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Observation of CaO corrosion by K_2O melts

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A qualitative investigation of CaO single crystal and hot-pressed polycrystal behaviour in high K_2O melts is presented. Under carefully controlled anhydrous conditions, no intermediate crystalline compound was detected at temperatures up to 800° C. Calcium oxide dissolves preferentially along grain boundaries and/or along $\langle 1\,0\,0\rangle$ directions on $\{1\,0\,0\}$ faces. The melt viscosity gradually increases with its CaO content. The single crystal corrosion rate, therefore, decreases with time and a protective glassy layer may eventually develop on its surface.

1. Introduction

Common metals and alloys as well as refractory oxide ceramics are known to be highly susceptible to hot corrosion by compounds of the alkali metals. Melts having high Na_2O or K_2O contents in particular, are very detrimental to all usual containers, including the noble metals. Very little precise information, however, has yet been published on the reaction mechanisms and dissolution kinetics in simple systems such as liquid K_2O or Na_2O in contact with a pure single phase oxide, and to the authors' knowledge, no direct observations were made on the behaviour of single crystal materials so that their ultimate resistance or intrinsic properties could be assessed.

The present paper reports preliminary results obtained on both single crystal and fully dense hot-pressed calcium oxide polycrystals in contact with potassium oxide melts in a carefully controlled anhydrous environment. Previous experience [1] had revealed that crucibles made from all commercially available oxide and non-oxide ceramics except MgO, were fully permeated within minutes in the 700 to 800° C temperature range. Magnesia behaved somewhat better and in an attempt to upgrade its corrosion resistance, LiF-doped hot-pressed polycrystals have been specially prepared. They were found to retain some integrity for hardly more than 1 h at 700° C and it was then decided to carry an exploratory investigation on the behaviour of CaO.

2. Experimental procedure

The starting materials were Verneuil-grown CaO single crystals* cleaved along at least one of the $\{1\,0\,0\}$ lattice planes. Dimensions of these crystals were in the 2 to 5 mm range. Crucibles, necessary for the experiments, were obtained by hot-pressing a high purity CaO powder† doped with 2 mol% NaF, following a procedure similar to those described by Rice [2] and Benecke *et al.* [3]. Satisfactory polycrystals were obtained with a 50 MN m^{-2} load applied for 2 h at 930° C under vacuum. The 1 cm diameter as-pressed theoretically dense blocks were subsequently annealed 48 h in air at 1500° C. Crucibles finally, were obtained by diamond machining. The potassium oxide was prepared as described by Rengade [4], by slow oxydation of the metal in anhydrous N_2/O_2 atmospheres. The produce obtained after distillation of

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* Supplied by Cristal-Tec, Grenoble, France.

† Prepared by calcination of $CaCO_3$, Prolabo, Paris, France.

the unreacted potassium was a greyish white powder consisting of K_2O 90%, with 3 to 4% KO_2, 5 to 6% K_2O_2 and 0.2 to 0.5% K_2CO_3.

Precautions were taken to avoid the presence of water during the corrosion tests which were conducted as given below after washing the crystals and crucibles in pure ethyl alcohol, followed by a 4 h calcining at 700° C under vacuum and introduction into a glove box. All experiments were carried out in a nitrogen atmosphere dried by passing over P_2O_5 columns. Phosphorous pentoxide was also placed in the glove box in order to trap any residual moisture. After weighing, the CaO single crystal was loaded with K_2O powder in a hot-pressed crucible and positioned in a vertical Vycor reactor as shown in Fig. 1. The reactor was flushed with anhydrous N_2 the pressure of which was finally set to 400 Torr. A corrosion test typically consisted in heating to 700° C in 1 h and holding at this temperature for 2 h. The furnace was then shut off and free cooling took about 10 h. It was checked that potassium oxide losses due to vaporization were always smaller than 10% (typically 6 to 7%).

After each run, the single crystal and crucible were thoroughly washed with ethanol, calcined under vacuum and their weight changes were determined. The progress of corrosion was followed by systematic microstructure observation in the scanning electron microscope, after a thin aluminium coating had been vacuum-evaporated on to the sample surfaces, following a standard procedure. At this stage, the samples could be stored for several days under vacuum before hydrated layers or crystals could be noticed.

