



Relation between Young's Modulus of set plaster and complete wetting of grain boundaries by water

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Abstract

The mechanical behavior of set plaster has been studied in humid atmospheres. This material is made of entangled needle-shaped gypsum crystals. At room temperature, Young's modulus of set plaster decreases as the coexistence of gypsum and water is approached by increasing the humidity of the surrounding air. Simultaneously, the thickness of the adsorbed water layer at the grain boundaries between the gypsum crystals is shown to diverge. It is suggested that the gypsum crystals are able to slide along certain grain boundaries because the viscosity of the water film approaches that of bulk liquid water. Small additions of D,L-tartaric acid prevent both the adsorption of water at grain boundaries of gypsum and the decrease of the Young's modulus of set plaster. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Complete wetting; Set plaster; Gypsum; Water adsorption; Grain boundary; Young's modulus

1. Introduction

The mechanical properties of polycrystalline materials depend, among others, on the chemical and physical characteristics of their grain boundaries. The determination of specific relationships requires consistent experiments to be performed on model materials at both the microscopic and macroscopic scales. This paper deals with set plaster, a material of simple chemistry and microstructure, which can be considered to

represent a model system. Set plaster is a generic term which refers to a porous solid made of entangled needle-shaped gypsum crystals connected by grain boundaries. It is produced by a simple process described in the following section.

The stiffness of the skeleton of needles which make up set plaster depends on two types of grain boundaries (GBs): so-called 'surface GBs', in which two needles are in contact at their surfaces or one needle lies in the mortise of another, and 'inside GBs' which display a mortise and tenon type joint between two needles. Fig. 1 displays a general view of the material (Fig. 1a) and two views of the different types of grain boundaries (Fig. 1b,c respectively).

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This paper addresses the phenomenon which produces a decrease in the Young's modulus of set plaster as the partial pressure of water in air increases. This is an important technological issue in Europe where plaster is widely used as a build-

ing material.

Experiments at 291 K on samples of pure plaster and of plaster containing 100 ppm by mass of D,L-tartaric acid ($\text{HOOC-CHOH-CHOH-COOH}$) are presented. The macroscopic behavior

