum hot-pressing. From kinetic analysis of these processes, it was found that application of external force makes an alternative mechanism of the transformation operative. Decrease in the activation energy with increasing applied external force suggests that mechanical force elevates the potential energy of the reactant particles by enhancing strains or defects in the crystal. Comparing the results to those on the mechanochemical transformation of PbO, reported previously by the authors, reveals that mechanical force acts on the polymorphic transformation at least by two different ways depending on the nature of the material, although the mechanism of transmission of the external force to the particles remains almost unchanged irrespective of the material.

## Introduction

The action of mechanical force on the powder particle during grinding or compressing often induces or enhances a solid state reaction, which is usually referred as a mechanochemical effects. However, the effect of the external force on the chemical properties or reactivities of powder has not yet been treated systematically nor quantitatively, except a few reports on this regard (DACHILLE and ROY 1960, 1961; NAESER and SCHOLZ 1962; SCHRADER and HOFFMAN 1966).

The polymorphic transformation process of the metastable phase of PbO, massicot, to the stable phase, litharge, in the isothermal wet ball mill was analyzed kinetically in the previous report by the present authors (SENNA and KUNO 1971). In these analyses, the process of transformation was compared with that of impact

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comminution (MATSUI 1966), and the effect of the mechanical force on the rate of reaction was discussed quantitatively. However, massicot never transforms to litharge only by heating, which makes the comparison between the rate of mechanochemical and thermal processes impossible. On the other hand, the rate of transformation was too fast when massicot was subjected to hot-pressing, which also is a drawback for the discussion on the effect of external forces.

The material treated in this report, maghemite ($\gamma$-$Fe_2O_3$) which is the metastable phase of $Fe_2O_3$, has an advantage over massicot since it transforms to the stable phase, haematite ($\alpha$-$Fe_2O_3$) with measurable rates irreversively by heating, hot-pressing, or isothermal wet ball-milling. Therefore, the effect of external force could be discussed quantitatively through kinetic treatment of the experimental results. Since the external force acts specifically on the material, the results were compared to those on PbO to understand the more general mechanism of the mechanochemical rate process.

## Experimental

### *Material:*

Maghemite was used as received from Toda Industrial Co., Ltd. (Commercial name, Memorix 400). A primary particle was rod-like in shape with 0.05−0.1 $\mu$m in diameter and 0.5−1 $\mu$m long.

### *Vacuum Hot-Pressing:*

Hot press was carried out in vacuum to avoid troublesome effects of water or any other vapors. About 0.40 g of $\gamma$-$Fe_2O_3$ (45/60 mesh fraction of aggregated particles) was filled into a cylindrical die cavity of $1cm^2$ in cross section and tableted under a relatively small pressure (about 200 $kg/cm^2$). The die, shown in Fig. 1, was placed between the aperture of two plates of 4 ton hand-press and heated externally to the predetermined temperature. A tablet of $\gamma$-$Fe_2O_3$ was put into the die cavity and evacuated to about $10^{-2}$ torr. When the temperature of the tablet was elevated to the predetermined value, the pressure ranging from 500 to 4000$kg/cm^2$ was applied. After pressing for desired time at constant pressure, the pressure was released and the sample was taken out of the die. Only the central part of the tablet was used for the X-ray analysis in order to avoid the effect of the die wall or of the pressure distribution in the tablet during pressing.

### *Isothermal Wet Ball-Milling:*

The apparatus for the isothermal ball-milling is the same as that used in the previous report (SENNA and KUNO 1971), except that the inner pot, 5.8cm I. D. and and 8.0cm long, was made of stainless steel and was charged with 1.5g of $\gamma$-$Fe_2O_3$,

