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Microstructures Occurring in Reduced Vanadium Dioxide

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Slightly oxygen-deficient VO_2 contains small clusters of (121) *CS* planes which ultimately order into the V_nO_{2n-1} series of oxides with increasing degrees of reduction. The fact that *CS* is limited to (121) planes within this system may be due to a specific degree of ionic relaxation within the *CS* plane. Nominal compositions near to M_xVO_2 in the Al–V–O, Ga–V–O, and Fe–V–O systems contain microstructures which are essentially similar to those of the binary system and no new *CS* plane types are found at temperatures of the order of 1400°K.

Introduction

X-ray studies, culminating in the paper by Andersson and Jahnberg (*1*), showed that reduction of the related oxides TiO_2 and VO_2 leads to the formation of homologous series of oxides, Ti_nO_{2n-1} ($10 \geqslant n \geqslant 4$) and V_nO_{2n-1} ($8 \geqslant n \geqslant 4$). These phases are structurally related to one another, and can be thought of as being made up of slabs of the parent oxide, TIO_2 or VO_2, joined along (121) planes. The width of the slab of parent oxide controls the value of *n* in the series formula and the (121) planes which demark the boundaries of the slabs have become referred to as crystallographic shear (*CS*) planes. Full details of the crystal chemistry of *CS* phases related to TiO_2 and VO_2 may be found in the review article by Bursill and Hyde (*2*).

Since these X-ray studies, a large amount of information has been gathered concerning the crystal chemistry of reduced and doped TiO_2, mainly by electron microscopy. It was found that initial reduction led to the appearance of *CS* planes on ($13\bar{2}$) planes and these ultimately ordered to form a new series of oxides, also having the general formula Ti_nO_{2n-1}. Between this group of phases and the earlier series containing ordered ($12\bar{1}$) *CS* planes, a structurally complex region occurs in which *CS* plane orientations pass from ($13\bar{2}$) to ($12\bar{1}$). The crystal chemistry of all these oxide phases has been described in detail by Bursill and Hyde (*2*).

One way of describing these *CS* phases is to regard them as intergrowths between elements of Ti_2O_3 (which has the corundum structure) and TiO_2. One would therefore expect that other oxides with the corundum structure would behave in a similar manner. This is not universally true, but the Cr_2O_3–TiO_2 (*2, 3*) and V_2O_3–TiO_3 (*4*) systems contain extensive *CS* phases analogous to the binary system, and the Fe_2O_3–TiO_2 system (*5*) also supports *CS* at higher temperatures. Although the Al_2O_3 system does not form *CS* phases, the Ga_2O_3–TiO_2 system also contains an extensive series of oxides, having the general formula $Ga_4Ti_{m-4}O_{2m-2}$, which can be regarded either as *CS* phases or as intergrowths between Ga_2O_3 and TiO_2 (*6*).

It is therefore surprising that the literature

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concerning the structural chemistry of reduced VO_2 is somewhat scanty. Bursill and Hyde (*2*) mention that reduction of VO_2 leads to isolated (121) planes but do not comment further on this feature. Kosuge *et al.* (*7*) carried out a brief electron microscope study on reduced VO_2 and confirmed the existence of the V_nO_{2n-1} series of oxides, which were based upon ordered (121) *CS* planes. Samples of composition $VO_{1.933}$ and $VO_{1.95}$ were reported to contain mixtures of VO_2 and V_9O_{17}, and this latter finding was substantiated by Horiuchi *et al.* (*8*). Finally, Plougonven (*9*) prepared one sample of composition $VO_{1.9948}$ and reported it to contain a small concentration of ordered (121) *CS* planes in a matrix of VO_2. Although the literature contains many other references to VO_2 and the V_nO_{2n-1} oxides, these are largely concerned with their physical properties or crystal structure and do not consider defect structures in depth.

In view of the quite different behavior between TiO_2 and VO_2 on reduction, and the lack of detailed reports in the literature, we undertook an electron microscope study of slightly reduced VO_2. A variety of preparation techniques and dopants were used, but in all cases only (121) *CS* planes were found. This result is discussed in terms of the interactions between *CS* planes, as described by Iguchi (*10*), and other features of the crystal chemistry of these oxides.

Experimental

Preparation of samples was carried out starting from vanadium metal chips and vanadium pentoxide powder, both of Specpure quality, supplied by Johnson Matthey Ltd. V_2O_3 was prepared by hydrogen reduction of V_2O_5, by heating for 2 hr at 873°K and then for an additional 6 hr at 1273°K. VO_2 was prepared by heating equimolar quantities of V_2O_5 and V_2O_3 in sealed evacuated silica ampoules for 3 days at 1273°K, followed by resealing and further heating for another 7 days at 1273°K. This produced blue-black well-faceted crystallites with edges of up to 1 mm in length. In doping experiments the oxides Al_2O_3 (B.D.H. Ltd., Analar); Ga_2O_3 (Koch–Light Ltd., 99.99%); Cr_2O_3 (Johnson Matthey Ltd., Specpure); and Fe_2O_3 (Cerac/Pure Inc., 99.5%) were used.