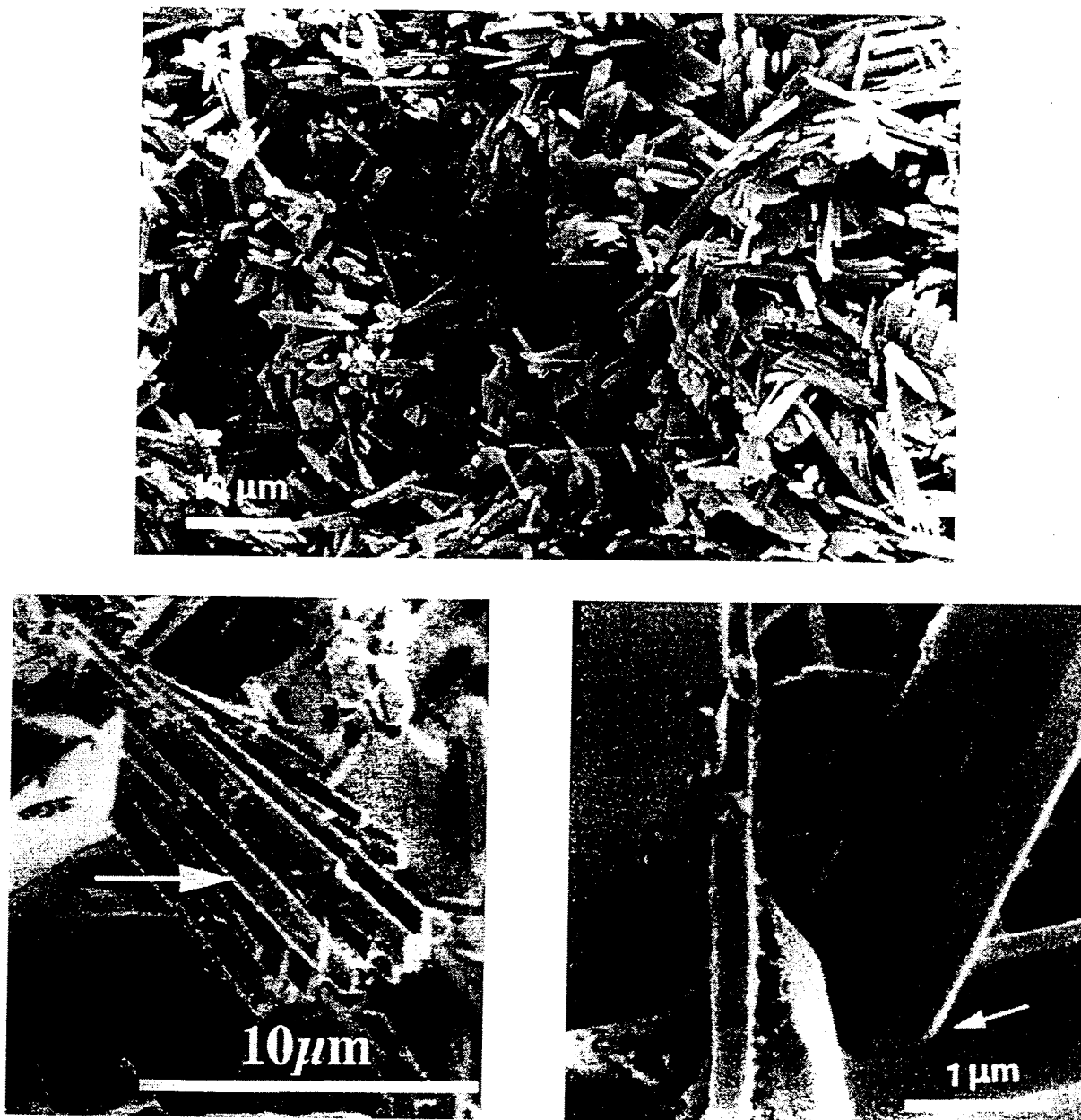


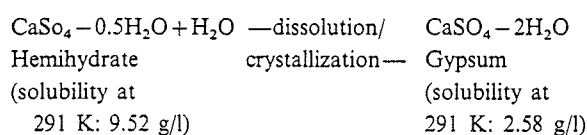
Fig. 1. (a) SEM photomicrograph showing typical view of the randomly arranged gypsum needles of a set plaster with a porosity of 57%. (b) SEM photomicrograph showing gypsum crystals in contact at grain boundaries parallel to the needle axis. (c) SEM photomicrograph showing gypsum crystals in contact at mortise and tenon joints.

of plaster is described through the change in Young's modulus as a function of relative humidity (directly related to the water partial pressure or to the water chemical potential). The microscopic characteristics of the grain boundaries are deduced from the water adsorption isotherms.

2. Results and discussion

2.1. Samples

Samples of pure set plaster were prepared from the β -hemihydrate of calcium sulfate (P23 of the Meriel quarry, France) and water, according to the following reaction sketch:



Hemihydrate mixed with water transforms into the dihydrate, generally referred to as gypsum. The mass ratio of water to hemihydrate, W/H , necessary to complete the hydration reaction is equal to 0.186. An excess of water allows porosity to form. In this study, a ratio W/H of 0.8 was chosen to produce a set plaster with a porosity of 57% (volume fraction of pores).

At 291 K, the relative humidity of air in which gypsum is stable ranges between 12 and 100%. Saturation of 1 atm of air by water corresponds to a partial pressure of water equal to 2×10^3 Pa at 291 K.

A second set of samples containing 100 ppm of D,L-tartaric acid were prepared by the same process. The additive was introduced into the solution prior to the calcium sulfate hemihydrate. Crystallization of gypsum in the presence of various carboxylic acids has been studied by different authors [1–4]. The morphology of gypsum crystals is observed to remain needle-shaped as in pure plaster at the present low concentration of additives.