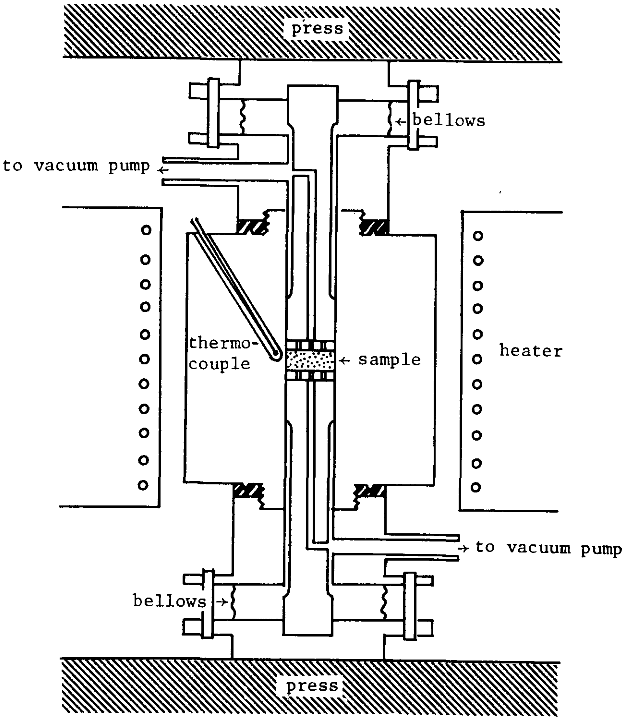

Fig. 1. Vacuum hot-pressing apparatus.

30ml of xylene as a medium liquid, as well as some milling balls of various number and sizes. The temperature of the inner pot and its contents was kept constant during whole milling process by circulating water at constant temperature into the annular space between outer and inner pots. The rate of rotation of the inner pot was fixed at 164 rpm. Three kinds of steel milling balls, S2 (0.67 cm in diameter), S3 (0.95 cm) and S4 (1.51cm) were used.

*Determination of Composition of Polymorphs:*

A composition of polymorphs or fractional conversion was determined by X-ray diffractometry, i.e., by comparing the intensity ratio of $\alpha$(111) to the sum of $\alpha$(111) and $\gamma$(220) with those of mixtures of known composition. Since substantial line broadening was observed on the milling product, as shown in Fig. 2D, the peak area measured with planimeter was used as the relative intensity. In other cases, line broadening was not significant, as shown in Fig. 2A, 2B and 2C, therefore the height of the diffraction peak was taken as the relative intensity.

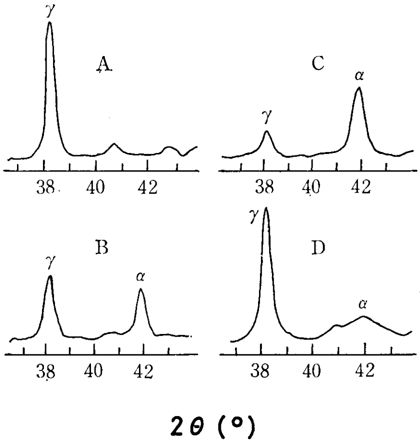

Fig. 2. X-ray diffraction profiles: A: $\gamma$-$Fe_2O_3$ (Memorix 400, as-received). B: 21.3% converted to $\alpha$-$Fe_2O_3$ after heating at 520°C for 20min in vacuum. C: 63.7% converted to $\alpha$-$Fe_2O_3$ after hot-pressing at 320°C, 2500kg/cm$^2$ for 30min in vacuum. D: 12.1% converted to $\alpha$-$Fe_2O_3$ after ball-milling at 73°C for 15h in xylene with 26 S4 balls.

## Results and Discussion

### *Vacuum Hot-Pressing:*

The relation between the fractional conversion, $a$, and the time, $t$, at constant pressure is given in Fig. 3. This relation is expressed with the following rate equation:

$$1-a=\exp[-kt]^{1/3} \qquad (1)$$

or taking logarithms,

$$\{\log(1/(1-a))\}^3=kt \qquad (2)$$

Equation (1) has the equivalent form as the Avrami's rate equation with its exponent, $n$, equal 1/3 (Avrami 1939, 1940, 1941). Although it is not clear whether the transformation takes place with a nucleation-growth mechanism, which is the theoretical basis of the Avrami's equation, eqn. (1) was applied empirically well to the present rate process. For instance, when $\{\log(1/1(1-a))\}^3$ is plotted against the reaction time, $t$, a series of straight lines through the origin were obtained, as shown in Fig. 4. The slope of these straight lines give the rate constant, $k$. An apparent activation energy for each applied pressure was obtained when log $k$ was plotted against $1/T$, as shown in Fig. 5. The value of the apparent activation energy thus obtained decreased nearly semi-exponentially with the applied external pressure as shown in Fig. 6.