Samples were prepared by mixing together appropriate weights of the above oxides or vanadium metal and compacting them into pellets of 5-mm diameter using a pressure of 18 kN. Some of these pellets were heated in sealed evacuated silica ampoules at temperatures between 1273 and 1474°K for times of 1 to 14 days, while others were melted under an argon atmosphere using a cold hearth arc melting technique. Arc melted beads were examined as prepared or else annealed in evacuated silica ampoules at temperatures in the range 1073 to 1373°K for times varying from 5 to 121 days. In some additional preparations crystals of VO_2 were heated in sealed evacuated silica ampoules with sufficient vanadium metal to give overall compositions in the range VO_2 to $VO_{1.9}$. These crystals were not compacted and their morphology was retained throughout the heating period, which was either 1 day or 3 days at a temperature of 1473°K. All annealed samples were quenched in cold water after heat treatment.

The compositions of binary oxide samples were determined after reaction by oxidation to V_2O_5 using a Sartorius Model 4102 microbalance. The composition of ternary oxides were estimated from a knowledge of the phases present in each sample, as determined by X-ray powder diffraction.

All samples were examined structurally by recording their powder X-ray photographs using a Guiner–Hägg focusing camera and strictly monochromatic Cu$K\alpha_1$ radiation, with KCl (a = 0.62923 nm at 298°K) as an internal standard. Film measurements were refined using least-squares techniques. The crystalline habit of materials was characterized using a Zeiss Ultraphot or Vickers 55 optical microscope. The microstructures of samples were determined using a JEM 100B electron microscope.

Results

Binary Oxides

All sample preparations made in the binary oxide system appeared to be in good accord with the literature data. The arc melted samples were most disordered and these preparations gave X-ray films with rather broad and diffuse lines. The solid-state preparations and the annealed arc melted preparations gave much sharper X-ray films which could be accurately measured. The lattice parameters of the phases present agreed well with the literature data. For example, the values found for VO_2 and V_8O_{15}, which coexisted in a sample of overall composition $VO_{1.9319}$ prepared by solid-state reaction at 1273°K for 14 days were

VO_2: $a = 0.5745 \pm 0.0003$ nm, $b = 0.4519 \pm 0.0004$ nm,
$c = 0.5372 \pm 0.0004$ nm, $\beta = 122.58 \pm 0.03°$;

V_8O_{15}: $a = 0.5432 \pm 0.0004$ nm, $b = 0.6989 \pm 0.0004$ nm,
$c = 3.7078 \pm 0.0004$ nm, $\alpha = 98.76 \pm 0.05°$,
$\beta = 128.39 \pm 0.06°$, $\gamma = 108.93 \pm 0.6°$,

X-ray results indicated that at the oxygen-rich end of the phase region VO_2 coexisted with V_8O_{15} while at compositions below about $VO_{1.9}$, homologs of the V_nO_{2n-1} series coexisted. Frequently, more than two phases were present in a sample, indicating that true thermodynamic equilibrium had not been achieved. In all samples, regardless of overall composition, no systematic changes in lattice parameter were found, and the X-ray data were in accord with the assumption that VO_2 and the V_nO_{2n-1} oxides were line phases.

In samples of overall composition between approximately $VO_{1.9}$ and $VO_{1.75}$ electron microscopy showed that the microstructures consisted of ordered or disordered intergrowths of the V_nO_{2n-1} homologs. The disorder was greatest in samples which had been arc melted only. Figure 1 shows an example. In this medium-resolution micrograph the dark lines represent the *CS* planes. It is seen that a variety of spacings between the *CS* planes occur, often grouped into bands of similar spacing. The spacings measured corresponded to those expected for the oxides V_6O_{11} to V_8O_{15}. Thus the crystal fragment can be

