Notes

Ordering Phenomena in U_4O_{9-y} Crystals studied by Transmission Electron Microscopy

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Striations observed during transmission electron microscopy of hyperstoicheiometric UO_2 have the same crystallographic orientation as the chains of oxygen defect clusters previously predicted in a co-ordination model of the structure based on chained clusters parallel to the $\langle 110 \rangle$ direction.

The arrangement of oxygen interstitials in hyperstoicheiometric UO_2 has been extensively investigated by *X*-ray [1,2] and neutron [3-5] diffraction techniques. Although a superstructure has been inferred from diffraction data based on a parent fluorite lattice, direct observations of this structure have not been reported. Recently a co-ordination model for the defect structure of the hyperstoicheiometric compound UO_{2+x} was proposed [6,7] which was based on the linear ordering of 2 : 2 : 2 oxygen defect clusters described by Willis.[3] Structures of this kind often manifest themselves in transmission electron microscopy (t.e.m.). Previous general t.e.m. studies, however, have been confined to stoicheiometric UO_2 in which striated structures were observed on heating and interpreted in terms of crystallographic shear [8] and surface faceting.[9] In this paper we present the results of a preliminary t.e.m. study of crystals of higher stoicheiometry than UO_2, nominally a mixture of UO_{2+x} and U_4O_{9-y}.

Experimental

Two polycrystalline samples of hyperstoicheiometric UO_2 were kindly supplied to us by courtesy of Dr. B. T. M. Willis, Atomic Energy Research Establishment, Harwell, Oxfordshire. The lattice parameter of these samples was determined by *X*-ray diffraction as $a_0 = 5.443$ Å, which from the relationship of Lynds *et al.* [10] indicates a composition $UO_{2.24}$ very close to U_4O_9. Specimens <2000 Å in thickness were prepared for t.e.m. by jet electropolishing.

Results and Discussion

Figure 1 shows a ' dark field ' image formed when a diffracted electron beam from the thinned crystalline sample was passed through the objective aperture of the electron microscope. Striations parallel to $\langle 110 \rangle$ with an approximate spacing of 30 Å were observed. Strong contrast can be seen in region A, near to a hole in the specimen, with the striations well defined in one $\langle 110 \rangle$ direction, whilst in region B an area of weaker contrast shows mutually orthogonal $\langle 110 \rangle$ striations. U_4O_9 superlattice reflections were present in the diffraction pattern of this area.

Striation contrast observed in the second specimen was similar to the above but was confined to local islands within some of the grains. In Figure 2, islands of banded contrast can be seen, with mutually orthogonal striations parallel to $\langle 110 \rangle$ and about 50 Å apart. The islands were present in the freshly polished specimen and their contrast varied as a function of specimen tilt and was stronger the thicker the section. U_4O_9 superlattice reflections were present in electron diffraction patterns from the islands, but not in those from the matrix. The islands were unstable under the heating effect of the focused electron beam. There were instances of a slow change of shape with the islands adopting a more regular crystallographic shape, and of sudden fragmentation into small irregular shapes possessing Miller indices. There was no reversion of the structure on cooling.

The above observations add weight to our view of oxidised UO_2 phases at room temperature comprising U_4O_{9-y} structures in which long-range ordered defect structures occur together with UO_{2+x} in which a more random defect structure is present. Moreover, the striated structure observed is entirely consistent with a bulk effect. This contrasts with the observations of Kraševec and Navinšek,[9] on UO_2, who considered that their striations were caused by the formation of surface facets during heating. Similarly, parallel striations have been observed during the annealing of UO_2 under reducing conditions.[6] The simultaneous observation of diffraction spot splitting was accounted for by the formation of planar faults by crystallographic shear. There was little evidence of the splitting of diffraction spots in the experiments reported here.

The model presented by Allen and Tempest [7] for the superlattice of U_4O_9 and possibly higher oxides was based on the linear ordering in chains of oxygen defect clusters parallel to $\langle 110 \rangle$. There is satisfactory agreement between crystallographic orientation predictions of the model and the present observations. Outwardly, however, the observed variable striation spacing of *ca.* 30—50 Å is larger than the anticipated spacing of *ca.* 13 Å required by the model for the composition of U_4O_9. However, restrictions imposed by chain nucleation and growth as well as overall symmetry requirements have yet to be applied rigidly. For instance, a unique [110] chain axis is not a prerequisite of the model and interleaved mutually orthogonal chains could be present producing parallel striations with a spacing of *ca.* 26 Å in better agreement with the smallest spacing observed.