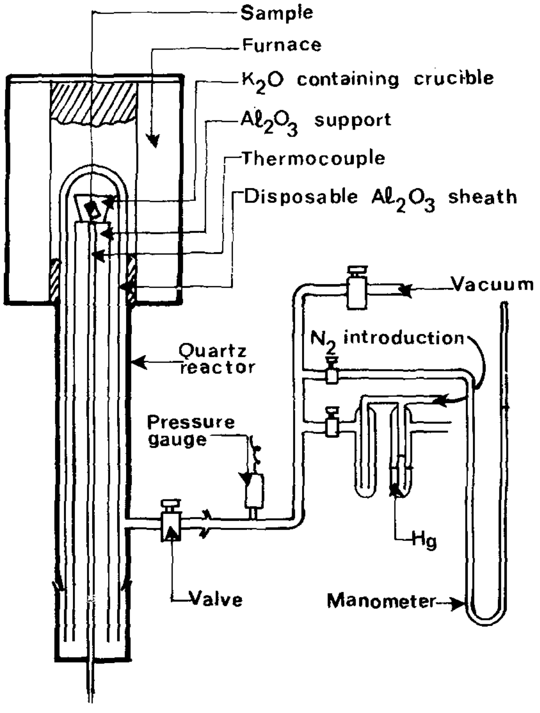

Figure 1 Schematic illustration of apparatus for studying dissolution.

3. Results and discussion

3.1. Behaviour of single crystals

Under conditions similar to those adopted in the present work, intermediate products have been observed to form when Al_2O_3 [1] or MgO [5] are heated above 600° C in K_2O melts, and it has been claimed that the respective chemical reactions could be written as follows:

$$K_2O + Al_2O_3 \longrightarrow 2KAlO_2$$

$$3K_2O + MgO \longrightarrow K_6MgO_4.$$

It is important to note that these only represent overall balances, not the actual chemical mechanisms which are much more complex and probably involve potassium peroxide, K_2O_2, as well. In the former case for example, depending upon temperature and the initial composition of the Al_2O_3–K_2O mixtures, other aluminates such as KAl_5O_8, K_3AlO_3 etc, have also been observed to form [1]. Similarly, it has recently been reported [6] that solid state reactions between K_2O and NiO yield K_2NiO_2 and K_2NiO_2 + K_2NiO_3 at 300 to 400° C. Such compounds [5, 6] can be easily hydrolysed into potassium hydroxide and the initial metal oxide or hydroxide.

In the case of CaO, no intermediate crystalline phase could be detected, either by X-ray or microstructure examinations in the corrosion residues, on the calcium oxide crystals or in reacted K_2O–CaO powder blends. It appears instead, that the solid readily dissolves into the melt, the composition of which is therefore gradually modified. Under the free convection conditions of the present work, it seems likely that the dissolution rate is diffusion controlled, as is the case in most practical situations of refractory corrosion by slags or glasses [7]. A boundary layer is then established, the thickness of which is some increasing function of the melt viscosity. The viscosity in turn increases as the calcium oxide concentration is raised. It thus follows that, for a given temperature, a CaO–K_2O glassy layer forms at the calcium oxide surface and in its immediate vicinity. The dissolution

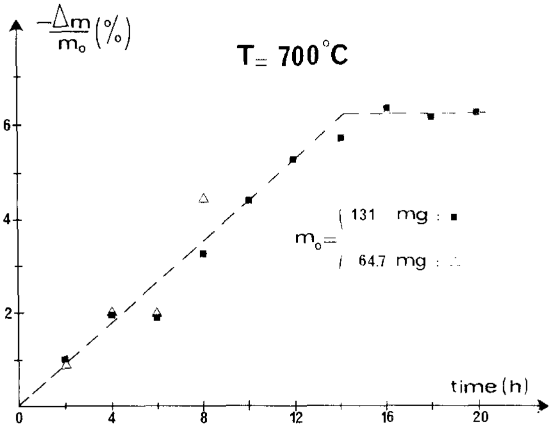

Figure 2 Weight loss of CaO crystals at 700° C.