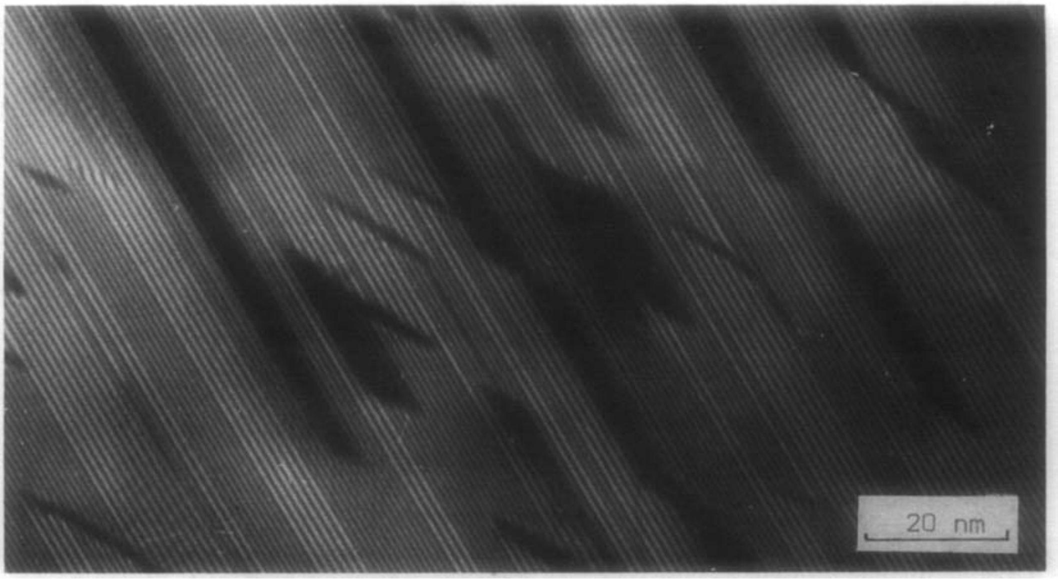

FIG. 1. Electron micrograph showing disordered intergrowths of the oxides V_6O_{11}, V_7O_{13}, and V_8O_{15} in a fragment of crystal from an arc melted sample.

considered to be a disordered intergrowth of these oxides and is clearly not at equilibrium. In contrast samples annealed for 121 days at 1373°K were usually well-ordered and crystal fragments showed only one *CS* plane spacing.

Samples with overall compositions lying between VO_2 and approximately $VO_{1.9}$ contained several types of microstructure. At the oxygen-rich end of this composition range, many fragments were unfaulted except for occasional damage associated with fracture. Diffraction patterns of these fragments could be indexed in terms of a tetragonal rutile cell which was therefore presumed to be VO_2. No boundaries of the type observed by Hayashi *et al.* (*11*) were observed, but these were not specifically sought. In samples with compositions nearer to $VO_{1.9}$ the predominent microstructure corresponded to the oxide V_8O_{15}. This was more or less disordered depending upon the history of the sample itself. The oxide V_9O_{17} was much more rarely found in all our preparations, and apart from isolated lamellae in very disordered crystals, oxides V_nO_{2n-1} with n values equal to or greater than 10 were never found.

The remaining type of microstructure found consisted of VO_2-like crystals containing small groups or packets of *CS* phases. These groups invariably consisted of between 2 and 7 or 8 parallel *CS* planes, as shown in Fig. 2, individual *CS* planes never being observed. Alignment of the *CS* plane packets parallel to the electron beam showed them always to lie upon (121) planes. The spacing of the *CS* planes in these small groups corresponded to that found in the oxides V_8O_{15} or V_9O_{17}. In the case of the crystals of VO_2 which were reduced by way of vanadium metal, identical microstructures resulted.

During normal observation of crystals containing small groups of *CS* planes, new *CS* planes were sometimes seen to grow laterally and be added onto the packet. It was noted that fragments of the V_nO_{2n-1} oxides and also those containing packets of about 7 or more *CS* planes were quite stable in the electron beam, even under fairly intense irradiation.

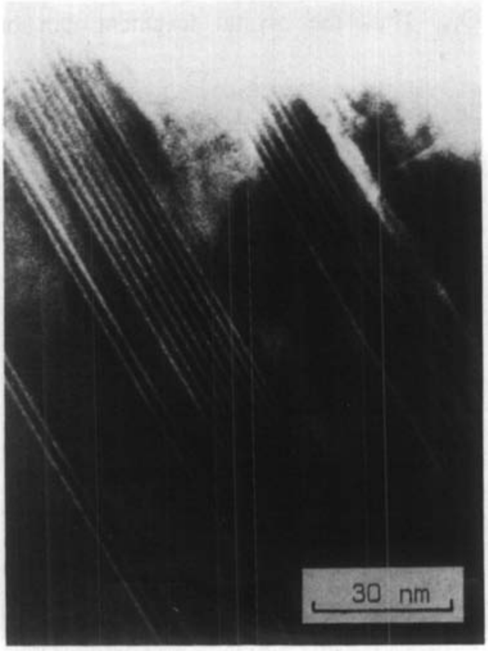

FIG. 2. Electron micrograph showing isolated groups of (121) *CS* planes in a VO_2 matrix.

