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STRAIN IN CRYSTALS DETECTED BY X-RAY

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STRAIN IN CRYSTALS DETECTED BY X-RAY

X-ray diffraction Laue photographs of deformed polycrystalline materials often show asterism. The Laue technique together with the polarizing microscope were employed to detect strains in samples of hydrated cement, Ca(OH)_2 , and analytical reagent grade NaCl in the form of compacts, powders and wafers. Distortion was detected in the crystal lattice of Ca(OH)_2 formed by hydration in excess water of a normal cement and in Ca(OH)_2 formed in cement hydrated as a paste. Microscopic examination showed symmetrically arranged inclusions in the Ca(OH)_2 formed by hydration in excess water. Strain was also detected in the compacted materials.

DETECTION AUX RAYONS X DES DEFORMATIONS EXISTANT A L'INTERIEUR DES CRISTAUX

Les photographies de substances polycristallines déformées, obtenues au moyen de la méthode de radio-cristallographie de Laue, indiquent souvent qu'il s'y produit de l'astérisme. La méthode de Laue et le microscope polarisant ont été utilisés pour mettre en évidence les déformations existant à l'intérieur d'échantillons de ciment hydraté, de Ca(OH)_2 , et de NaCl de qualité analytique, sous forme de comprimés, de poudres et de paillettes. On a décelé une certaine distortion dans le réseau cristallin du Ca(OH)_2 formé par hydratation dans l'excédent d'eau d'un ciment normal et dans le Ca(OH)_2 formé dans le ciment mouillé à la consistance d'une pâte. L'examen au microscope a permis de découvrir des inclusions disposées symétriquement à l'intérieur du Ca(OH)_2 obtenu par hydratation dans un excédent d'eau. On a également décelé des déformations à l'intérieur des produits agglomérés.

STRAIN IN CRYSTALS DETECTED BY X-RAY

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IT is useful to know whether the crystals forming a rigid polycrystalline body are strained, especially when such bodies are formed by compaction of the powdered microcrystalline material at moderate pressures. Residual internal stress in the crystals may have an influence on its mechanical properties, particularly its stability, when subjected to cyclical conditions.

X-ray diffraction transmission Laue photographs of deformed polycrystalline materials often show astorism, the radial distortion of the spots^{1,2}. This article discusses the use of this technique to detect strains in samples of hydrated cement, $\text{Ca}(\text{OH})_2$, and analytical reagent grade NaCl in the form of compacts, powders, and wafers.

In this technique, unfiltered copper X-radiation was employed and the diffraction patterns were recorded on film held either by a flat-plate holder mounted at a distance of 4 cm from the sample or by a cylindrical cassette of 5.73 cm diameter. The samples were also examined on the petrographic microscope.

A normal portland cement was used which was hydrated by two procedures. In the first the cement was hydrated essentially to completion in an excess of water by continuous rotation in a bottle on a wheel. The hydrated cement was recovered as a powder. In the second the cement was hydrated in the normal fashion as a paste with a water/cement ratio of 0.5 by weight.

Two varieties of $\text{Ca}(\text{OH})_2$ were investigated. One variety formed as a hydration product of cement. When hydration was carried out in an excess of water the crystals reached a size of about 1 mm. They were separated by sieving from the hydrated cement powder. The second variety of $\text{Ca}(\text{OH})_2$ crystals was grown by the diffusion technique of Johnston³ using CaCl_2 and NaOH .

The compacts were made in a mould 1.25 in. in diameter and the quantity of powder was adjusted so that after compaction the sample had a thickness of 0.25-0.5 mm when pressures in the range of 5,000-100,000 lb./in.² were employed. Some compacts of NaCl were annealed in a muffle furnace at a temperature of 500° C. Wafers of dimensions similar to the compacts were cut from a cylinder of normally hydrated cement by means of a diamond saw. Powder samples were gently pressed by

hand into a flat-plate holder and held in place by admixture with a small quantity of gum.

Laue photographs obtained from wafers of the cement hydrated as a paste showed marked asterism (Fig. 1a). This was also present on Laue photographs of the compacted and uncompact samples of cement powder hydrated in an excess of water. A Laue photograph of the uncompact $\text{Ca}(\text{OH})_2$ separated by sieving from the cement hydrated in an excess of water also showed asterism (Fig. 1b). The film was remarkably similar in appearance to that obtained from the cement powder hydrated in an excess of water, suggesting that in this case the observed diffraction effects resulted largely from the $\text{Ca}(\text{OH})_2$ crystals. The radial distortion of spots was even more marked on a photograph obtained from this material after it had been compacted at 20,000 lb./in.². The powder sample of $\text{Ca}(\text{OH})_2$ crystals grown by the slow diffusion process gave Laue photographs which showed very little asterism. Laue photographs of this material after compaction at 20,000 lb./in.² showed a similar amount of asterism to that observed on films of the uncompact $\text{Ca}(\text{OH})_2$ separated from the cement powder by sieving. A single crystal of the $\text{Ca}(\text{OH})_2$ separated from the hydrated cement powder showed distorted spots on discontinuous Debye-Scherrer powder rings; Laue spots showed asterism.

The NaCl (reagent grade) uncompact powder sample gave a Laue photograph which showed some asterism. Compaction at 800, 6,000 and 20,000 lb./in.² was accompanied by a progressive increase in the amount of asterism shown on the Laue photographs. Annealing the compact for 1 h at 500° C removed a large amount of the asterism from the corresponding Laue photograph. Annealing for 42 h was required before the Laue photograph of the compact showed no asterism. There was only a very slow decrease with time in the amount of asterism present on Laue photographs of an NaCl compact conditioned in a desiccator held at 50 per cent relative humidity. This result is in accord with that of Lewis and Pearson⁴, who studied X-ray diffraction-line broadening in the alkali halides.