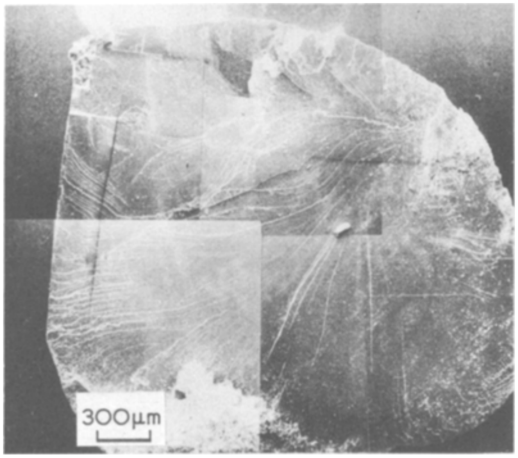

Figure 3 Cleaved {1 0 0} surface of CaO crystal.

rate will, therefore, gradually slow down and eventually stop. It may even prove practically useful for obtaining longer life times, to submit CaO to a preliminary partial corrosion at a temperature higher than the desired service temperature. Support for this behaviour is believed to be given by the single crystal weight loss curve of Fig. 2 and the following microstructural evidence.

Fig. 3 shows the typical river pattern of a cleaved single crystal along one of the {1 0 0} planes. Another cleavage crack is developing normal to the plane of the figure in the upper part of the sample. Such cracks have frequently been observed and can be penetrated by the corrosive melts as will be discussed below. On short time exposure to liquid K_2O, preferential dissolution takes place along ⟨1 0 0⟩ directions as Fig. 4 suggests. The continuous boundary layer is then progressively built and after 1 h at 700° C the CaO-rich glassy phase is about 10 to 20 μm thick. Fig. 5 gives an idea of the crystal surface at this stage: the ⟨1 0 0⟩ grooves have disappeared and cracking of the sample normal to the exposed surface makes the glassy layer visible. After several hours this layer has grown thicker and appears rough. A pattern of wide, deep grooves running in random directions with respect to crystal axes had developed (Fig. 6a). Once formed this network remains fairly stable. However, observation at higher magnifications (Fig. 6b) suggests that partially wetting secondary deposits grow on the initial glass whose degree of coverage increases with time. Neither the continuous glass nor the deposits seem much affected by mositure at this stage. Because of the surface roughness, no quantitative microprobe analysis could be made, but it was qualitatively confirmed that both Ca and K were present, exclusive of other metal impurities. Since the corrosion experiments were made in hot-pressed CaO crucibles, it is

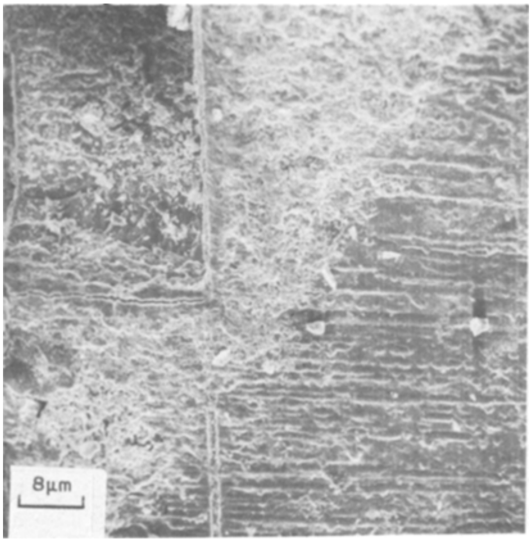

Figure 4 Preferential dissolution along ⟨1 0 0⟩ directions (700° C, 0.5 h).

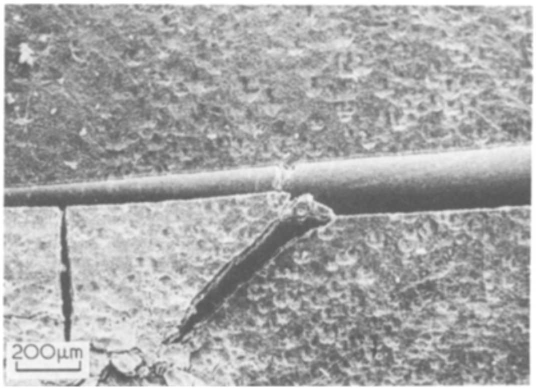

Figure 5 Continuous glassy layer on {1 0 0} surface (700° C, 1 h).

