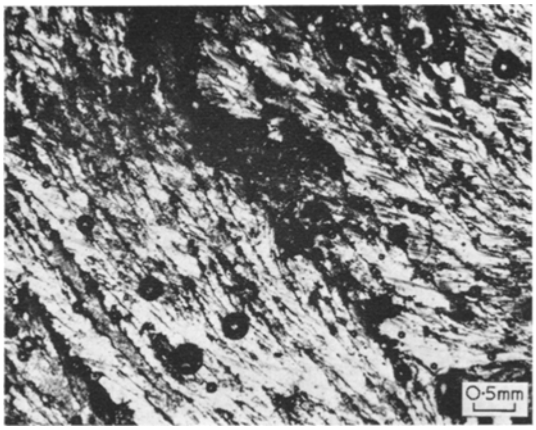

Figure 4 Secondary markings on the main fracture surface.

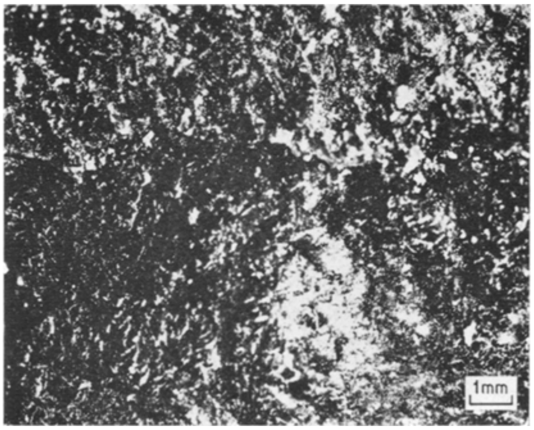

Figure 5 Surface of the secondary fracture.

of the type shown are generally associated with cleavage involving extensive local deformation.

It is well known that at high deformations natural rubber becomes partially crystalline [4]. Therefore a possible explanation of the observed fracture characteristics is that the localised high strain ahead of the progressing crack causes crystallisation and that failure is then through material which can undergo cleavage. It should be noted, however, that this places a restriction upon the crack-propagation rate because of the time necessary to allow for the development of the local crystalline regions. The size of the facets on the rubber fracture are larger, by a factor of several hundreds, than those in the steel fractograph.

The secondary fracture face (CEF in fig. 1) shows quite different characteristics (fig. 5). The surface is generally rough and no features of the type discussed above are to be seen and it appears to be a typical tearing fracture.

We may summarise by noting that a comparatively smooth fracture surface was created in a direction perpendicular to the principal tensile stress and a rough surface was created perpendicular to the principal comprehensive stress. The markings on the smooth surface have some features similar to a cleavage-type failure in a crystalline material. It is possible however that the presence of the secondary tear type of crack is fortuitous, having started as a flaw at F′ (fig. 2) and propagating towards C′, within the time scale of propagation of X′D′.

References

1. R. S. RIVLIN, "Rheology", Vol. 1 (Academic Press, New York, 1965).
2. M. M. HALL, College of Aeronautics (Cranfield) Note Mat. No. 17, 1968.
3. E. H. ANDREWS, "Fracture in Polymers" (Oliver & Boyd, 1968) p. 121.
4. L. R. G. TRELOAR, "The Physics of Rubber Elasticity", 2nd edition (Clarendon Press, 1958).
5. H. C. BURGHARD and N. S. STOLOFF, "Electron Fractography" ASTM (STP 436) (1968) p. 32.

Received 12 March
and accepted 7 April 1970.

M. M. HALL
A. R. SOLLARS
Department of Materials,
Cranfield Institute of Technology,
Cranfield, Bedford, UK

Variations in the Lattice Constant of Calcium Oxide

The paucity of reliable data for lattice constant changes in ionic microcrystals is due to the experimental difficulties involved in their measurement, e.g. the preparation of microcrystals sufficiently small to exhibit lattice changes, coupled with the instantaneous adsorption of gases by vacuum calcined powders when exposed to air. In the absence of adsorbed gases, the lattice constant of MgO has been shown to contract with decreasing crystallite size [1]. The magnitude of this contraction is in agreement with that predicted by Anderson and Scholz [2] from calculations involving the minimising of the energy of the crystals with respect to interionic separation. The lattice dilation of MgO, observed by several workers [1, 3, 4] results from the presence of chemisorbed gases, in particular H_2O. Garvie [5] considered that this dilation was due to lattice relaxation and cited the data of Cimino, Porta, and Valigi [4] to confirm his theory.

