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THERMAL EFFECTS INDUCED BY IMPERFECTIONS IN POWDERED SOLIDS

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ABSTRACT

The effects induced in the thermal behaviour of solids by alterations to their crystallinity are discussed. The thermal behaviour of different alkaline earth metal carbonates changes considerably after mechanical treatment of the samples. Release of the energy stored as imperfections in the ground solids takes place at fixed temperature intervals for dolomite and the polymorphs of calcite. On the other hand, the defects present in iron oxides and oxyhydroxides condition their thermal behaviour. In several instances, crystallinity is recovered with an appreciable release of energy, as in ex-akaganeite haematite.

INTRODUCTION

The imperfections present in the crystalline state have major effects on the thermal behaviour of solid samples. These effects include changes in the kinetic parameters of chemical reactions in which the solid is involved, such as thermal decompositions or phase transitions, and/or the development of new effects of heat release during the thermal treatment of the samples.

In connection with the latter point, it is well known that lattice defects are a common way of storing energy in metals [1,2] and other solids [3,4]. The determination of average structural parameters such as the size of the coherently diffracting domains or microstrain content [5] may be used to quantify the level of imperfections in high volumes of powdered samples. These parameters may be correlated with the values of stored energy under certain conditions [6,7]. Additionally, experimental determination of the energy stored as defects may be carried out by measuring the difference between the power required to heat deformed and undeformed samples [1] or the difference between their heats of reaction [4].

An alternative procedure for quantifying a process of release of stored energy may also be used with those samples in which the content of

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imperfections is high and they are released in a sufficiently short temperature interval to be detected by conventional DTA or DSC techniques. This procedure requires prior interpretation of the thermal effects and the study of the thermal evolution of the above-mentioned structural parameters. Thus, a precise knowledge that no chemical change is involved is necessary. Similarly, the possibility that a surface recordering process, related to a marked decrease in specific surface area or a change in the pore texture, may be responsible for the liberation of energy [8,9] should be considered.

ALKALINE EARTH METAL CARBONATES

Alkaline earth metal carbonates show good examples of the above characteristics of energy storage in samples submitted to mechanical treatment such as grinding or pressure procedures. Several thermal effects originate from grinding in dolomite [10–12]. The DSC curves of ground samples show an exothermic peak placed at ca. 300°C (Fig. 1a). This effect cannot be ascribed to a surface reordering as evidenced by textural determinations. Instead, a partial restoration of crystallinity takes place [12]. A kinetic

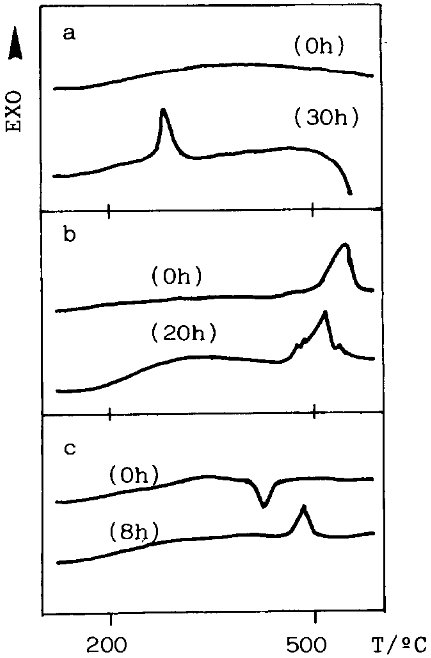

Fig. 1. DTA and DSC traces of alkaline earth metal carbonates: (a) dolomite; (b) vaterite; and (c) aragonite. The time of prior mechanical treatment is shown in parentheses. The ordinate is in arbitrary units.

analysis of this process showed that its activation energy takes low values (ca. 20 kcal mol^{-1}) indicating, according to the criteria of Gross [4], that the process is a recovery of crystallinity instead of a recrystallization phenomenon. On the other hand, the grinding process leads to an unusual decomposition behaviour of dolomite [10]. A first endothermic effect attributed to the decomposition of the $MgCO_3$ component becomes broadened and appears at lower temperatures. The curves for ground samples approach those found for iron-bearing dolomite [13].

