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Mechanochemical Reactions at High Pressures. IV. Transformation of Lead Monoxide

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Synopsis. The mechanochemical phase transformation of lead monoxide has been studied by the X-ray diffraction method. It is established that the transformation of lead monoxide proceeds by a stress-induced martensitic mechanism.

Lead monoxide exists in two familiar forms: litharge (L, a red tetragonal form) and massicot (M, a yellow orthorhombic form). Most of the studies of phase transformations in PbO have involved milling, comminution, and abrasion. High pressure studies have not been carried out except for an experiment to determine the equilibrium pressure-temperature relation for the L⇄M reaction by White *et al.*[1] These authors reported that L could be converted into M either by raising the temperature above 540 °C or the pressure above 6000 atm, although the reaction was slow at low temperature. Furthermore, they suggested that purely hydrostatic pressure causes the L→M transformation, whereas bond breakage at low pressure gives the M→L transformation.

In the present work, we investigated the L⇄M transformation at room temperature under high pressure with simultaneous shear deformation.

Experimental

The experimental high pressure apparatus combined with simultaneous shear deformation (HP+SSD) consists of Bridgman's type anvils. Details of the apparatus and procedure have been described previously.[2] All experiments were carried out up to 20 kbar (1 kbar = 10^8 Pa) at room temperature. In these experiments, the reactions proceeded at a constant shearing velocity of 2.51 rad h^{-1} (2.4° min^{-1}).

As specimens of lead monoxide, the litharge starting material was kindly supplied from Dai Nippon Toryo Co. Ltd. and the massicot was the commercial reagent. The specimens were sieved to 100 mesh and molded in 12-mm diameter pellets. The sample tablet was placed in the HP+SSD apparatus, and the experiment was carried out at the desired pressure. The volume fraction increment of L(or M), after M(or L) was sheared under high pressure, was determined by X-ray diffraction analysis. The lines chosen for comparison were, for M, $2\theta = 37.82°$ for the (020) plane and a relative intensity of 20, and for L, $2\theta = 35.74°$ for the (002) plane and a relative intensity of 18.[3] According to Lins' report,[4] the relation between the volume fraction of massicot, C_M, and that of litharge, C_L is given by:

$$C_M/C_L = 2(I_M/I_L)\,,$$

where I_M and I_L are the intensity of a chosen diffraction line for M and L, respectively.

Results and Discussion

Figures 1 and 2 show the relations between the static pressure and the shear stress for M and L, respectively. In Fig. 1, the curve exhibits a characteristic change at about 2 kbar, which corresponds to the M→L phase-transition. In Fig. 2, the characteristic variation at about 2 kbar and a slight variation at about 5 kbar were observed. These facts suggest that a large transition energy is required for L in comparison with M→L transformation because M is more stable than L at high pressures. Therefore, the energy required for L→M transformation will be accumulated over the range from 2 to 5 kbar of static pressure. This consideration is supported by the conversion curve of L as shown in Fig. 3. Consequently, the apparent transformation pressure of lead monoxide exsists in the vicinity of 2 kbar, and is smaller than the 5.6 kbar, obtained by extrapolation of the pressure-temperature phase diagram.[1] In conclusion, the forced shear deformation is responsible for the decrease in the transition pressure of lead monoxide.

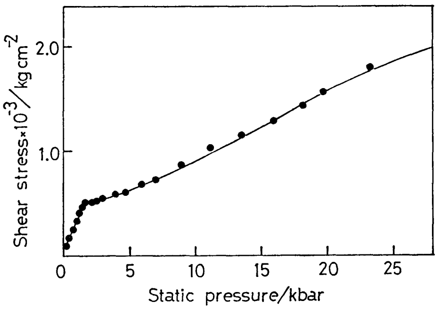

Fig. 1. Relation between the static pressure and the shear stress for massicot.

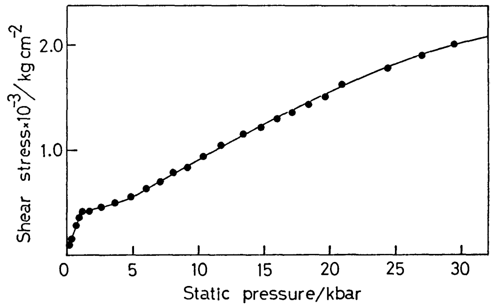

Fig. 2. Relation between the static pressure and the shear stress for litharge.