2.2. Young's modulus

Young's modulus, E , has been determined from

the mechanical resonance frequency of a sample of set plaster of dimensions $125 \times 50 \times 30$ mm, using a GrindoSonic apparatus [5]. E is related to the longitudinal and flexural resonance vibrations of the sample. It is calculated from relationships given by Spinner and Tefft [6] for a bar of rectangular cross-section. For the sake of brevity the set of equations is not reproduced in this paper.

The sample is enclosed in a chamber in which the partial pressure of water is fixed by equilibrating saturated salt solutions with the atmosphere.

An initial set of experiments was performed on nine samples of pure set plaster. For a given water partial pressure, the scatter in Young's modulus was found to be $\pm 13\%$. However, Young's modulus as a function of the water partial pressure behaved in the same manner for all the samples. Thus, we considered the relative value of Young's modulus, $\Delta E/E$, instead of its absolute value. This may be written as follows:

$$\Delta E/E = \frac{E_{\text{HR}} - E_{\text{HR} = 12\%}}{E_{\text{HR} = 12\%}}$$

E_{HR} is the value of Young's modulus at a given relative humidity HR, and $E_{\text{HR} = 12\%}$ is the value of Young's modulus at a relative humidity of 12%, where the dihydrate is in equilibrium with the hemihydrate at 291 K [7]. This is the highest value of Young's modulus in the range of water partial pressure where gypsum is stable.

Fig. 2 displays the relative value of Young's modulus of pure set plaster as a function of the relative humidity in air. This value decreases slowly as humidity increases up to about 80%. As coexistence of water and gypsum is approached, the relative value of Young's modulus decreases at an increasing rate.

Fig. 3 shows the relative value of Young's modulus of set plaster containing 100 ppm of D,L-tartaric acid, as a function of the relative humidity, in comparison with the data obtained for pure set plaster. The two curves display a similar shape, but in the case of set plaster with the additive, the decrease in the relative value of Young's modulus is clearly less rapid as coexistence of gypsum and water is approached.

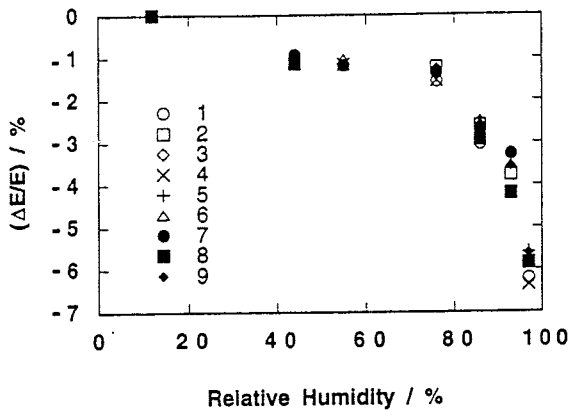


Fig. 2. Decrease of the relative value of Young's modulus versus relative humidity for nine samples of pure set plaster with a porosity of 57%.

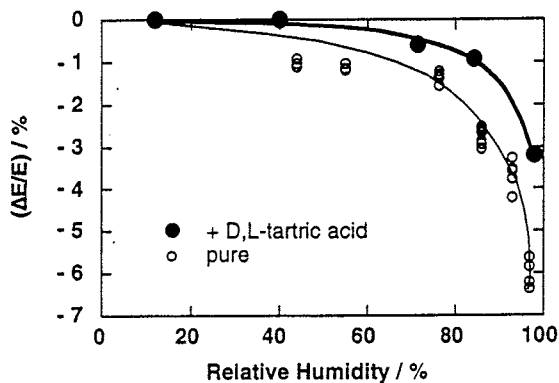


Fig. 3. Decrease of the relative value of Young's modulus versus relative humidity for a sample of pure set plaster and for a sample containing 100 ppm of D,L-tartaric acid with the same porosity of 57%.

