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PHASE TRANSFORMATIONS AND THERMAL RECRYSTALLIZATION OF HYDRATED COBALT MOLYBDATE

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The thermal evolution of a very fine-grained hydrated cobalt molybdate, $CoMoO_4 \cdot 0.9H_2O$, has been studied by dilatometry, DTA, X-ray crystallography and scanning electron microscopy. Four principal stages have been detected between 25 and 1000°: dehydration, polymorphism (or precipitation), recrystallization, and high-temperature phase change. Such phenomena also occurred with some other hydrated molybdates (Ni, Mn).

This work is part of a general series of experiments dealing with the dilatometric behaviour of hydrated inorganic compounds.

The experiments were carried out with a hydrated cobalt molybdate, $CoMoO_4 \cdot 0.9H_2O$, obtained by adding (at boiling temperature) a cobalt nitrate aqueous solution to molybdenum trioxide dissolved in ammonia, at $pH \leq 6$ [1]. The fine-grained powder obtained after washing and drying the precipitate is purple coloured. Its thermal behaviour in air was studied by four experimental techniques: dilatometry (Chevenard apparatus) [2], DTA. Apparatus constructed in this Laboratory and already described. This apparatus was designed for working in sealed tubes under vacuum. In the experiments described here the tubes were not sealed [3], X-ray crystallography (Guinier diagrams), and scanning electron microscopy (MEB Cameca).

The following results were obtained:

1) The thermal expansion curve of compacts (Fig. 1a) exhibits three phenomena:

a) a slight contraction AB between 25° and 310°;

b) a rapid and large contraction BC between 320 and 340 ($\Delta L/L \sim 3\%$);

c) a slow contraction which becomes more and more important with the increase of the temperature ($\Delta L/L > 30\%$ at 700°).

2) The phenomenon b) appears in the DTA curve as a small, sharp exotherm immediately followed by a large, sharp endotherm (Fig. 1b). The X-ray diagrams of the products A and B (after cooling) are not very different, in good agreement with the fact that no important structural change takes place during dehydration [1]. The X-ray diagram of the cooled product C is quite different from that

of cooled *B*. This observation let us to suppose that the DTA peak and the contraction *BC* can be assigned to a polymorphic transformation (or perhaps to a "precipitation process" phenomenon, which is often the final step of a dehydration reaction [4]).

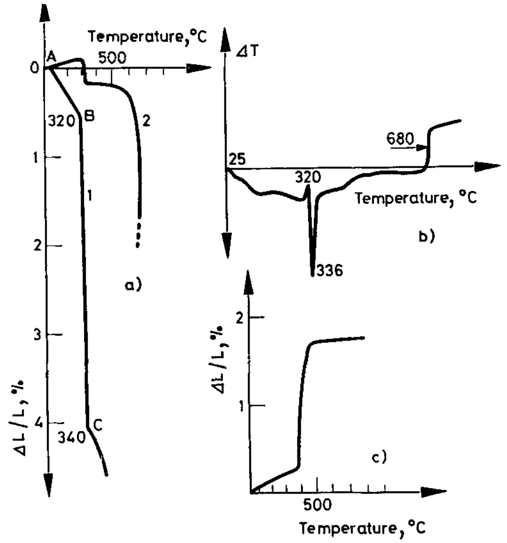

Fig. 1: a) Thermal expansion curves of $CoMoO_4 \cdot 0.9H_2O$ compacts (compacting pressure: 1000 bar) 65 mm in length (curve 1) and 5 mm in length with an alumina coin 60 mm in length (curve 2). Heating rate: 300°/hour. In curve 2 the thermal expansion between 25 and 320° is the sum of the thermal expansion of the 60 mm alumina coin and the contraction of the 5 mm molybdate sample. This sum is positive owing to the great length of the alumina coin and the small length of the molybdate sample.

b) DTA curve in air of 150 mg of $CoMoO_4 \cdot 0.9H_2O$ powder. Heating rate: 300°/hour.

