Letters

The direct observation of the reduction of $LaCoO_3$ using high voltage transmission electron microscopy

The study of the oxidation and reduction of oxide materials has in the past employed a variety of methods. Unfortunately none of these techniques allow the microstructure of the oxides to be directly and continuously observed during the reduction or oxidation and as a consequence it is possible for disagreements to arise as to the exact role, nature and sequence of microstructural changes that are associated with these reactions. The structural features that are relevant in this context are normally only observable using transmission electron microscopy; if they are to be viewed during reduction, a specialist stage is required which can maintain a local gaseous environment inside the electron microscope. This condition is fulfilled by the environmental cell, developed by Swann [1] at Imperial College, London, for use inside the AEI high voltage electron microscope. Using this cell it is possible to keep specimens under observation whilst at temperatures up to 1000° C and surrounded by a controlled atmosphere.

The reduction of lanthanum cobaltate can be studied using this technique. This material has been shown by Sis [2] to undergo a change in structural symmetry during reduction which may be associated with the formation of oxygen-deficient structures. In order to identify the presence of these structures as a consequence of reduction, and to determine their nature and role in the subsequent breakdown of the oxide, a study has been made using the environmental cell inside a high voltage electron microscope.

Samples of lanthanum cobaltate were prepared by mixing the proper proportions of lanthanum and cobalt acetate in a vibrating blender. The mixed powders were then successively calcined in air at 600° C for 2 h, reground and fired in air at 1200° C for 48 h. The resulting material was then arc melted to a button, sliced on a diamond saw and reoxidised, the final crystalline product being identified as lanthanum cobaltate using X-ray diffraction. Specimens suitable for transmission electron microscopy were prepared by mechanical grinding followed by ion-beam thinning, using argon ions at a voltage of 6 kV. The heating of the specimen inside the high voltage electron microscope was achieved using a platinum/rhenium strip heater and a controlled atmosphere of 10 torr hydrogen balanced helium was maintained using a Swann environmental cell. During the reduction the temperature was kept at a constant 500 ± 50° C and the observations recorded using standard video and film techniques. Since these observations are made using a high voltage electron beam it is important to establish whether this itself is perturbing the results. For this to be the case, the accelerating voltage used in the electron microscope would have to produce electron displacement damage. In order to avoid this possibility the minimum voltage necessary to produce observable electron irradiation damage was determined prior to reduction studies. This voltage was found to be 500 kV and all the reduction observations were made at an operating voltage of 400 kV.

Prior to examination under reducing conditions in the environmental cell, the initial microstructure of the as-prepared lanthanum cobaltate was observed. The material was found to have an

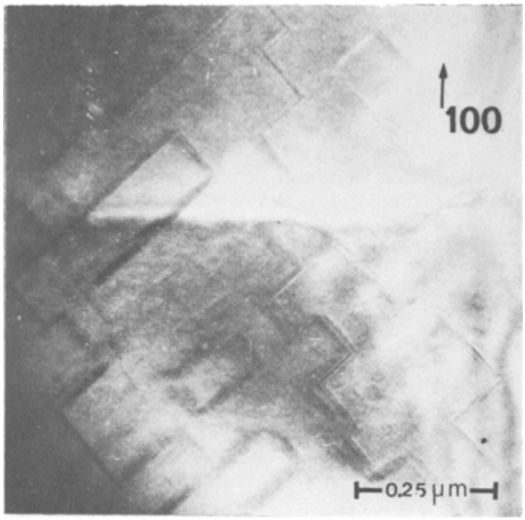

Figure 1 ⟨1 0 1⟩ anti-phase boundaries observed in as-prepared lanthanum cobaltate.

overall grain size of between 1 and 2 μm with varying amounts of defect microstructure within the grains. One of the main types of defect that was observed is shown in Fig. 1. The fringe contrast from the planar interfaces shown in this figure and the extra spots in the {1 1 1} electron diffraction pattern obtained from the same area show that they are ⟨1 0 1⟩ anti-phase boundaries (APBs). Whilst this particular planar defect does not itself accommodate any oxygen deficiency its relevance is that it is a member of the "crystallographic shear" (CS) family of defects, which although not reported previously as occurring in perovskite lanthanum cobaltate, have been shown [3] to be present in many other ReO_3 based structures as a means of accommodating anion deficiencies. In view of the large number of the ⟨1 0 1⟩ APBs that were observed, a careful search was made for the presence of other CS faults. It has been found that in the starting material there are small numbers of ⟨0 0 1⟩ CS planes, indicated by the presence of extra spots, in the ⟨0 0 1⟩ direction in the {1 0 0} diffraction pattern, obtained from an area where faults on the {0 0 1} planes could be resolved in the electron microscope. Since reducing conditions do not occur during thin foil preparation it must be concluded that these ⟨0 0 1⟩ CS faults are produced during the preparation of the bulk material and if they are to be identified as a dynamic means of incorporating oxygen deficiencies it must be further shown that they can also occur as a consequence of reduction.

Unfortunately, the other techniques that can be used to study reduction, such as thermogravimetry, magnetic measurements and X-ray diffraction cannot unambiguously identify small regions containing ⟨0 0 1⟩ CS planes, especially as they are also present in the starting material. In order to overcome this problem by using the environmental cell, the grains that were selected for study were initially defect free and were orientated as close to ⟨1 0 0⟩ as possible. On reduction, the first observable microstructural change was the formation of areas of faulting which occurred during the first hour of reduction. The individual faults that are produced at this stage cannot be resolved in the electron microscope due to thermal vibrations and tilt limitations imposed by the use of the environmental cell. However, the onset of faulting is accompanied by the formation of extra spots in the diffraction pattern, as shown in Fig. 2, which are identical to the extra spots which have previously been shown to correspond to ⟨0 0 1⟩ CS planes. Also associated with this stage of reduction was the presence of small amounts of cobalt oxide and free cobalt, identified from electron diffraction evidence.