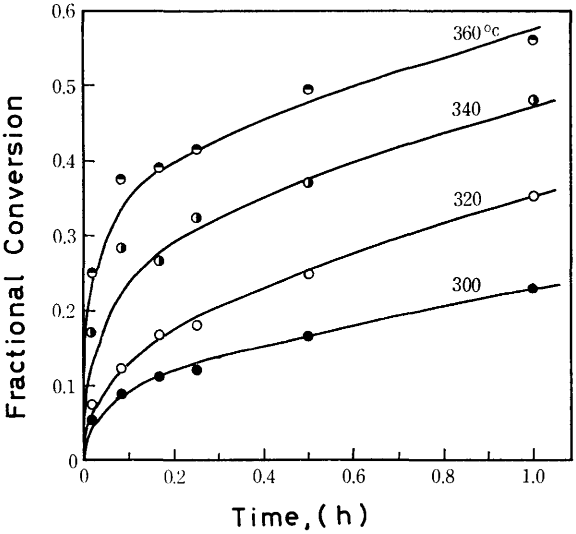

Fig. 3. Relation between fractional conversion by hot-pressing and time. Pressure: 1000kg/cm².

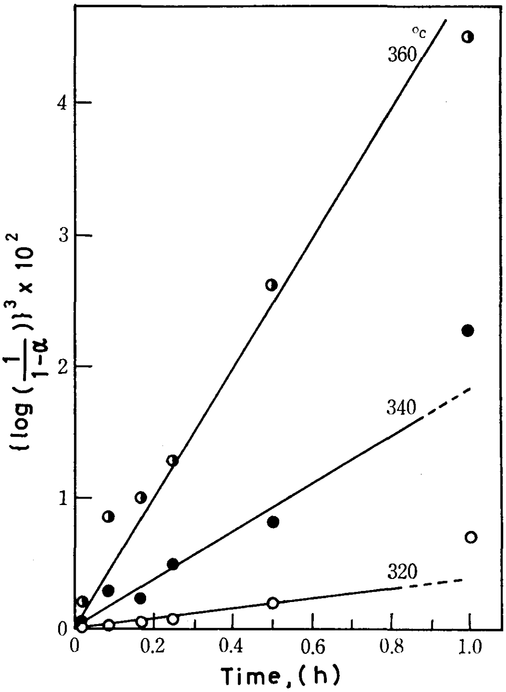

Fig. 4. Relation between $\{\log(1/(1-\alpha))\}^3$ and time. Pressure: 1000kg/cm².

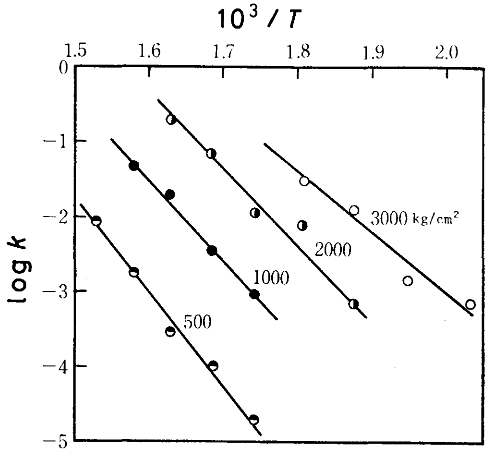

Fig. 5. Relation between log $k$ and $1/T$.