c) Thermal expansion curve of a mixture of $CoMoO_4 \cdot 0.9H_2O$ (heated to 850 or 1000° and cooled) and zirconia powder: weight percentage of molybdate in the mixture: 10%; compacting pressure: 3400 bar; heating rate: 300°/hour

3) When the temperature of the thermal treatment reaches 650–700°, the morphology and the texture of the compacts (which have not changed during the transformation *BC* (Fig. 2), are greatly affected: large crystals emerge from the powder (Fig. 3), the grain size of which has grown (Fig. 4)). The X-ray diagram of the cooled product is characteristic of a well-crystallized solid (this was not the case with a thermal treatment limited to 300 or 340°). This recrystallization process can explain the decrease of some adsorption properties [5].

4) After heating at 850 or 1000° and subsequent cooling, the fine-grained texture of the powder has entirely disappeared: only very large crystals with many "cracks" can be observed (Fig. 5). These cracks are certainly due to the reversibility, on cooling, of the (b)–(a) polymorphism of anhydrous cobalt molybdate [6].

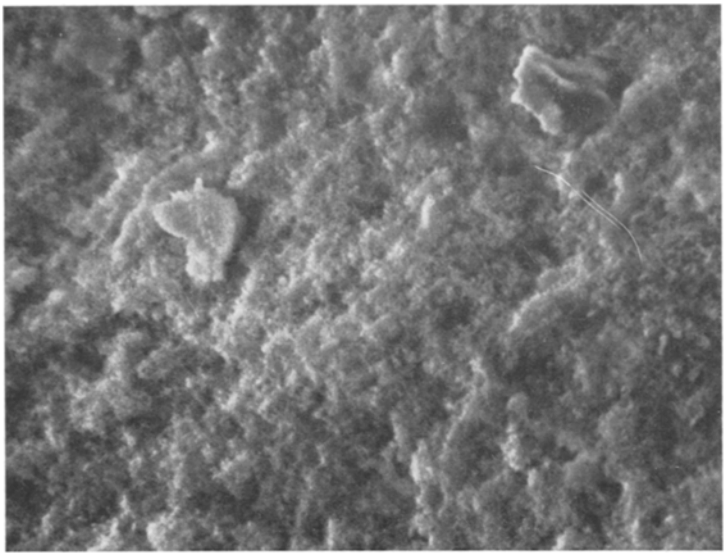

Fig. 2: Scanning electron microscopy photograph of hydrated cobalt molybdate compacts heated before point B (310°) or after point C (360°) and cooled at 25° (×3000)

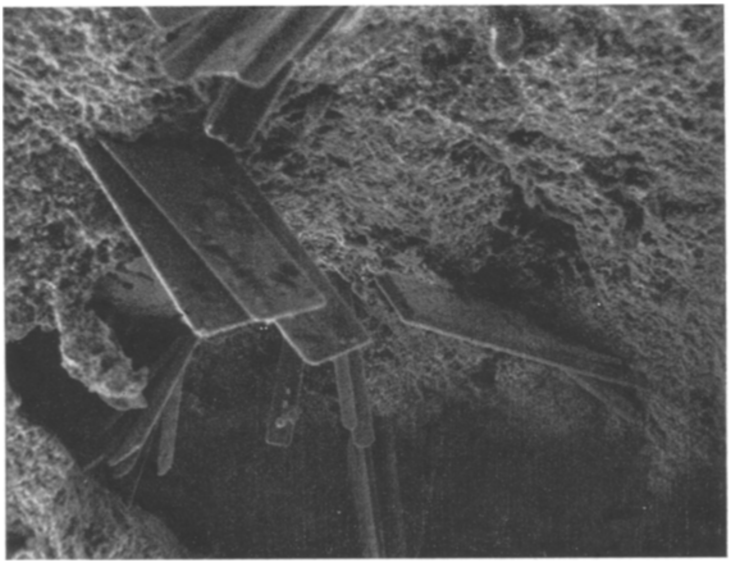

Fig. 3. Scanning electron microscopy photography of hydrated cobalt molybdate compacts heated to 680° and cooled at 25° (×800)