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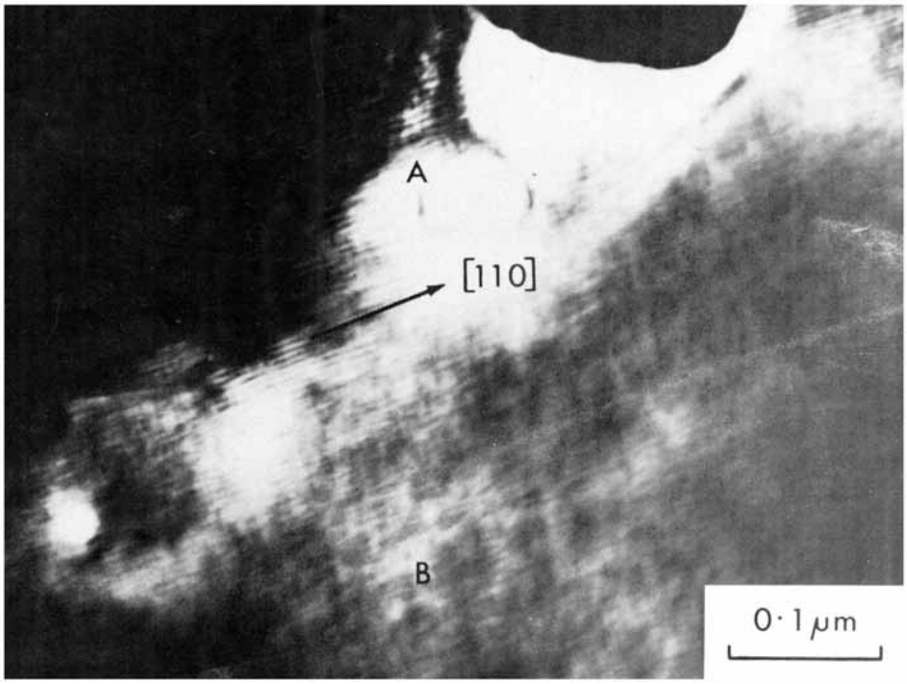

Figure 1. Dark field image of striated area showing the marked contrast from striations parallel to [110] in region A and the weaker contrast in two orthogonal ⟨110⟩ directions in region B

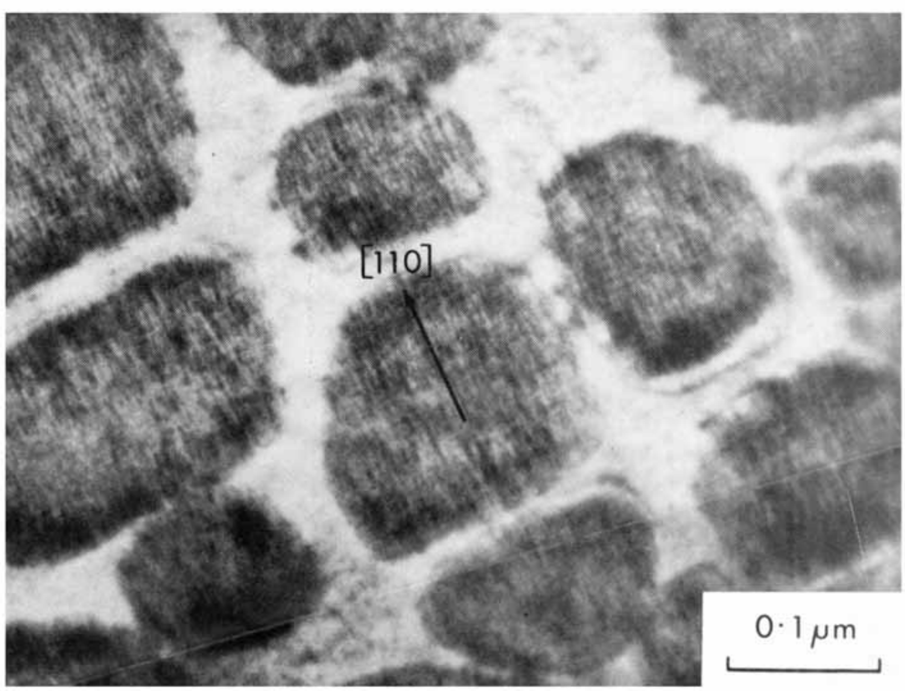

Figure 2. **Bright field image of islands showing striation contrast; striations are parallel to [110]**

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