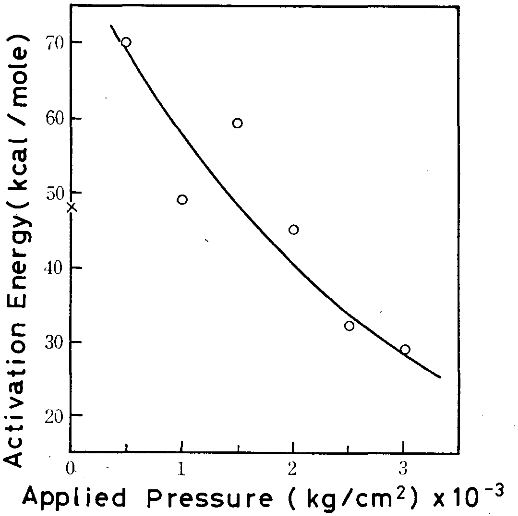

Fig. 6. Variation of apparent activation energy with applied pressure.

GOTO (1964) has reported that the rate process of the transformation of $\gamma$-$Fe_2O_3$ to $\alpha$-$Fe_2O_3$ by hot-pressing in air has an exponential form, and obtained the rate constant, $k$, for each applied pressure. He analyzed the results from the thermodynamic point of view with the aid of the semiempirical equation of VOLMER-WEBER ;

$$k=A\exp(-E_D/RT)\cdot\exp(-C/RT(\Delta F)^{-2}) \tag{3}$$

where, $E_D$ is the activation energy for diffusion, $C$, the function of interfacial energy stored at the interface between the precipitate and the matrix, and $\Delta F$, the free energy difference between two phases. By assuming $E_D$ and $C$ as independent of the temperature and pressure, GOTO obtained a linear relation between log $k$ and $(\Delta F)^{-2}$. However, it is doubtful whether the effect of mechanical compressive force could be treated thermodynamically, since the mechanical force is by no means hydrostatic but acts locally to the powder particles through their contact points. Furthermore, the effect of the mechanical force is still marked even when $\gamma$-$Fe_2O_3$ was heated after the application of some mechanical forces at room temperature (SENNA and KUNO 1972). For these reasons, we reanalyzed GOTO's data by applying eqn. (2). A series of straight lines through the origin were obtained like the present case, and the apparent activation energy was obtained for each applied pressure, as shown in Table 1. The effect of applied pressure on the apparent activation energy was similar to our case although the absolute value were somewhat different.

As shown by preceeding two examples, the rate process of the transformation of maghemite to haematite under mechanical pressure can be expressed by eqn. (1). Although the mechanism corresponding to the eqn. (1) is still open to the question, it can be stated at least, that the mechanism of the transformation is to be changed by applying the mechanical force, since, without external force, eqn. (4);

Table 1. Apparent activation energy, $\Delta E$ obtained by applying eqn. (2) to GOTO's data (1964).

| Applied pressure (kg/cm$^2$) | $\Delta E$ (kcal/mole) |
|---|---|
| 5000 | 52 |
| 13000 | 16 |
| 26000 | 13 |
| 33000 | 9 |

$$\{\log(1/(1-\alpha))\}^{1/2}=kt \tag{4}$$

instead of eqn. (2) was applied. Equation (4) has the form similar to the AVRAMI's equation with its exponent, $n$, equal 2. The apparent activation energy of transformation without external force, obtained from the rate constants in eqn. (4), for various temperature, is considerably small as shown with the mark 'X' in Fig. 6. But the absolute value itself cannot be compared directly with those with applied pressure since the mechanisms are different.

