differing impurity incorporation is present in the vibrating reigion.

The growth cell boundary, which also appears to be an impurity boundary, and the gsb may be alike in structure judging qualitatively from the similarity in their X-ray topographical image contrast. However, the nature of the former has not yet been fully investigated.

A simple X-ray image converter capable of permitting the rapid detection of gsbs in quartz has recently been reported [12].

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References

- 1. W. J. SPENCER, Physical Accoustics 5 (1968) 111.
- 2. D. B. FRASER, ibid 5 (1968) 59.
- 3. A. R. LANG and V. F. MIUSCOV, J. Appl. Phys. 38 (1967) 2477.
- 4. D. Y. PARPIA, Phil. Mag. 33 (1976) 715.
- 5. W. J. SPENCER and K. HARUTA, J. Appl. Phys. 37 (1967) 549.
- 6. M. TAKAGI, H. MINO and M. SATO, J. Crystal Growth 24, 25 (1974) 541.
- 7. W. J. CADY, "Piezoelectricity" (McGraw Hill, London, 1946).
- 8. A. J. COHEN, J. Phys. Chem. Solids 13 (1960) 321.
- A. R. LANG "Modern Diffraction and Imaging Techniques in Material Science", edited by S. Amelinckx, R. Gevers, G. Remant and J. van Landuyt (North-Holland, Amsterdam, 1969) p. 407.
- 10. U. BONSE, Z. Phys. 184 (1965) 71.
- 11. C. S. BROWN and L. A. THOMAS, J. Phys. Chem. Solids 13 (1960) 337.
- 12. D. Y. PARPIA and B. K. TANNER, *Phys. Stat. Sol.* (a) 6 (1971) 689.

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Acoustic emission activity during accelerated conversion of high alumina cement pastes

High alumina cement (HAC) owes its high initial strength to the formation of monocalcium aluminate decahydrate, dicalcium aluminate octahydrate and alumina gel, on hydration. These high strength aluminates are metastable, however, and decompose gradually to tricalcium aluminate hexahydrate and gibbsite (aluminium hydroxide) which are stable up to about 200° C. This process, termed "conversion", entails a crystallographic change from hexagonal to cubic and is accompanied by the evolution of water. Conversion takes place very slowly at normal ambient temperatures but is accelerated at higher temperatures. In recent years it has been established that under adverse conditions conversion leads to a serious loss of strength in HAC pastes and HAC concretes [1, 2]. The major factors affecting the strength loss

during conversion are (a) the temperature of conversion, and (b) the water/cement ratio of the paste or concrete.

Pastes with a high water/cement ratio contain very little residual unhydrated cement. The water evolved during conversion, therefore, cannot be absorbed, and appears as free water in the interior of the paste. The main effect of increased temperature is to increase the conversion rate. This leads to a larger aluminate crystallite size, which is thought to adversely affect the strength.

Acoustic emissions (AE) are elastic stress waves generated within a material by rapid discontinuous relaxation of local stress. Common examples of processes emitting AE are (a) dislocation motion during plastic deformation of metals, (b) martensitic phase transformations and twinning, and (c) crack nucleation and propagation. It was not considered likely that the conversion process in HAC would itself be a source of acoustic emission, since the reaction proceeds continuously with little or no build up of local stress at the reaction interface. The crystallographic change from hexagonal to cubic during conversion entails a decrease in volume, with consequent pore formation. It was considered that the formation of pores and voids, especially in the presence of excess water, could give rise to detectable AE activity. For this reason, AE monitoring was carried out during accelerated conversion of two HAC pastes. The paste mixes were chosen to give high and low levels of excess water after conversion.

To the best of our knowledge, the application of AE techniques to studies of the conversion of HAC pastes and concretes has not previously been reported.

Two HAC pastes having water/cement ratios of 0.35 and 0.65 were mixed, and cast into $20 \text{ cm} \times 10 \text{ cm} \times 7.5 \text{ cm}$ rectangular wooden moulds. As soon as possible after casting, the slabs were removed from the mould and left to cure for 24 h in running water at 17° C. After curing, the slabs were immersed for 72 h in a stirred water bath maintained at 60° C. During this time the slabs were monitored for AE activity by attaching an Endevco D140B resonant AE transducer. The rate of AE energy release was recorded using an Endevco 3000 module, with a sampling time of 120 sec. A

control experiment was carried out to determine any background AE, by attaching the transducer to a household brick immersed in the water bath.

The observed AE rate as a function of time for the two samples is shown in Fig. 1 and 2. The background emission rate determined by the control experiment, over a 5 h period, fluctuated between 0 and 10 events/sec. The sample with low water/cement ratio (Fig. 1) did not exhibit any significant AE activity above the background level. The sample with a high water/cement ratio (Fig. 2) showed a long period of greatly increased AE activity, between 18 and 40 h at 60° C. Peak activity, with a maximum recorded emission rate of 135 events/sec occurred after about 26 h. Large fluctuations in AE rate were often observed between consecutive sampling periods.

The background AE rate (10 events/sec, max.) is almost certainly due to turbulence and mechanical noise from the water bath stirrer. With the stirrer switched off, the AE rate became negligible.

After 72 h at 60° C, conversion is expected to be virtually complete in both samples [1]. The work of Alegre [3] has shown that with a water/ cement ratio of 0.35, no excess water is liberated during full conversion. Below this value, termed "critical water/cement ratio", incomplete hy-



Figure 1 Variation of acoustic emission rate with time, for water/cement ratio of 0.35.



Figure 2 Variation of acoustic emission rate with time, for water/cement ratio of 0.65.

dration takes place, whilst above the critical value, free water is evolved.

The experimental work has shown that no acoustic activity was generated during conversion of HAC paste with a water/cement ratio of 0.35. It may, therefore, be inferred (a) that the conversion process *per se* is not a source of AE activity, and (b) the formation of voids and pores owing to the smaller volume of the cubic aluminate does not cause AE activity.

In the case of the paste with a high water/ cement ratio, conversion was accompanied by a high level of AE activity. The occurrence of this high amplitude AE indicates the probability that fracture processes take place in the cement during conversion; this is thought to be associated with the liberation of excess water. The means by which free water causes cracking is not certain. It is possible that this occurs due to the build-up of hydrostatic pressure as the water is evolved; alternatively the presence of water may lower the critical surface energy requirement for crack nucleation at existing internal voids. In the presence of applied stress, microcracking during conversion will be enhanced; this could lead to eventual failure of HAC concrete load-bearing structures manufactured using mixes with a high water/cement ratio.

References

- 1. Building Research Establishment CP34/75 (1975) Garston, UK.
- C. M. GEORGE, "The Structural use of High Alumina Cement Concrete" (Lafarge Fondu International, 1973).
- 3. R. ALEGRE, Rev. Mater. Construct. 630 (1968) 104.

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