The lattice constant changes in microcrystals of CaO have been investigated in different atmospheres at selected temperatures. $Ca(OH)_2$ powder of stated purity Fe, Al and Pb < 10 ppm was thermally decomposed under a vacuum of 10^{-6} mm Hg in a Rigaku-Denki attachment to a Philips 1050/25 goniometer. The CaO (200) diffraction peak was step-scanned at temperature and the position of the peak centroid determined [6]. The size of the CaO microcrystals was calculated at various stages of growth from the Fourier integral breadth of the (200) peak using a computer programme developed by Harrison [7]. This method of analysis corrects for absorption, Lorentz and polarisation effects, but entails no assumptions of the profile shape. A standard high-temperature calcined sample of CaO was used to compensate for absorption and the data of Dolloff [8] were employed to correct for the thermal expansion of CaO. A more detailed description of the procedures involved is given elsewhere [1, 9].

The results are given in table I and a plot of the change in lattice parameter, a, against N is shown in fig. 1. The microcrystals were assumed to be cubes containing N^3 ions, N being calculated from the formula $N = (D/d) + 1$, where D is the crystallite size and d is the interplanar spacing, calculated from the CaO (200) reflection. After decomposition at 300° C, the size of the CaO microcrystals was 95 Å and at room temperature *in vacuo* the lattice constant of these crystallites was normal. As the sample temperature was gradually raised to remove any adsorbed gases, the lattice constant decreased until a minimum value was reached at 870° C, fig. 1. Simultaneously, considerable crystallite growth occurred and the magnitude of the lattice contraction was therefore not as large as that observed with MgO [1], but was still of the same order as that predicted by the Anderson and Scholz model [2]. On cooling to room temperature, whilst still under vacuum, the CaO lattice dilated and further dilation occurred when the sample was exposed to a small partial pressure of water vapour, table I. When moist (laboratory) air was admitted to the 95Å material, rehydration was rapid, the smooth powder bed fragmented and no parameter measurements were possible.

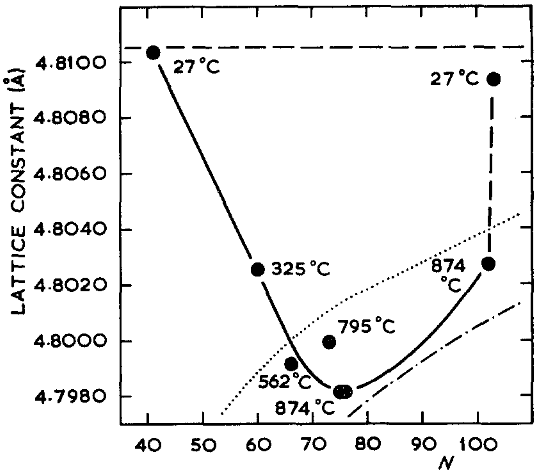

Figure 1 Change in lattice constant with N for cubic microcrystals of CaO containing N^3 ions. ------ normal lattice constant of CaO; ...... upper and – · – · – · lower limits of calculated values of Anderson and Scholz [2].

After initial decomposition at 300° C, the lattice constant measured at room temperature *in vacuo* although normal is, in effect, dilated due to the affinity of CaO microcrystals for water vapour. Complete removal of hydroxyl ions is not facilitated until temperatures around 800° C are reached, when the minimum lattice parameter values are obtained. Thus, our experimental evidence in this and previous work shows that the lattice dilation observed in ionic microcrystals is due to the presence of adsorbed water vapour, and is not an inherent property of the material as suggested by Garvie [5].

