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RECRYSTALLIZATION EFFECT DURING THE DEHYDRATION OF MAGNESIUM HYDROXIDE

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The thermal decomposition of finely divided $Mg(OH)_2$ does not occur smoothly. Several maxima of the gas evolution rate are observed, when microgram quantities of $Mg(OH)_2$ are heated under ultrahigh vacuum conditions. This phenomenon is attributed to the formation of an overlayer of partially decomposed hydroxide $Mg(OH)_{2-x}O_{x/2}\square_{x/2}$ with $x \rightarrow 2$ ($\square$: anion-sized neutral vacancy left by H_2O molecules in the hydroxide lattice). This defect layer represents a diffusion barrier for further H_2O molecules. When a critical thickness is reached, it spontaneously recrystallizes to cubic MgO exposing fresh $Mg(OH)_2$ surface.

The differential thermal analysis of magnesium hydroxide, $Mg(OH)_2$, in the usual quantities, namely a few milligrams, yields a smooth endothermic reaction just as one would expect for the simple dehydration reaction $Mg(OH)_2 \rightleftarrows MgO + H_2O$. However, we have repeatedly observed [1, 2] that the dehydration of microgram quantities of magnesium hydroxide under ultrahigh vacuum conditions, as measured mass-spectroscopically by the gas evolution rate, does not result in a smooth curve.

Experimental

The samples consisted of very high purity MgO-powder (total cation impurity content <5 ppm) either superficially hydroxylated or bulk hydroxylated and deuteroxylated to $Mg(OH)_2$ and $Mg(OD)_2$ respectively. The diameter of the individual hexagonal platelets was well below 1 μm, and their thickness in the 0.1 μm range.

The samples were heated in a fused-silica capillary tube attached to an oil-free, all-glass ultrahigh vacuum system operating at a base pressure of 10^{-10} mbar. In case *A* a step mode with 25° intervals and 7 min. isothermal heating periods was used [1] whilst in case *B* a linear heating rate of 2°/min. [2] was used.

The gas evolution from the sample was monitored by a memory-free, all platinum Omegatron mass spectrometer [3]. In case *A* the gases evolved were pumped away rapidly through a wide tube of large conductance, whilst in case *B* pumping was carried out more slowly through a capillary of known conductance for quantitative evaluation.

Results and discussion

Typical results obtained in case *A* and *B* are shown in Figs 1 and 2 respectively. In Fig. 1 the behaviour of a nearly fully deuteroxylated $Mg(OD)_2$ sample is shown, in Fig. 2 that of a partially deuteroxylated sample and of pure $Mg(OH)_2$. In all cases we find several maxima in the gas evolution curves which indicate changes in the gas evolution rates and, hence, some irregularities in the dehydration kinetics. The effect is most pronounced in case *A* where the reaction gas was pumped away at a higher rate than in case *B*.

After the steep initial rise of the dehydration curves, starting shortly above 230°, the first maximum occurs at about 330°, followed by an equally steep decrease with a valley at 380°. The second maximum lies at 460° and there is a pronounced shoulder at about 570°. Under the special heating conditions used here, the dehydration is completed by 700°.

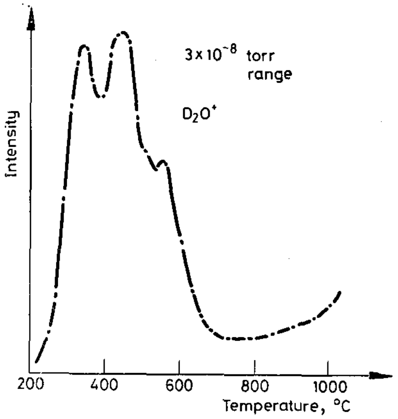

Fig. 1. Variations in the gas evolution curve from $Mg(OH)_2$ in ultrahigh vacuum as measured by the H_2O^+ signal intensity by means of a mass spectrometer (3×10^{-8} mbar)