2.3. Water adsorption isotherm

The adsorption isotherm of water has been determined by differential gravimetry using an electronic micro-balance (Setaram MTB 10-12). The weight change of a sample of set plaster about $10 \times 10 \times 40$ mm in size, was measured as a function of the humidity in air. The balance was enclosed in a sealed chamber in which the partial pressure of water was fixed by equilibrating a mixture of water and glycerin with the atmosphere. It is worth noting that neither salt nor

glycerin interfere with the values of the quantities measured (Young's modulus and water adsorption). When saturated salt mixtures are used to fix the partial pressure of water, the type of salt has to be changed for each humidity level. In the case of gravimetry experiments, the glycerin/water mixtures are more convenient because the humidity level can be adjusted by changing the ratio water/glycerin without opening the sealed chamber to ambient air.

The zero weight was taken to correspond to the so-called adsorption free state. This is measured at the lower end of the humidity range at which gypsum is stable, i.e. 12% at 291 K, and is obtained by evacuating the chamber down to $P = 10^3$ Pa. The kinetics of dehydration of the dihydrate into hemihydrate is slow enough that the zero-adsorption equilibrium can be reached by this means. This is consistent with the Controlled Transformation Rate Thermal Analysis experiments performed previously [8].

The water adsorption isotherm of pure set plaster is shown in Fig. 4, which displays the variation of water mass per g of set plaster as a function of the relative humidity. Each point in Fig. 4 was plotted after a 72 h waiting period. Equilibrium was reached within 24 h. The adsorption curve in the figure corresponds to a type II isotherm in the classification of Brunauer [9]. The weight of the sample increases slightly as the relative humidity increases from 12 to 80%. At higher humidity levels, the quantity of adsorbed water diverges as water–gypsum coexistence is approached. In such

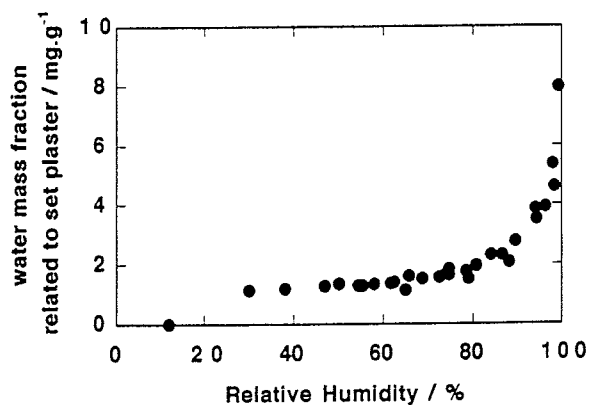


Fig. 4. Water adsorption isotherm for a sample of pure set plaster with a porosity of 57%, recorded at 291 K.

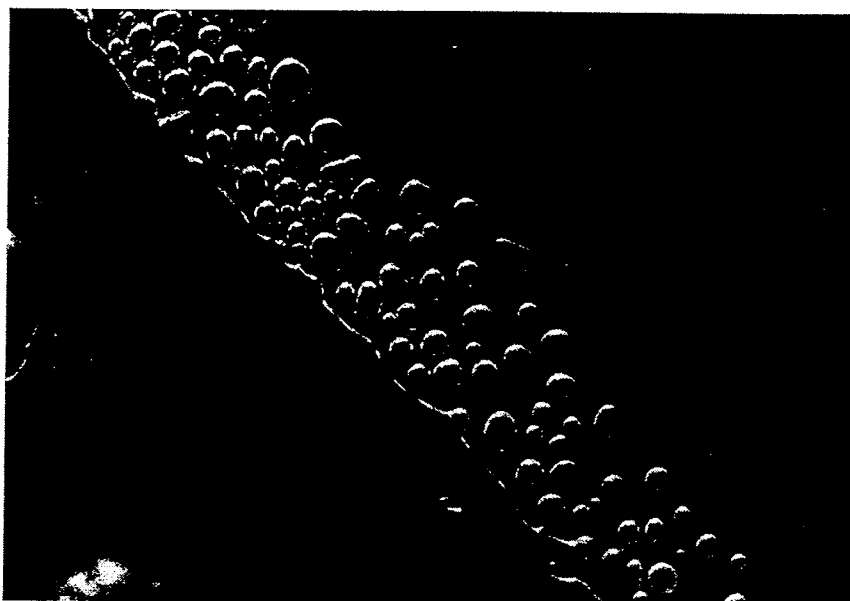


Fig. 5. Optical photograph showing water droplets condensed on the (010) face of a single crystal of gypsum.

an experiment, the increase in weight of the sample results from two contributions: water adsorption at the free surfaces of the gypsum needles and water adsorption at the grain boundaries of the gypsum crystals. Capillary condensation does not play a role in these measurements, as indicated by the absence of any plateau on the diverging part of the isotherm [9].