After approximately 1 h, the formation and movement of the faults was followed by a gradual breakdown of the grain size to 0.1 μm. It was only towards the end of this grain size change that the presence of lanthanum oxide could be identified. This sequence of events is illustrated in Fig. 3, which shows three areas which have reached different stages of reduction, and Fig. 4, which shows in more detail the final fine-grained microstructure. Following the decrease in grain size there is a further breakdown producing variations of thickness. After this stage the specimens did not retain sufficient rigidity and broke up under the action of the electron beam and the thermal stresses produced by the heater.

Whilst the observations that have been described above represent only a broad outline of the sequence and nature of the microstructural breakdown due to reduction, they have shown that in

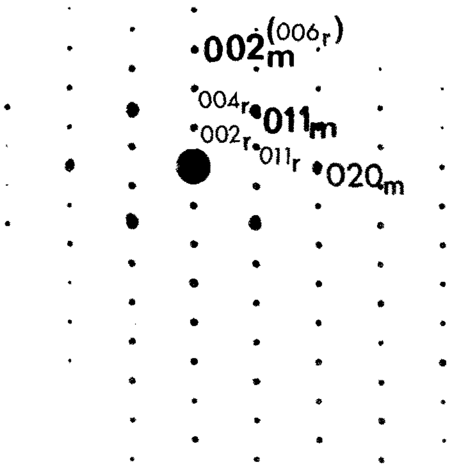

Figure 2 {0 0 1} electron diffraction pattern showing the presence of extra spots due to the reduction induced formation of ⟨0 0 1⟩ CS planes. Spots from the original unreduced pattern are indexed with the subscript m, and those observed to form during reduction with the subscript r.

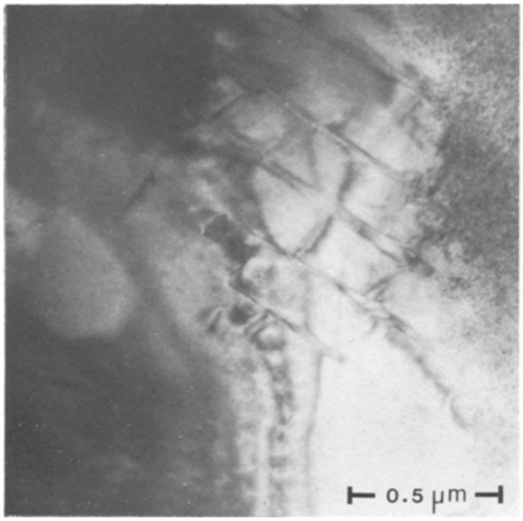

Figure 3 Micrograph showing regions where reduction has proceeded at different rates resulting in areas of faulted unreduced and fine grained $LaCoO_3$. It should be noted that this micrograph was taken at temperature in the environmental cell which precluded the accurate setting of diffraction conditions.

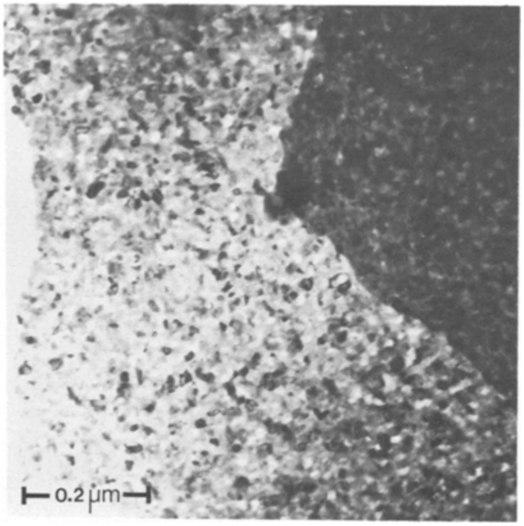

Figure 4 Fine grained oxides of cobalt and lanthanum resulting from reduction.

the early stages of reduction there is a change in structure due to a systematic faulting mechanism. Although other workers [4], have shown that ABO_{3-x} polytypes of the basic ABO_3 perovskite structure can occur when regular faulting is present, for example $BaFeO_{2.8}$ [5], the current work has demonstrated that this systematic faulting can also be produced to accommodate a reduction-induced anion deficiency in lanthanum cobaltate. Another significant observation is that immediately after the faulting, only cobalt oxide is detected in the electron diffraction pattern and lanthanum oxide is only determined to be present just prior to the final complete breakdown of the microstructure. This sequence of events requires that in reduction a structural change occurs which produces cobalt oxide yet retains the lanthanum in a stable mixed oxide form. In this context it is significant to note that the formation of two contiguous ⟨0 0 1⟩ shear planes in an ReO_3 structure, a not unlikely event in view of the ⟨0 0 1⟩ faulting already observed, results in a localized face centred cubic oxygen lattice which could allow some atomic ordering to keep the lanthanum in a stable form. Since the hydration characteristics of lanthanum oxide have a direct influence on the final mechanical breakdown of lanthanum cobaltate, due to reduction, a careful study is being made of this intermediate stage of reduction. This work will be reported at a later date.

References

1. P. R. SWANN and N. J. TIGHE, *Jernkont Ann.* **155** (1971) 502.
2. L. B. SIS, Ph.D. Thesis, University of Illinois (1972).
3. J. S. ANDERSON, "Reactivity of Solids", (Chapman and Hall, London, 1972) p. 23.
4. J. L. HUTCHISON and A. J. JACOBSON, *Acta. Cryst.* **B31** (1975) 1442.
5. J. L. HUTCHISON, "Development in Electron Microscopy and Analysis", (Academic Press, London, 1976) p. 241.

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