The rapid growth of CaO microcrystals during vacuum decomposition above 300° C prevents the measurement of lattice constant changes in crystallites less than ~ 150 Å. Anderson, Horlock, and Avery [10] have shown that $Ca(OH)_2$ is only 90% decomposed at 300° C *in vacuo* and also noted that the crystal growth of CaO is more sensitive to the presence of water vapour than MgO. It is difficult to see how very small crystallites of CaO (~ 50 Å) can be prepared without the presence of chemisorbed water vapour, since our results indicate that this is

TABLE I Lattice constant and crystallite size values of CaO microcrystals

Temperature (° C)	Atmosphere	Lattice* constant a (Å)	Change in lattice constant Δa (Å)	Crystallite size (Å)	N
27	vacuum	4.8103	−0.0002†	95	41
325	vacuum	4.8025	−0.0080†	142	60
562	vacuum	4.7991	−0.0114	158	66
795	vacuum	4.7999	−0.0106	175	73
874	vacuum	4.7981	−0.0124	179	75
874	vacuum	4.7981	−0.0124	183	76
874	vacuum	4.8027	−0.0078	245	102
27	vacuum	4.8093	−0.0012	246	103
27	moist air	4.8127	+0.0022	246	103

* Lattice constant corrected to 27° C.
† Minimum lattice parameter values not reached due to incomplete removal of hydroxyl ions (see text).

present at temperatures up to at least 600° C. There is some evidence to suggest that the size of the original hydroxide platelets influences the initial size of the oxide microcrystals [11], hence smaller hydroxide crystallites are necessitated. However, a more fruitful approach may rest on decomposition under ultra-high vacuum at low temperatures.

Acknowledgement

The authors are grateful for the bursary awarded to one of them (I.F.G.) by the UKAEA.

References

1. I. F. GUILLIATT and N. H. BRETT, *Trans. Faraday Soc.* **65** (1969) 3328.
2. P. J. ANDERSON and A. SCHOLZ, *ibid* **64** (1968) 2973.
3. M. M. NICOLSON, *Proc. Roy. Soc.* **228** A (1955) 490.
4. A. CIMINO, P. PORTA, and M. VALIGI, *J. Amer. Ceram. Soc.* **49** (1966) 152.
5. R. C. GARVIE, *Mat. Res. Bull.* **1** (1966) 161.
6. E. R. PIKE and A. J. C. WILSON, *Brit. J. Appl. Phys.* **57** (1959) 10.
7. J. W. HARRISON, AERE Report 4918 (1965).
8. P. T. B. SCHAFFER, "High Temperature Materials, Index" (Plenum Press, New York, 1964), p. 327.
9. I. F. GUILLIATT and N. H. BRETT, *Phil. Mag.* **21** (1970) 671.
10. P. J. ANDERSON, R. F. HORLOCK, and R. G. AVERY, *Proc. Brit. Ceram. Soc.* **3** (1965) 33.
11. I. F. GUILLIATT, unpublished work.

Received 5 March
and accepted 17 April 1970.

I. F. GUILLIATT
N. H. BRETT
Department of Ceramics with
Refractories Technology,
University of Sheffield, UK

---

*Subgrain Growth on Annealing of Thin Foils of Cold-rolled Aluminium**

The mechanism of subgrain growth on annealing of cold-rolled metals has been studied by several investigators after the invention of transmission electron microscopy. Reviews are found in [1] and [2]. Li [3] has proposed that subgrains grow by coalescence. The theory is supported by experimental observations made by Hu [4, 5] and Koo and Sell [6] in 3% silicon-iron and Weissmann [7] in aluminium. Walter and Koch [8, 9] have also studied 3% silicon-iron. They are of the opinion that subgrains grow by sub-boundary migration.

The author's intention was to investigate the problem of subgrain coalescence further. Thin foils of cold-rolled aluminium were observed

---

* The experimental work was done at The Laboratory of Metallurgy, The Technical University of Denmark, Lyngby, Denmark. The author is now at The Technical University of Denmark, DIA-M, Lyngby, Denmark.