The thickness of an adsorbed liquid layer on a substrate surface reaches a maximum at coexistence of the bulk liquid with the substrate (e.g. water on the surface of gypsum). It is connected to the value of the contact angle of a drop of the bulk liquid on the substrate. In general, one expects that the adsorbed liquid layer will thicken with decreasing contact angle [10]. A zero contact angle will correspond to an 'infinitely' thick adsorbed layer [10]. Thus, in order to separate the contributions of surfaces and grain boundaries, the wetting behavior of water on the (010) cleavage plane of a gypsum crystal was determined.

The freshly cleaved single crystal was enclosed in a chamber the atmosphere of which was first saturated with water at 313 K, then cooled down to 291 K in order to produce water condensation. As shown in Fig. 5, water forms on the surface of

gypsum as droplets. The contact angle is about 15° . It was measured on a water sessile drop, 5 mm in contact diameter deposited, in air, on a freshly cleaved surface of gypsum. The measurement was performed from the drop profile captured by a camera, using image analysis software. The non-zero value of the contact angle clearly means that as water–gypsum coexistence is approached, the thickness of the water layer adsorbed on the free surface of gypsum will tend to a finite value which can be guessed to be several monolayers thick, as observed for other ionic crystals [11,12]. The (010) plane is one of the prismatic planes present on the surface of the gypsum needles, the Miller indices of the other surfaces of the needles are (120), $(\bar{1}11)$ and (011). As large enough surfaces of these orientations were impossible to prepare from a single crystal, no contact angle data on these dense planes could be measured. However, partial wetting of water on these planes is hypothesized, based on experimental results of Naidich et al. [13] who showed that a systematic partial wetting is present on dense planes of different solids by their own melt.

By considering the adsorption isotherm of Fig. 4 and the finite adsorption expected at the free

surfaces of gypsum, it can be deduced that the divergence of the weight of water in the adsorption isotherm corresponds to a thickening of the water film at the grain boundaries of gypsum. The physical and chemical properties of this water film are likely to be different from those of bulk water, nevertheless the thicker the film, the closer it will be to bulk liquid water.

The type of interactions at grain boundaries of gypsum wetted by the water layer can be determined from the shape of the divergence [10]. First, the adsorption isotherm has to be replotted as a function of the chemical potential of water, $\mu_{\text{H}_2\text{O}}$, which is related to the relative humidity, HR, as

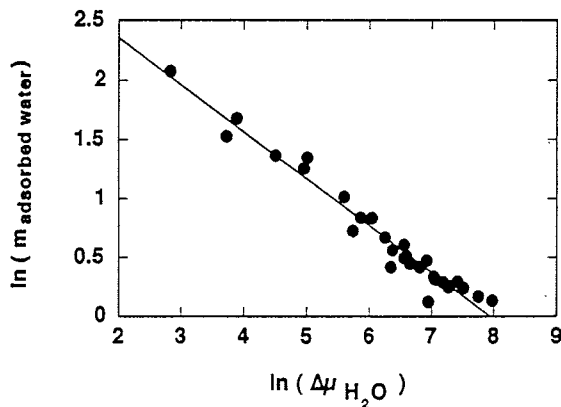


Fig. 6. Water adsorption isotherm for a sample of pure set plaster as a function of the chemical potential of water plotted on logarithmic scales.