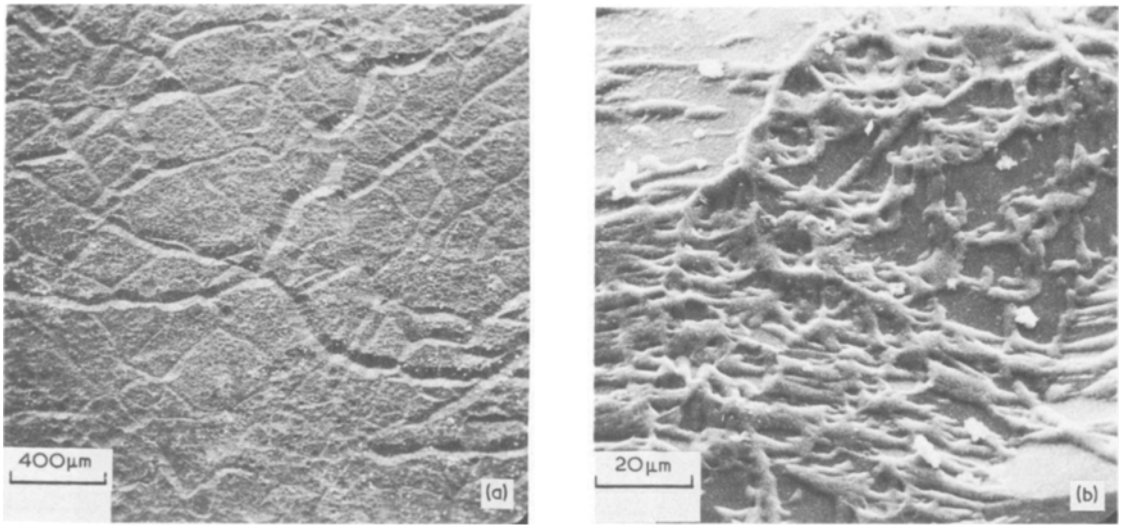

Figure 6 Thick rough glassy layer with secondary deposits (700° C, 4 h): (a) groove pattern; (b) secondary glassy deposits.

believed that the secondary deposits result from crucible dissolution and transport through the melt by natural convection.

3.2. Influence of defects and impurities

Structural imperfections in the solid as well as impurities, either in the melt or in the solid, obviously can markedly affect the corrosion rates and mechanisms, and the present system is no exception to this general rule. When grain boundaries are present, for example, they provide short circuit paths for penetration of the corrosive liquid. Fig. 7 shows typical fracture surface features of a used CaO crucible. In the uncorroded material, fracture is intergranular as evidenced on the bottom of Fig. 7a, which corresponds to the outer part of the sample. The K_2O melt is clearly seen to have penetrated from the top of the photograph where individual grains seem to have been "extracted" from the polycrystalline matrix: they are no longer bonded to their neighbours. It was also found (Fig. 7b) that preferential dissolution occasionally occurs on some grain faces along particular directions, in a manner similar to the early stages of the previously described single crystal attack. Finally, Fig. 7c shows a group of three grains in the process of being separated from each other as a result of rapid dissolution in the vicinity of the grain boundaries. This, presumably, has not yet reached the stage where exposure to moisture is no longer of consequence. The corrosion produces appearing as entanglements of plate-like crystals, are deposited in the vicinity of the grain boundaries. Such a morphology is typical of many hydrated mineral compounds [8]. Residual impurities of the initial CaO polycrystals, if locally present in excess of the solubility limits will also have taken part in the process and might have influenced the growth of the plate-like crystals.

Attempts at obtaining polished sections of the CaO single crystals with their glassy corrosion layers, that would be suitable for quantitative microprobe analysis proved unsuccessful because of the pre-existing cleavage cracks (Fig. 3) and/or the ease with which they were found to develop on grinding thus producing sample chipping. It was, however, found that cracks in the starting crystals can readily by penetrated by the corrosive melt, probably at early stages. Fig. 8 shows dendrite-like deposits on a crack plane after the upper part of the sample has been removed. The X-ray picture (Fig. 8b) was obtained with the characteristic potassium $K\alpha$ line. It appears that pure liquid K_2O is sufficiently fluid and has a small enough contact angle with CaO for a liquid film to be infiltrated into the cracks. There, some CaO dissolution will take place and it is believed that the observed coalesced drops result, at least partly, from a change in the surface tensions of CaO/melt, and/or vapour/melt, brought about by the dissolution.

