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LIBERATION OF EXCESS ENERGY AND RETRANSFORMATION OF MECHANICALLY ACTIVATED CADMIUM SULPHIDE

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ABSTRACT

On heating vibro-milled CdS containing the strained high-pressure rock salt phase, the excess energy was gradually liberated accompanied by the retransformation into more stable phases and the restoration of their crystallinity. Profiles of DSC curves, inter-relationships between thermal and crystallographical properties, the stability of each phase and the mechanism of the mechanochemical activation are discussed. A direct retransformation of the strained high-pressure phase was found to accompany the liberation of the excess energy.

INTRODUCTION

By vibro-milling the stable phase of CdS (wurtzite) in air or in cyclohexane, distorted metastable phases, particularly the rock salt phase, appear, accompanied by an increase in enthalphy [1,2]. With increasing atomic mobility during subsequent heating, a "quenched" metastable state is released. It is important to examine the process of energy release, not only to elucidate the mechanism of the mechanochemical activation but also for the development of mechanochemical technology. The purpose of the present study was to scrutinize the above-mentioned processes during annealing by examining changes in the differential scanning calorimetry (DSC) curves and the phase compositions at various stages of the annealing process.

EXPERIMENTAL

Cadmium sulphide was prepared by two different methods. CdS-A was precipitated by bubbling gaseous H_2S into 40 wt.% $CdCl_2$ solution in 3 mole dm^{-3} HCl. The sample was tempered in N_2 at 823 K for 2 h. CdS-B was

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prepared from 10 wt.% $CdSO_4$ in 6 mole dm^{-3} H_2SO_4 and H_2S. The latter was tempered in N_2 at 873 K for 24 h. Unless otherwise stated, the starting material was always CdS-A.

Samples were ground in cyclohexane with a laboratory vibro-mill. The detailed method of grinding is described elsewhere [1]. Differential scanning calorimetry was carried out using high-temperature DSC (Rigaku, Thermoflex). The sample was heated in N_2 at a constant heating rate of 10 K min^{-1}. Because of the superimposition of X-ray diffraction peaks from different phases, quantitative phase analysis of the ground and annealed samples was not simple. The method has been reported elsewhere [3].

RESULTS AND DISCUSSION

DSC curves

When the ground CdS was heated linearly in N_2 in the DSC furnace, a broad exothermic peak was always observed, as shown in Fig. 1. From the DSC curves the amount of energy liberated during heating was obtained. The profile of the exothermic peak reflects, furthermore, the distribution of the excess energy stored during the previous grinding. Clarebrough et al. [4] have shown from DSC curves of deformed aluminium that plateau-like exothermic peaks at lower temperatures correspond to recovery, whereas sharper exothermic peaks at higher temperatures correspond to recrystallization.

From Fig. 1 it can be seen that the temperature range of the energy distribution is almost independent of the milling time, since all exothermic peaks except that for the very short period began at ca. 373 K and ended at

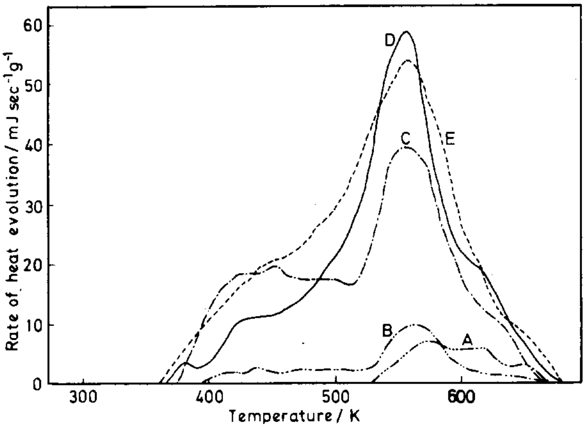

Fig. 1. DSC curves of CdS ground for A, 0.5 h; B, 1 h; C, 3 h; D, 6 h; and E, 9 h.

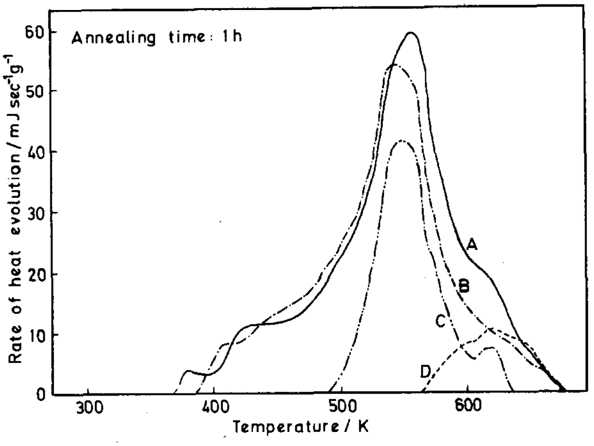

Fig. 2. DSC curves of ground and annealed CdS. Grinding time 6 h; annealing time, 1 h. A, As-ground; B, annealed at 373 K; C, 473 K; and D, 573 K.

ca. 673 K. The main peak at 553 K became higher with milling time, but a shift of the peak temperature was not observed. This suggests that with increasing milling time the extent of the crystallographic imperfection simply increases, without changing its nature.