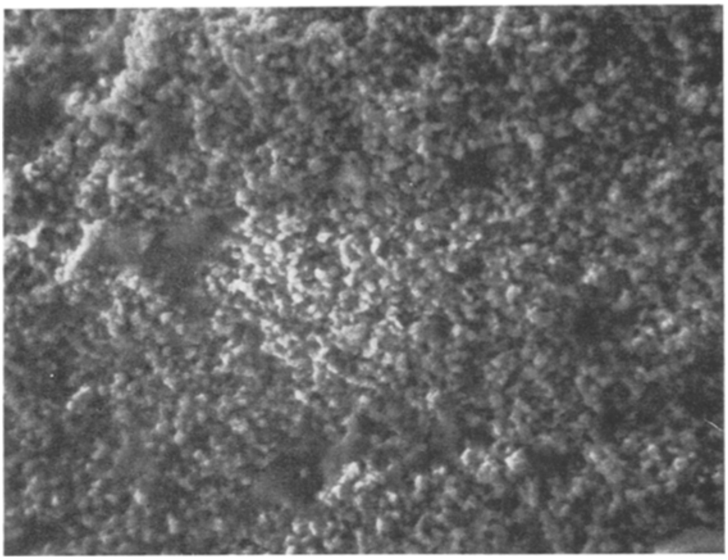

Fig. 4. Scanning electron microscopy of hydrated cobalt molybdate compacts heated to 680° and cooled at 25° (×3000)

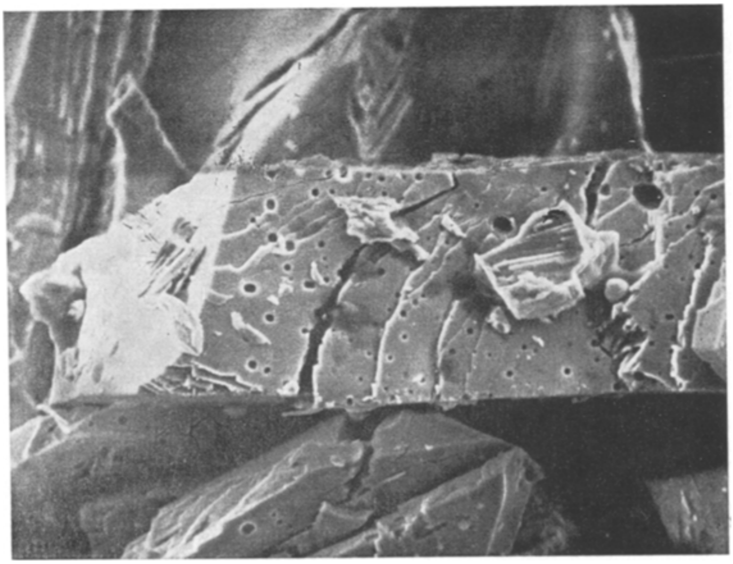

Fig. 5. Scanning electron microscopy photograph of hydrated cobalt molybdate heated to 1000° and cooled at 25° (×1800)

This reversibility entirely destroys the compact texture of the sample, which loses its mechanical strength. Such observations led us to believe that, during the first heating at high temperature, the molybdate is transformed into the anhydrous modification (a). If the product is compacted again, after cooling, in a ZrO_2 matrix* the (b) – (a) transformation appears in the dilatometric curve (Fig. 1c) at about 400° (expansion).**

A study of the phase change with a high-temperature X-ray camera is necessary to obtain more information on what happens between 650 and 1000° (explanation of the discontinuity observed on the DTA curve at about 680° (Fig. 1b).

These results do not seem specific for cobalt molybdate. Thermal expansion curves of hydrated nickel or manganese molybdates present the same aspect: dehydration, polymorphic transformation (or precipitation) and thermal recrystallization.

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* If the product is not dispersed in a matrix, but compacted alone, the (b)—(a) transition (expansion) at 400° is so large that the compact texture is destroyed.

** The extrapolated value of L/L, at 100% of $CoMoO_4$, gives an expansion value $\frac{L}{L}$ 7%. for the (b) – (a) polymorphism (monoclinic—monoclinic transition).