Impurities present in the melts may also markedly affect the course and kinetics of the corrosion process. In the present case, however, very little may be said on this particular point. The

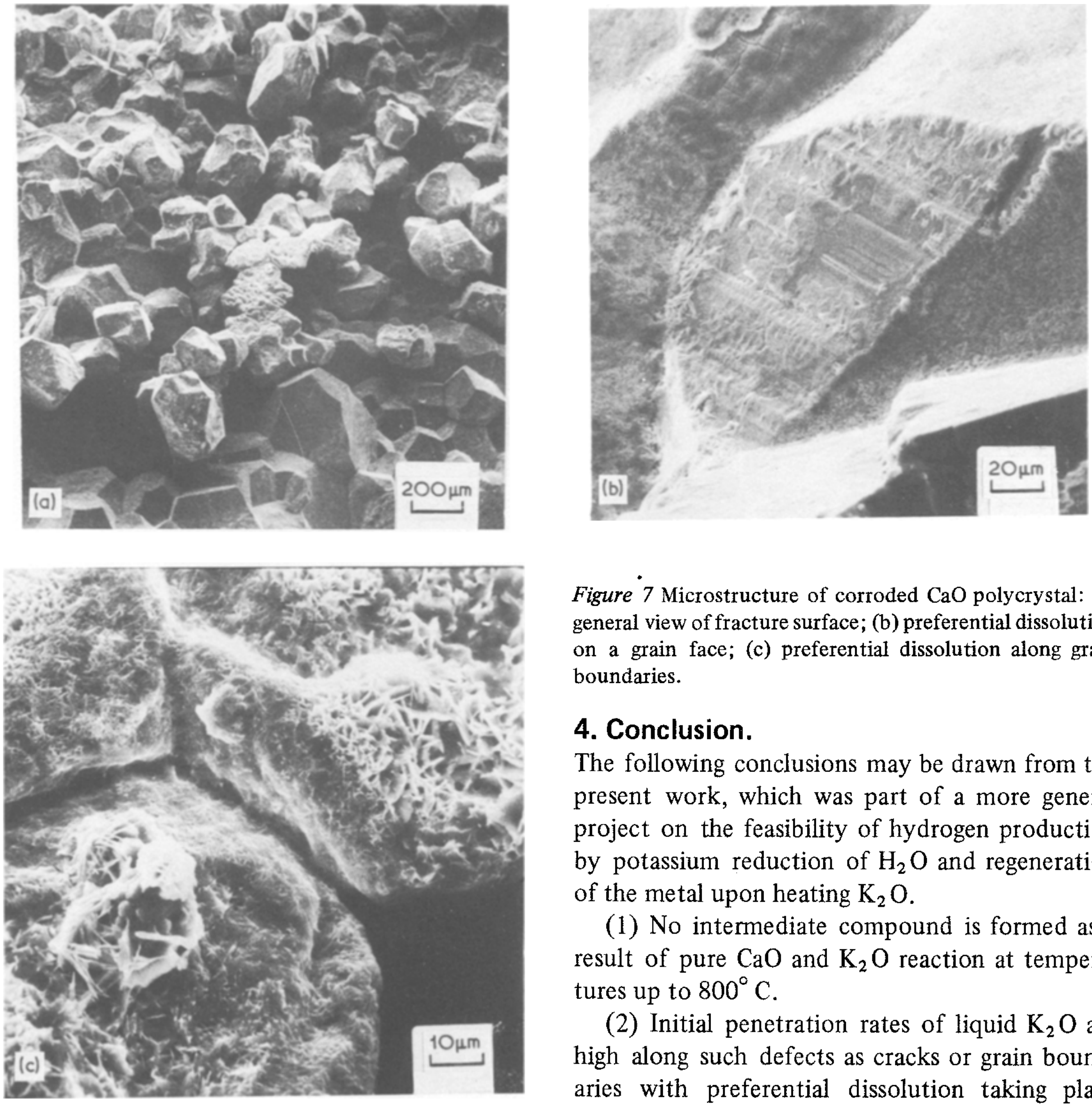

Figure 7 Microstructure of corroded CaO polycrystal: (a) general view of fracture surface; (b) preferential dissolution on a grain face; (c) preferential dissolution along grain boundaries.

high temperature behaviour of the potassium–oxygen system is still a matter of controversy, especially with respect to the stabilities and properties of its more oxygenated compounds. These may (or may not) have an influence on the overall chemical evolution and kinetics.