X-ray photographs of the polycrystalline samples examined showed discontinuous Debye-Scherrer rings, but these were sometimes only visible in the back reflexion region. Their absence in the front reflexion region on some photographs was attributed to absorption in somewhat thicker or denser samples. Spots were commonly distorted around the circumference of the circle. After annealing the circumferential streaks on the photographs from the NaCl compacts were replaced by small sharp spots, the extent of the replacement depending on the length of annealing time. Photographs of the $\text{Ca}(\text{OH})_2$ separated by sieving from the cement powder showed this effect though no attempt was made to anneal the

sample. The Debye-Scherrer rings were generally more continuous on photographs of compacted samples than on photographs of uncompacted samples and the size of the spots was often reduced.

Most of the samples were examined under low power magnification under the binocular and at higher magnification under the petrographic microscope. The $\text{Ca}(\text{OH})_2$ crystals which grew as a product when the cement was hydrated in an excess of water were plate-like. Those grown by the diffusion technique of Johnston³ were of different morphology. They were elongated normal to the base (0001) in the form of hexagonal prisms which were sometimes hollow. Differences in shape of $\text{Ca}(\text{OH})_2$

Fig. 1. X-ray diffraction photographs showing asterism. *a*, Cement wafer hydrated as a paste; *b*, $\text{Ca}(\text{OH})_2$ sieved from cement hydrated in excess water

Fig. 2. Photomicrograph of oriented inclusions in Ca(OH)_2 , separated from cement hydrated in excess water

crystals have been discussed by Hedin⁵ in terms of differences in growth rate on different faces. He suggested that the presence of a very low concentration of impurities which absorb on growth steps such as screw dislocations may affect the growth mechanism⁵. He found that growth of prism faces began at a lower concentration of solution than did growth on the prism bases. Once growth had started, however, an increase in solution concentration caused a more rapid increase in growth rate on the basal surface than on the edges of the crystals. Predominant growth on basal surfaces favours long rod-like crystals whereas, if the growth is mainly on the edges, plates are produced. Differences in concentration between the CaCl_2 - NaOH and hydrating cement system and much higher concentration in the latter of impurities with possible growth-interfering properties may have influenced the difference in morphology of the two types of Ca(OH)_2 . The Ca(OH)_2 sieved out from the cement powder contained small inclusions symmetrically arranged in hexagonal form. Some of the inclusions within the hexagons appeared to show a spiral arrangement (Fig. 2). This is suggestive of rotation during growth and may result from a screw dislocation type of growth mechanism. Alternatively, the method of preparation may be responsible as this involves continuous rotation on a wheel. A few of the Ca(OH)_2 crystals contained randomly oriented lath-shaped inclusions of larger size than the symmetrical inclusions. The Ca(OH)_2 showed undulatory extinction on rotation of the microscope stage under crossed polars.

The classical interpretation of asterism is that it is due to diffraction from crystals in which the lattice is bent. Annealing removes the distortion and the diffraction

streaks are replaced by sharp spots characteristic of diffraction from an undeformed crystal. The separation of the streaks into a number of sharp spots is attributed to polygonization or the fragmentation of the larger distorted crystal into a number of well-defined sub-grains which differ slightly in orientation.

On the basis of this view it appears that there is distortion in the crystal lattice of the $\text{Ca}(\text{OH})_2$ formed during hydration of cement in an excess of water. This conclusion is supported by the undulatory extinction observed under crossed polars on the petrographic microscope. The similar effects observed on the X-ray photographs of the cement hydrated as a paste suggest that distorted $\text{Ca}(\text{OH})_2$ was also formed during the paste hydration process. The polygonization in the separated unannealed crystals implies that partial recrystallization also took place when an excess of water was present. Very little lattice distortion was present in the crystals of $\text{Ca}(\text{OH})_2$ grown by slow diffusion. Compaction resulted in deformation and a reduction in the size of the crystals. Similar conclusions apply to the results obtained with the NaCl powders and compacts.

The evidence of distortion in the crystal lattice leads to the conclusion that the crystal was subjected to some form of stress at some stage in its formation. This was certainly the case during compaction, but such stress is difficult to account for when crystals grow from solution in a free medium, as was the case for the $\text{Ca}(\text{OH})_2$ formed by hydration of cement in a rotating bottle. The fact that inclusions were observed in the crystals of $\text{Ca}(\text{OH})_2$ (Fig. 2) may account for the presence of strain. When cement hydrates as a paste it is acceptable to consider that stress is applied on the growing crystal, because the products must accommodate to the spaces formed by the structure of the unhydrated particles as well as to the primary hydration products.

The important question is whether distortion in crystals is evidence for the presence of residual internal stress. If so, one would anticipate that such crystals would be more reactive, might recrystallize (age) more readily, and would be less stable dimensionally especially under cyclical conditions of temperature or moisture change, than crystals of the same size having no residual internal stress.

Certainly in the case of NaCl , the lattice distortion tended to disappear after annealing, indicating that the distortion resulted from residual internal stress. Residual internal stress in crystals may have a significant influence on the mechanical properties of a rigid polycrystalline body.

¹ Barrett, C. S., *Structure of Metals*, 414 (McGraw-Hill, 1952).

² Taylor, A., *X-ray Metallography*, 757 (J. Wiley, 1961).

³ Johnston, J., *J. Amer. Chem. Soc.*, **36**, 16 (1914).

⁴ Lewis, D., and Pearson, H., *Nature*, **196**, 162 (1962).

⁵ Hedin, R., *Swedish Cement and Concrete Res., Inst. Proc.*, No. 33 (1962).