The effects of the static pressure on the conversion and the shearing degree for L→M, and M→L transformations are shown in Figs. 3 and 4, respectively. As shown in Fig. 3, the L→M transformation curves possess the following features:

(1) At 5 kbar, L was not converted into M in most experiments. These results are correlated with those in Fig. 2.

(2) The percent of M formed did not decrease

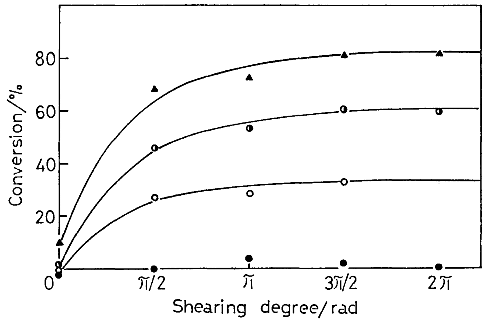

Fig. 3. Relation between conversion and the shearing degree at various static pressures for the litharge to massicot transformation.
● 5 kbar; ○ 10 kbar; ◑ 15 kbar; ▲ 20 kbar.

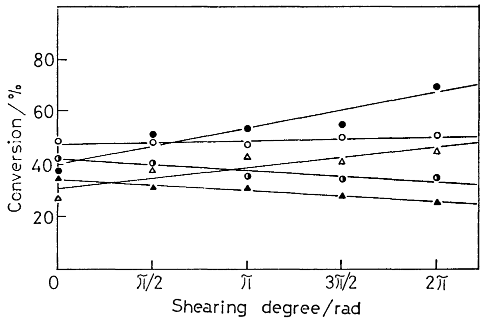

Fig. 4. Relation between conversion and the shearing degree at various static pressures for the massicot to litharge transformation.
△ 2 kbar; ● 5 kbar; ○ 10 kbar; ◑ 15 kbar; ▲ 20 kbar.

with the shearing degree, as was found for the M→L transformation in Fig. 4, but it tended to approach an equilibrium value similar to the value in the literature.[5] Judging from Fig. 3, L will be completely converted into M at about 30 kbar static pressure under our experimental conditions.

(3) The higher the static pressure, the more the transformation proceeds.

(4) The curves all have a parabolic shape.

The M→L transformation in Fig. 4 is characterized as follows:

(1) All relations are linear.

(2) At all static pressures, M is considerably transformed to L even without the forced shear deformation. It can be assumed that the energy required for the M→L transformation is less than that for the L→M transformation because L has a lower potential energy than M.[6]

(3) The conversion of M→L becomes small with the increase the static pressure as a general tendency. Furthermore, the conversion tends to decrease as the shearing proceeds at 15 and 20 kbar static pressure. This fact suggest a transformation back to M. Thus, it can be assumed that the transformation of M to L is an equilibrium reaction, if the transformation can be called the reaction. Judging from Fig. 4, the equilibrium shifts to M with increasing pressure. This consideration agrees with the Le Chatelier principle since M is a high-pressure modification.

The following two mechanisms can be proposed for the transformation of lead monoxide. The one is a nucleation and growth mechanism and the other is a stress-induced martensitic type transformation. When the experimental results fit Avrami equation, the transformation must proceed by a nucleation and growth mechanism.[5] Our experimental data did not fit the Avrami plot, therefore, the transformation of lead monoxide is a martensitic type transformation induced by the strong shear force. This conclusion is consistent with the result for M→L transformation during comminution.[4]

We also carried out some experiments on the transformation of calcium carbonate. The phase diagram of $CaCO_3$ has been studied since Bridgman's work in 1939, but regardless of many studies it is still not completely determined. Burns and Bredig[8] have found calite to be transformed to aragonite by grinding at room temperature, and estimated the pressure necessary for the transformation of calcite to arragonite at 4600 kg cm^{-2}. Ahrens and Katz[9] reported that the transformation of calcite occurs at pressures above 5 kbar. However, our X-ray examination revealed that calcite was not transformed into aragonite under 2π rad shearing at 15 kbar static pressure.

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