The melting point of the K_2O material used in the present work was experimentally checked and consistently found to equal 674 ± 20° C, in good agreement with Natola and Touzain's result [9]. It is thus our opinion that residual water, which was shown to decrease the temperature of liquid formation to 420° C, has been satisfactorily eliminated.

4. Conclusion.

The following conclusions may be drawn from the present work, which was part of a more general project on the feasibility of hydrogen production by potassium reduction of H_2O and regeneration of the metal upon heating K_2O.

(1) No intermediate compound is formed as a result of pure CaO and K_2O reaction at temperatures up to 800° C.

(2) Initial penetration rates of liquid K_2O are high along such defects as cracks or grain boundaries with preferential dissolution taking place along such directions as $\langle 1\,0\,0 \rangle$ on $\{1\,0\,0\}$ faces.

(3) As corrosion proceeds at 700° C, the K_2O melt is progressively enriched with CaO. This brings about a gradual increase in its vicosity and possibly a change in its surface energy.

(4) Upon prolonged exposure, a binary CaO–K_2O glass eventually forms which seems sufficiently adherent to the CaO substrate for the dissolution rate to be effectively reduced or even stopped.

Acknowledgements

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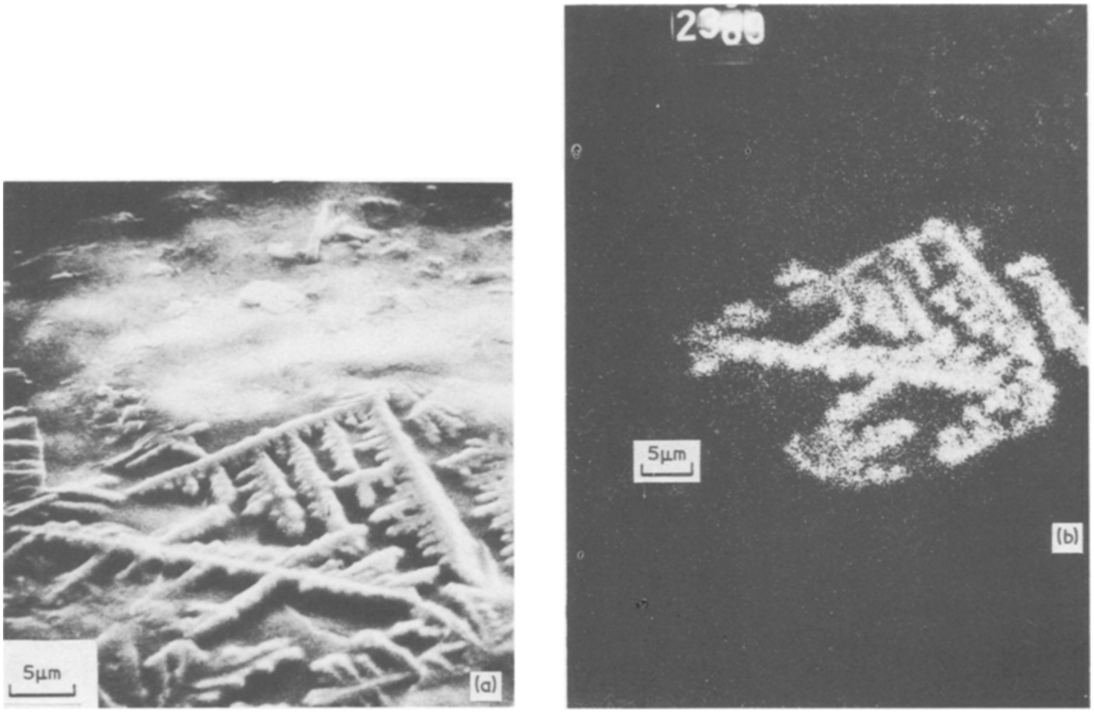

Figure 8 Corrosion products within a $\{100\}$ cleavage crack: (a) dendrite-like deposits on crack plane; (b) electron microprobe image; potassium $K\alpha$.

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