If the ground sample is annealed, however, not only the peak area, i.e. the amount of heat liberated, but also the temperature range of energy evolution is changed, as shown in Fig. 2. A similar tendency has been observed for ground γ-Fe_2O_3 [5]. This indicates that the degree of activation may be different, even when the overall excess enthalpy is the same. If, for instance, nucleation is the rate determining step, a highly disturbed region with a high energy concentration may be indispensable for the nucleation. The same total excess energy may not promote nucleation if only less disturbed regions exist in larger quantity. A suitable example was found in comparing the excess enthalpies of CdS ground in cyclohexane to that in air [2].

Phase change

For the purpose of closer examination of the energy liberation process, DSC measurements were interrupted at various temperatures and quenched samples were analyzed with an X-ray diffractometer. As shown in Fig. 3, CdS ground for 6 h has the phase composition 34% wurtzite, 30% zinc blende and 36% rock salt phase. During annealing, the rock salt phase decreased at first, and disappeared at 573 K, followed by a monotonical decrease, and vanished at 673 K. The stable wurtzite phase, on the other hand, increased constantly and the sample was almost single phase wurtzite at 673 K.

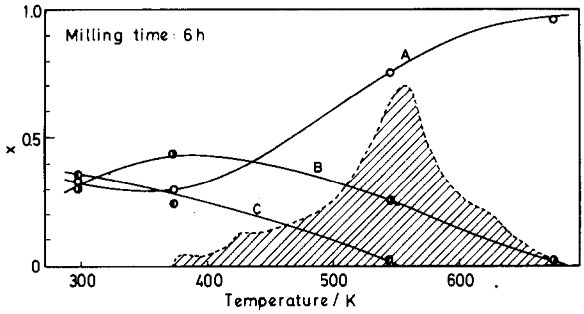

Fig. 3. Variations of phase composition with temperature during DSC analysis. A, Wurtzite; B, zinc blende; and C, rock salt. Hatched area denotes the corresponding DSC profile (cf. Fig. 1).

As a measure of the recovery and recrystallization, the change in the net half-breadth, β, of the representative X-ray diffraction peak of each phase is given in Fig. 4. Little change in β for each phase was found until immediately before the peak temperature of energy liberation.

Contents of excess energy

From the foregoing discussion, it can be concluded that the largest fraction of excess enthalpy is held within the distorted rock salt phase. The restoration of the rock salt phase does not occur separately from the retransformation. This would indicate that the nuclei of the more stable phase are formed directly from the highly distorted rock salt phase. This is possible because the necessary atom transport distances for the retransformation are smaller than or similar to those for the recovery and recrystallization. This is also the case for the transformation of distorted γ-Fe_2O_3 to α-Fe_2O_3 [5].

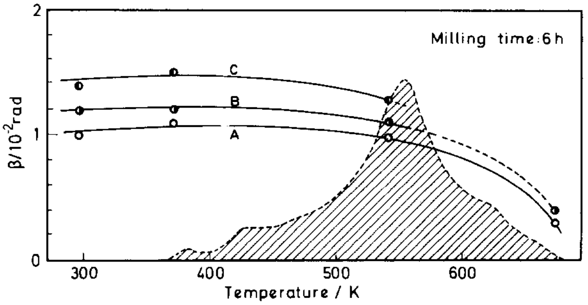

Fig. 4. Variations of X-ray net half-breadth with temperature during DSC analysis. A, Wurtzite (100); B, zinc blende (111); and C, rock salt (200). Hatched area denotes the corresponding DSC profile (cf. Fig. 1).

Energy liberation at temperatures higher than 573 K, where no rock salt phase was found, would seem to be associated with the recovery of zinc blende and wurtzite and the retransformation of zinc blende to wurtzite. However, for CdS-B, where no excess enthalpy was observed even after extensive grinding, the extent of the line broadening of the wurtzite and zinc blende phases was similar. Therefore the contribution of zinc blende and wurtzite does not seem very significant. On the other hand, it is not correct to assume that the whole exothermic process at temperatures higher than 573 K is due to retarded heat evolution caused by the strained rock salt phase. Even when the sample was annealed at 573 K for 1 h, ca. 11% excess enthalpy was observed, in spite of the absence of the rock salt phase (cf. Fig. 2). Because of Cl^- ion contamination in CdS-A, the rock salt phase is capable of absorbing a large amount of strain without losing its phase identity [1], resulting in the enthalpy increase. Since Cl^- is effective for the retardation of the retransformation by forming complexes with the cadmium ions [6], it is possible that the other phases, particularly the strained zinc blende phase of CdS-A, carries a part of its excess enthalpy in contrast to CdS-B.

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