Recently Sperling [4, 5] has confirmed that fine-grained $Mg(OH)_2$, when heated carefully in vacuum, first dehydrates to a defect structure which is chemically MgO (with some residual OH^--groups) but crystallographically retains the hexagonal CdI_2-type hydroxide structure:

$$Mg(OH)_2 \rightleftharpoons Mg(OH)_{2-x}O_{x/2}\,\square_{x/2} + x/2\ H_2O \text{ with } x \to 2$$

($\square$ designates a neutral, anion-sized lattice vacancy). Such residual hexagonal diffraction patterns have been observed before [6–8]. There is only a slight, but sharp lattice contraction in the c-direction and almost none in the a-direction, when this defect structure forms. The persistence of this very interesting defect structure could be followed by X-ray diffraction methods up to 480°. It has also been characterized by soft X-ray spectroscopy [9] and photoelectron spectroscopy [10].

When the cubic MgO nucleates from this defect phase, there is a very large lattice contraction by about 50 Vol%. The cubic MgO is formed in very small crystallites, the size of which appears to be related to the size of the parent $Mg(OH)_2$ crystals, but always smaller than 10 nm [11]. These small MgO crystallites contain numerous imperfections, including V-type centers, i.e. OH^--groups trapped in the vicinity of Mg^{2+}-vacancies which eventually dissociate to give molecular H_2 and O^--ions [1, 12] and Mg^{2+} on tetrahedral sites [13, 14].

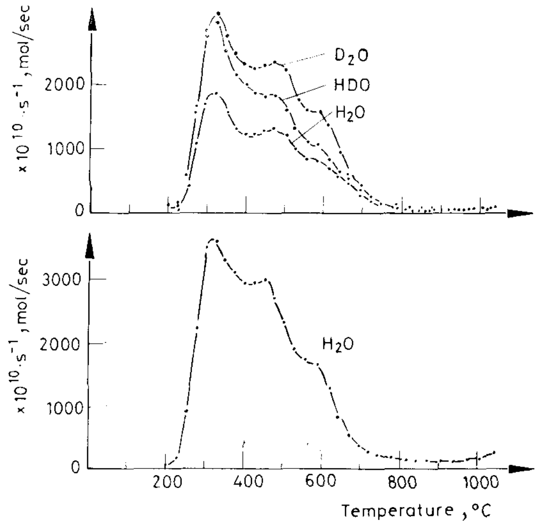

Fig. 2. Variations in the gas evolution rate (in molecules per sec) from 69 μg of partially deuteroxylated magnesium hydroxide (top) and 38 μg of $Mg(OH)_2$ (bottom)

The irregularities in the dehydration kinetics of $Mg(OH)_2$ are probably due to the formation of the defect phase and its subsequent recrystallization to cubic MgO.

Anderson and Horlock [7] have shown that small $Mg(OH)_2$ platelets dehydrate preferentially along the (001) basal plane. Combining this observation with the occurrence of the above-mentioned defect phase we come to the following conclusion for the observed irregularities in the dehydration curves:

As the reaction interface moves inwards, a reaction rim grows which is made out of the defect phase $Mg(OH)_{2-x}O_{x/2}\square_{x/2}$. There will be no disruption across the reaction interface because x is variable and the lattice contraction is small. The water molecules generated at the reaction interface will have to diffuse through this rim of growing thickness to reach the surface. During this time the dehydration kinetics is diffusion controlled by the build-up of this rim and the gas evolution rate slows down. At a given moment, or thickness of the rim, crystallization of cubic MgO occurs which is accompanied by the above-mentioned 50 Vol% lattice contraction and, hence, disruption occurs across the reaction interface. Thus fresh, undecomposed $Mg(OH)_2$ surface is exposed to the vacuum, and the gas evolution rate may become large again. This process repeats itself rhythmically until the reaction front reaches the core of the $Mg(OH)_2$ crystallites and all the origin substance is used up.