*Isothermal Ball-Milling:*

Maghemite also transformed partially to haematite by isothermal wet ball-milling

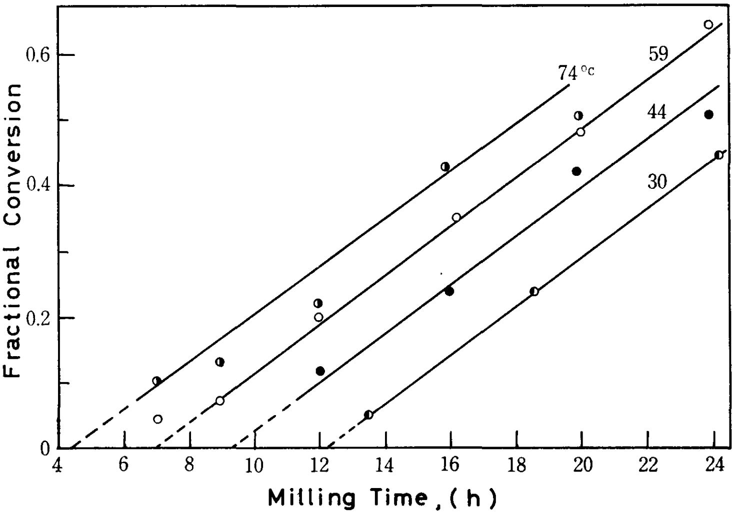

Fig. 7. Relation between fractional conversion and milling time. Ball: S2, $N$=300.

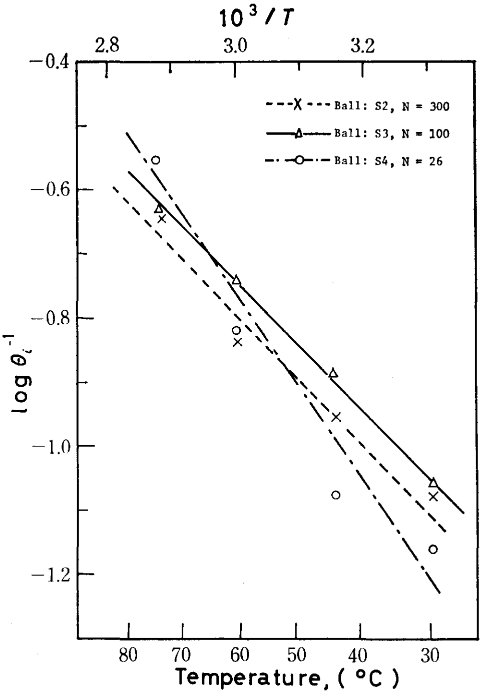

Fig. 8. Relation between $\log \theta_i^{-1}$ and $1/T$.

even at room temperature. However, for the process of the conversion by ball-milling, none of the equations of AVRAMI's type were applicable, as in the cases of the transformation of maghemite by hot-pressing ($n=1/3$), by simple heating ($n=2$), and of massicot by ball-milling ($n=1$). As shown in Fig. 7, the relation seemed to be zero-order with an induction period. The slope of the straight line, i.e., the zero-order rate constant shows no substantial change with temperature, indicating that the apparent activation energy of this zero-order process is nearly equal to zero. On the other hand, for the reciprocal of the induction period, $\theta_i^{-1}$, which could be interpreted as a kind of rate constant, Arrhenius plots resulted in a straight line for each milling condition, as shown in Fig. 8. The values of the activation energy thus obtained were 4.8, 4.8 and 7.5 kcal/mole for 300 S2, 100 S3, and 26 S4 balls, respectively. The data were not enough for the discussion on the effect of the number and the size of the milling balls on the activation energy, but these effects on the rate constants are similar to those on the transformation of massicot to litharge as decribed below. The reciprocal of the induction period divided by $N^{1.75}$, where $N$ is the number of milling balls, is considered to be a kind of rate constant independent of the number $N$. When logarithm $\theta_i^{-1}/N^{1.75}$ is plotted against log $V$, where $V$ is the volume of a single ball, a straight line was obtained for each temperature, as shown in Fig. 9. These lines had approximately equal slopes of 1.8. Thus the resulting relation between the rate constant independent of the number of balls, and the volume of the ball is expressed as:

$$\theta_i^{-1}/N^{1.75} \propto V^{1.8} \tag{5}$$

or,

$$\theta_i^{-1} \propto N^{1.75} \cdot V^{1.8} \tag{5a}$$

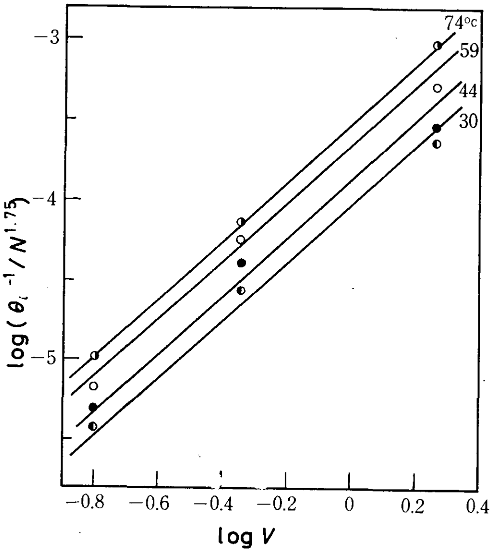

Fig. 9. Relation between log($\theta_i^{-1}/N^{1.75}$) and log $V$.