The effect of grinding on the shape of the DSC curves of synthetic vaterite, the least dense polymorph of $CaCO_3$, is also significant (see Fig. 1b) [14]. For ground samples, the exothermic effect at the temperature of vaterite–calcite transformation becomes more complex. The heat evolved in the complete process remains almost unaltered, although a partial mechanochemical transformation of vaterite into calcite takes place. This fact has been interpreted in terms of a recovery of crystallinity of both phases, on the basis of X-ray line broadening analysis. Deformed samples also suffer an alteration in the kinetics of the thermal phase transition [15].

Grinding of aragonite, another metastable phase of $CaCO_3$, dramatically changes the shape of its DTA curve (Fig. 1c). Whereas for an unground sample a small endothermic peak is developed at 420 °C, owing to its transformation into calcite, the endotherm does not appear for a sample ground for 8 h [9], although its composition remains almost unaltered. Instead, an exothermic peak at ca. 480 °C is observed. An explanation based on surface reordering may be consistent with the experimental data.

IRON OXIDES AND OXYHYDROXIDES

The different phases of iron oxyhydroxide and their decomposition products provide new proof of the relationships between crystallinity and thermal behaviour. It is well known that the dehydration of goethite (α-FeOOH) leads to haematite. According to Mackenzie and Beggren [16], well crystallized samples of this mineral give a single large endothermic peak. Other workers [17,18] have found that pure goethites show a pronounced double peak in the DTA traces throughout their dehydroxylation to haematite. This alteration has been related to the degree of crystallinity of the samples.

The recovery of crystallinity in haematite is also reflected in energy-release processes, such as the exotherm found in the DTA and DSC curves of synthetic akaganeite (β-FeOOH) in air, N_2 and O_2 atmospheres (Fig. 2a) [19]. The determination of crystallite size and strain content in several crystallographic directions, assessed by the observation of a drastic change in particle morphology throughout the exotherm, are in agreement with this interpretation. On the other hand, the thermal decomposition of akaganeite in vacuo leads to a poorly crystallized product, structurally related to

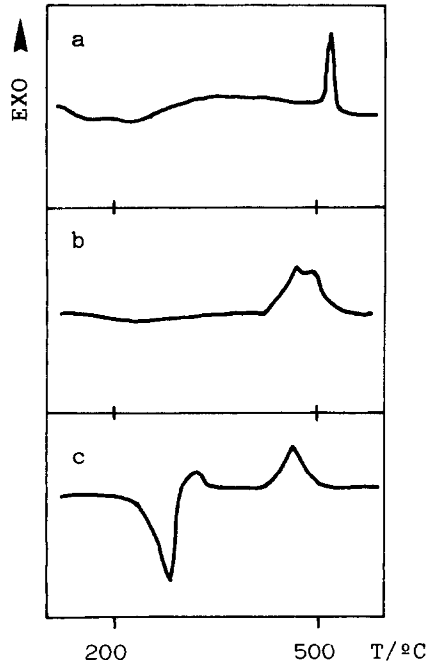

Fig. 2. DSC diagrams for iron compounds: (a) akaganeite; (b) the product of the thermal decomposition of akaganeite in vacuo at 350°C; and (c) lepidocrocite. The ordinate is in arbitrary units.

γ-Fe_2O_3, whose thermal evolution also implies a recovery of crystallinity besides its conversion into haematite. These changes are reflected in a complex exothermic effect in its DSC diagrams (Fig. 2b) [20].

The DTA curves of natural and synthetic lepidocrocite (γ-FeOOH) show essentially two thermal effects: endothermic dehydration to γ-Fe_2O_3 and exothermic transformation of this phase into haematite. A new, low-area exotherm has been found in the DSC traces of this solid (Fig. 2c) and a surface reordering process seems to be responsible for the released heat [21]. A more direct influence of crystallinity seems to be present in the thermal behaviour of γ-Fe_2O_3 samples derived from the mechanochemical dehydration of lepidocrocite in cyclohexane medium [22]. Thus, a greater thermal stability, shown by the temperature of conversion into haematite, is evident for mechanically produced samples. This result is probably related to the lower broadening of the maghaemite reflections in these samples, as compared with the product of the thermal dehydroxylation.

Finally, the thermal dehydration of δ-FeOOH leads to haematite, which has been found to have a high content of imperfections, reflected in line broadening and alteration of the intensity ratios in the powder X-ray diffractograms [23]. However, no quantitative evaluation of the changes in structural parameters or the energy liberated during the thermal treatment of these samples has been carried out.

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