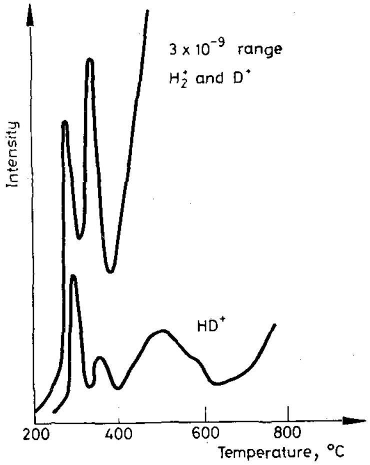

Fig. 3. Variations in the gas evolution curve from superficially hydroxylated MgO (3×10^{-9} mbar)

Curves like those shown in Figs 1 and 2 can only be obtained from very minute samples consisting of a small number of individual $Mg(OH)_2$ grains. If there is a large number of individual $Mg(OH)_2$ crystallites, a smooth envelope will result due to the superposition of the more-or-less rhythmic dehydration curve of each individual $Mg(OH)_2$ grain.

If well-annealed, fine grained MgO is only superficially hydroxylated or deuteroxylated by exposure to 26 mbar water vapor pressure at 80° [1], the irregularities in the dehydration curve become even more marked than for bulk $Mg(OH)_2$ as shown in the last Fig. 3. The reason is that in this case the MgO surface will be covered by an $Mg(OH)_2$ layer of near-uniform thickness which dehydrates in the manner described above.

It should be noted that in the case of large $Mg(OH)_2$ single crystals, measuring a few tenths of a millimeter or more, the dehydration is further complicated by another cracking process by which the large single crystals are first broken down into 2–3 μm diameter particles [15]. The probable reason for this process is the same in that strains are induced by the formation of a thin layer of the defect phase. Elsewhere it has been discussed [16] that the average size of these particles can be calculated from the elastic constants of $Mg(OH)_2$ and the relative lattice contraction upon defect phase formation.

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Résumé — Lors de la décomposition thermique sous ultravide de $Mg(OH)_2$ pulvérulent, plusieurs maximums apparaissent sur la courbe de déshydratation. On ramène ce phénomène à la formation d'une couche réactionnelle consistant en $Mg(OH)_{2-x}O_{x/2}\square_{x/2}$ partiellement décomposé, avec $x \rightarrow 2$ ($\square$: lacune neutre, due au départ de H_2O du réseau d'hydroxyde), qui constitue une barrière de diffusion à l'élimination de l'eau. Pour une épaisseur critique cette couche recristallise en MgO cubique. Cette recristallisation s'accomplit graduellement, en plusieurs étapes, jusqu'à la décomposition de la totalité de $Mg(OH)_2$.

Zusammenfassung — Bei der thermischen Zersetzung von pulverförmigen $Mg(OH)_2$ im Ultrahochvakuum treten in der Entwässerungskurve mehrere Maxima auf. Dies wird zurückgeführt auf die Bildung einer Reaktionsschicht von partiell zersetzten $Mg(OH)_{2-x}O_{x/2}\square_{x/2}$ mit $x \rightarrow 2$ ($\square$: neutrale Leerstelle durch H_2O-Austritt aus Hydroxidgitter), die eine Diffusionsbarriere für den Austritt des H_2O darstellt. Bei einer kritischen Dicke rekristallisiert diese Schicht zu kubischen MgO. Diese schubweise Rekristallisation erfolgt mehrmals, bis alles $Mg(OH)_2$ zersetzt ist.

Резюме — Термическое разложение тонко измельченной $Mg(OH)_2$ не протекает гладко. Особая максимальная скорость выделения газа наблюдалась, когда микрограммные количества $Mg(OH)_2$ нагревались в условиях сверхвысокого вакуума. Это явление приписано образованию особого поверхностного слоя частично разложенной гидроокиси $Mg(OH)$ $Mg(OH)_{2-x}O_{x/2}\square_{x/2}$ с $x \rightarrow 2$ ($\square$: анион-класифицированная нейтральная вакансия, оставленная молекулами воды в решетке гидроокиси). Этот дефектный слой является диффузионным бавьером для последующих молекул воды. Когда достигается критическая толщина, происходит самопроизвольная рекристаллизация в кубическую MgO, экспонируя тем самым новую поверхность $Mg(OH)_2$.