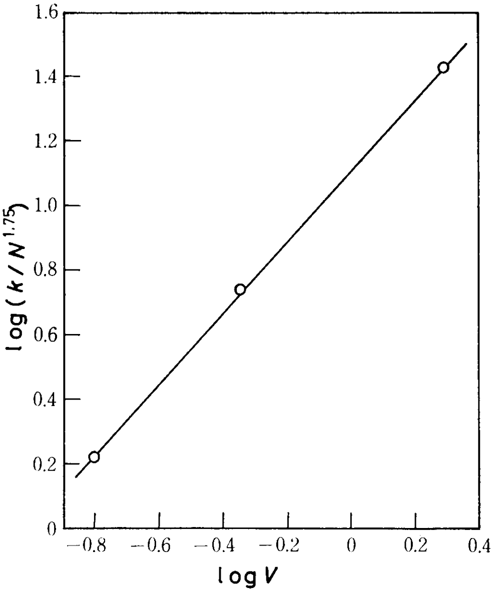

Fig. 10. Relation between $\log(k/N^{1.75})$ and $\log V$.

Equation (5a) can be compared with Matsui's equation relating the rate constant of surface area increase in impact comminution, $A_{r_1}$, and the number or the volume of the balls:

$$A_{r_1} \propto N^{1.75} \tag{6}$$

and

$$A_{r_1} \propto V^{1.58} \tag{7}$$

Furthermore, the logarithms of zero-order rate constant $k$ (average value for each temperature) divided by $N^{1.75}$ varied with $\log V$ linearly with its slope equal to about 1.1 as shown in Fig. 10. Thus the relation between $k$, $N$ and $V$ can be expressed as:

$$k \propto N^{1.75} \cdot V^{1.1} \tag{8}$$

which also can be compared with equns. (6) and (7).

Equations (5a) and (8) are similar to those obtained in the transformation of massicot to litharge by isothermal ball-milling (SENNA and KUNO 1971). This fact suggests that the mechanism of transmission of the external force to the particles remains almost unchanged irrespective of the material.

### *Comparison of the Effect of External Force on the Rate of Transformation of* PbO *and* $Fe_2O_3$:

The effects of external force on the transformation of PbO and $Fe_2O_3$ are compared and illustrated in Fig. 11.

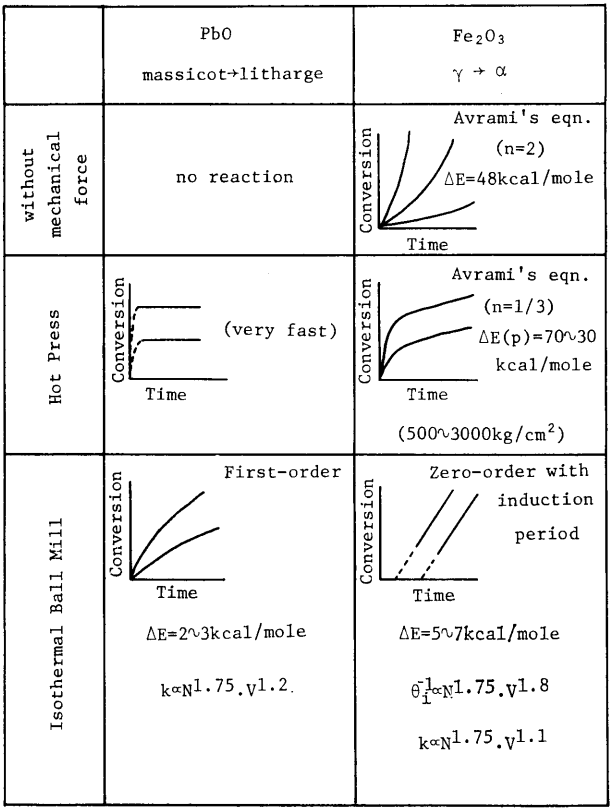

Fig. 11. Comparison of the effects of applied mechanical force on the rate of transformation of PbO and $Fe_2O_3$.