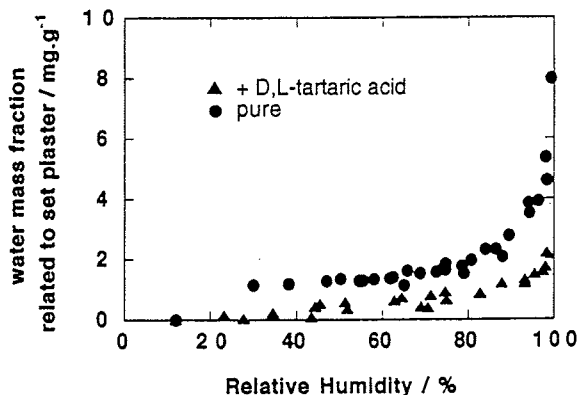


Fig. 7. Water adsorption isotherm of a sample of pure set plaster and of a sample containing 100 ppm of D,L-tartaric acid, with the same porosity of 57%, recorded at 291 K.

follows:

$$\Delta\mu_{\text{H}_2\text{O}} = \mu_{\text{H}_2\text{O}} - \mu_{\text{H}_2\text{O}}^{\circ} = RT \ln(\text{HR}/100)$$

In this equation, $\mu_{\text{H}_2\text{O}}^{\circ}$ is the chemical potential of liquid water (at a relative humidity of 100%), R is the gas constant and T is the temperature.

Fig. 6 shows this adsorption isotherm on logarithmic scales. The experimental points lie on a straight line, the fitted slope of which is found to be -0.396 . This value is close to $-1/3$ which is the exponent corresponding to long-range interactions at the wetted grain boundaries [10]. These interactions are established either between the ionic gypsum grains through the water layer, or in this layer if it contains dissolved sulfate anions and calcium cations.

Fig. 7 shows the water adsorption isotherm of set plaster containing 100 ppm of D,L-tartaric acid additive in comparison with the data obtained for pure plaster. The weight of adsorbed water for set plaster with additive increases slightly, in a linear manner, up to 95% relative humidity. This is followed by an acceleration in the increase of adsorbed water weight as coexistence is approached, but there is no evidence of a divergence. Comparison of this isotherm with that of pure plaster shows that the weight of adsorbed water at 98% of humidity is more than three times smaller. It is concluded that the adsorbed layers of water at both the free surfaces and the grain boundaries of gypsum are finite when set plaster contains 100 ppm of D,L-tartaric acid. This additive thus appears to block water adsorption at gypsum grain boundaries by adsorbing at these interfaces.

2.4. Comparison between macroscopic and microscopic data

There is an obvious correlation between the shapes of the curves obtained for Young's modulus and the water adsorption as a function of relative humidity. Since we interpret the adsorption isotherm as a measure of water adsorption at the grain boundaries of gypsum, it is possible to conclude that the decrease in Young's modulus of pure set plaster at high humidity levels is due to the thickening of the water layer at grain

boundaries. As its thickness increases, this water layer tends to approach the 'bulk-like' state, which allows the gypsum needles to slide along the so-called 'surface GBs'. The tenon-mortice GBs maintain the rigidity of set plaster.

A phenomenon of dissolution-precipitation of gypsum at grain boundaries was previously suggested for explaining the damage of the mechanical properties of set plaster in humid atmospheres [14,15]. Coquard and Boistelle discarded this hypothesis [16]. Moreover they observed a reversible swelling of $200 \mu\text{m m}^{-1}$ for a set plaster of ($W/H=0.8$) as the maximum humidity is approached. This observation is consistent with the behavior of water at grain boundaries deduced from the adsorption isotherm.

The experiments performed on set plaster containing 100 ppm of D,L-tartaric acid provide additional evidence for the present conclusions: if the thickening of the water film is prevented by a pre-adsorption at grain boundaries, the decrease of Young's modulus of set plaster is not as significant at high humidity levels.

3. Conclusions

A correlation between the increase in the thickness of an adsorbed water layer at grain boundaries of set plaster, and the deterioration in the mechanical properties of this material, has been identified. A simple process for the prevention of the deleterious effects of humidity on mechanical properties, which involves small additions of pre-segregating species, has been proposed. This work is also relevant to understanding the mechanism of damage to solids by so-called Liquid Metal Embrittlement, in which a solid fractures prematurely after a liquid penetrates along its grain boundaries.

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