JOURNAL OF MATERIALS SCIENCE LETTERS 11 (1992) 150–151

Gypsum crystals grown in silica gel in the presence of citric acid as additive: a study on microhardness

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Since microstructures and microconstituents of surfaces of crystals exercise considerable influence on indentation measurements, testing involving microhardness has recently been popular in this field of scientific research. Crystalline physical properties, such as hardness, glide and anisotropy, have been studied employing the indentation technique [1–3]. Mineral gypsum (calcium sulphate dihydrate, $CaSO_4 \cdot 2H_2O$) is a monoclinic (point group 2/m) crystal with hardness 2 on the Mohs scale. As they find wide applications in industry, agriculture and research [4–6], we made microhardness measurements on these crystals obtained under two different growth conditions to estimate the extent of perfection in them.

Two types of crystals of gysum were grown in silica gel medium [7], one in the absence of additive and the other in the presence of citric acid as additive, hereafter referred to as G1 and G2, respectively. The (0 1 0) faces of fairly large single crystals of G1 and G2 cleaned with acetone were used for the study. Static microindentations (15 s) and diagonal measurements were made using a Vickers microhardness tester-cum-projection metallurgical microscope (Cooke, Troughton and Sims, York, UK). Using the relationship [8]

$$\mathrm{VHN} = 1.854\, P/d^2$$

where P denotes the load applied in kg and d is the indentation diagonal in mm, the Vickers hardness number (VHN) was calculated for each observation. The data for the two samples are listed in Table I.

TABLE I Microhardness data for gypsum crystals[a]

Load P (kg)	Mean diagonal of the indentation mark, d (μm) Crystal G1	Crystal G2	VHN (kg mm^{-2}) Crystal G1	Crystal G2
0.005	15.0	17.6	41.0	29.9
0.010	15.6	20.3	76.2	45.2
0.015	15.9	22.8	110.0	53.5
0.020	16.6	25.5	134.6	57.0
0.025	22.3	28.1	93.2	58.7
0.030	28.4	Crack develops	69.0	

[a]G1, crystal grown in the absence of the additive; G2, crystal grown in the presence of the additive (citric acid).

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Using the computer software AXUM and a laser printer, plots were drawn with these data. A perusal of Fig. 1 shows that the plots of log d versus log P are straight lines below and above the critical load region of 20 g. The values of the slope for sample G2 is 14.7 and that for G1 is 3.5. These values are higher than the $n = 2$ in the Meyer relation, viz.

$$P \propto d^n,$$

and so both cases satisfy it in the region below the critical load. However, the above relationship is not satisfied by the two samples in the region with $P >$ 20 g. The abnormally large value of n for G1 for $P <$ 20 g shows that the absence of the additive in the gel has caused crystal G1 to grow with a higher degree of microhardness than the crystal in the presence of the additive (crystal G2).

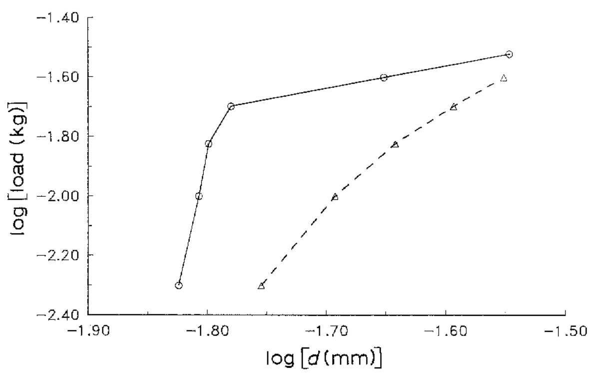

Figure 1 The effect of the additive (citric acid) in gel on log d versus log P plot for gypsum crystal G2, (○) G1 and (△) G2.

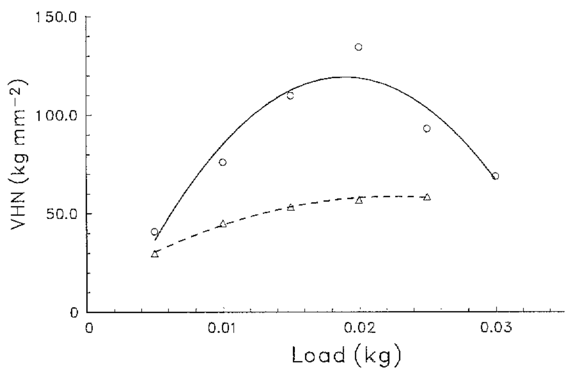

Figure 2 Variation of VHN with load for the gypsum crystals grown in the absence ((○)G1) and in the presence ((△)G2) of citric acid as additive in gel.

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Crystals having large surface energies are known to possess greater microhardness at low values of load [9]. Furthermore, studies on interatomic distance and microhardness [10] have shown an inverse relationship between them. There is also found a direct relationship between the degree of gel inclusion and hardness in the case of gypsum crystals [11]. A look at Fig. 2 reveals that for crystal G2 both the surface energy; and the gel inclusion are larger than those for crystal G1. We therefore conclude that the presence of the additive in the silical gel medium favours growth of crystals of calcium sulphate dihydrate in it towards a higher degree of perfection than one grown without the additive.

Acknowledgements

The authors thank Professor K. S. Viswanathan of the University of Kerala for his encouragement, Professor M. S. Joshi, Sardar Patel Universtiy, Vallabhnagar, for useful discussions and Dr S. Narayana Kalkura, University of Kerala, for his interest in this work.

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Received 12 March
and accepted 25 April 1991