Only by heating, massicot phase of PbO never transforms to litharge phase, although with the aid of mechanical force, transformation starts rather easily and proceeds quite rapidly as stated in the previous report. Therefore, mechanical force seems indispensable for massicot—litharge transformation. On the other hand, $\gamma$-$Fe_2O_3$ does transform by simple heating. But the application of mechanical force to $\gamma$-$Fe_2O_3$ results in the change in the mechanism of the transformation accompanied with the decrease in the apparent activation energy with increasing external pressure as shown above.

The above-mentioned difference in the effects of mechanical force on the transformation kinetics could be explained, if it is assumed that the mechanical force on massicot acts anisotropically and causes the breakage of the specific bondings, while on $\gamma$-$Fe_2O_3$ it enhances the formation of crystal defects or lattice distortion. These ideas do not seem unrealistic taking the crystal structure and the mechanism of the transformation of the ordinary thermal process into consideration. Massicot, having apparent layer structure parallel to (001) plane of its orthorhombic lattice, is said to transform with short range diffusion of oxygen atom with lead atom substantially fixed (SOEDERQUIST and DICKENS 1967), while $\gamma$-$Fe_2O_3$, having a spinel structure with considerable vacancy in $B$ sites, requires the restacking of the oxygen layer with simultaneous diffusion of ferric ions between oxygen layers for the transformation to $\alpha$-$Fe_2O_3$ (KACHI et al 1963).

The difference in the ways of the application of the external force has also important effects on the kinetics of the transformation. By pressing in the die with constant pressure, the external force is applied to the most of the particles simultaneously through their contact points. While by ball-milling, only a small fraction of particles was subjected to the mechanical stimulus at one time, and both the number of the particles receiving the stimulus and the number of stimuli received by the single particle increase with milling time. These differences well explain the difference in the kinetic behavior of transformation of PbO and $\gamma$-$Fe_2O_3$ between hot-pressing and ball-milling processes. Furthermore, first-order rate process of PbO by ball-milling is explained by assuming that a single particle of massicot transforms to litharge only by one hit of the ball. On the other hand, if the accumulation of the crystal defects or distortion, to some extent, is necessary for the transformation of $\gamma$-$Fe_2O_3$, the reason of the existence of the induction period could be interpreted.

## Conclusions

Polymorphic transformation of $\gamma$-$Fe_2O_3$ to $\alpha$-$Fe_2O_3$ with applied external mechanical force was carried out either by vacuum hot-pressing or isothermal ball-milling and the rate constants and apparent activation energies were obtained through usual kinetic analyses.

The rate equation of the type similar to that of AVRAMI with its exponent, $n$, equal 1/3 was applied to the transformation process by hot-pressing, while AVRAMI-type equation with $n$ equal 2 was applied to the transformation without external force. Therefore, the application of external force should alter the mechanism of the transformation. The apparent activation energy in hot-pressing decreased nearly semi-exponentially with increasing applied external pressure, suggesting that mechanical force elevates the potnetial energy of the reactant particles by enchancing strains or defects in the reactant crystals.

By isothermal ball-milling, the transformation of maghemite to haematite also occured even at room temperature, and its process was expressed with another rate equation, i.e., zero-order with considerable induction periods. The reciprocal of the induction period was interpreted as a kind of rate constant from which the apparent activation energy was obtained.

Comparison of the results to those on the mechanochemical transformation of PbO, reported previously by the present authors, reveals that mechanical force acts at least with two different ways on the polymorphic transformation processes depending on the nature of the material, although the mechaism of transmission of the external force to the particles remains almost unchanged irrespective of the material.

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