Ternary Oxides

Four ternary systems were studied, the Al–V–O, Ga–V–O, Cr–V–O, and Fe–V–O systems. Here we are not intending to discuss the phase equilibria in general but only the microstructures of the *CS* phases present. Despite the variety of preparation techniques and conditions used, the only *CS* structures found were identical to those in the bindary system. That is, either small isolated groups of (121) *CS* planes were seen in what appeared to be a matrix of normal VO_2, or else more or less disordered V_nO_{2n-1} *CS* phases were found. In no samples were *CS* planes or any other planar faults observed which were not on (121) planes.

X-ray diffraction studies on these materials yielded complex films and suggested the presence of a number of previously unreported phases. However, in the region close to the

M_xVO_2 line of the phase diagram, reflections from the V_nO_{2n-1} phases could be readily detected. Where it was possible to measure these reflections accurately, they showed no indication of any systematic deviation of the unit cell size from those of the pure binary oxides. This suggests that large amounts of doping by the M^{3+} ions does not take place, but it does not rule out small degrees of incorporation of the dopant metal into the *CS* structures.

Only one other microstructure was noted. This consisted of a complex twinned material which was observed in arc melted samples from all four systems studied. This material is similar in appearance to some of the high-temperature phases found in the Cr_2O_3–TiO_2 (*2*, *3*) and Fe_2O_3–TiO_2 (*4*) systems and it may be a new structure type or a complex *CS* type which is stabilized by the presence of the ternary metal ions. Its structure is at present unknown.

Discussion

Our investigations show that over a wide range of preparative conditions, reduction of VO_2 results in the formation of small groups of *CS* planes. The *CS* planes lie only on (121) planes. The same result holds good when ternary Al–V–O, Ga–V–O, Cr–V–O, and Fe–V–O samples are prepared, although in these latter systems it is not certain how much ternary ion has entered the reduced VO_2 matrix. The small groups of *CS* planes can be considered to be coherent intergrowths between VO_2 and the oxides V_9O_{17} or V_8O_{15} and in this sense the system can be regarded as behaving in a classical fashion. In our experiments we found no evidence for an oxide $V_{10}O_{19}$ or any other higher oxide, but it may well be that the phase range over which the V_nO_{2n-1} oxides exist broadens somewhat at higher temperatures, and previous reports of the existence of $V_{10}O_{19}$ may be due to such differences in the preparation conditions.

Although our results do not give direct evidence for the transformation of VO_2 into V_8O_{15} or V_9O_{17} they do suggest a mechanism. It would seem reasonable to suppose that initial reduction leads to the formation of a *CS* plane nucleus at the crystal surface which then grows by a dislocation mechanism similar to that proposed by Anderson and Hyde (*12*) to pass through the crystal. However, as single *CS* planes were not observed, pairs of *CS* planes being the smallest number seen, the possibility arises that the initial nucleation is of a pair of *CS* planes. These could grow through the crystal in a hairpin arrangement as suggested by Van Landuyt and Amelinckx (*13*). However, our results do not discriminate definitely between these two possibilities.

Once this initial stage has been reached, it seems that further *CS* planes can add to the pair, causing it to grow into distinct lamellae of V_9O_{17} or V_8O_{15}. The new *CS* planes seem to nucleate preferentially at such a position that little lateral movement is needed. Results on the tungsten oxides (*14*) strongly suggest that this position is governed by elastic strain and that new *CS* planes nucleate in a position of minimum strain energy. Continued reduction would then cause these lamellae to grow into large volumes of V_9O_{17} and V_8O_{15}, so that the microstructure of a reduced VO_2 crystal is likely to contain a mosaic or more or less disordered grains of these oxides.

As was noted in the Introduction, only two oxides with the rutile structure support *CS*, namely, VO_2 and TiO_2. It is therefore of some interest to compare these results with those of the titanium oxides. The most obvious difference is that reduction of TiO_2 leads to *CS* formation on (132) planes while in the case of VO_2, reduction leads directly to (121) *CS* planes and to the formation of V_9O_{17} or V_8O_{15}. Iguchi (*10*) has estimated the formation energy of CS planes in an idealized rutile structure by calculating both the elastic strain energy due to the *CS* planes in the parent matrix and the energy required to lose oxygen from the matrix to form a unit area of *CS* plane. Both of these pointed to the fact that (132) *CS* planes should form in preference to (121) *CS* planes.

If we now consider the differences between the VO_2 system and the idealized system it is clear that the relative energy required to lose oxygen per unit area of *CS* plane in any oxide will always be in the sequence $(121) > (132)$ because the geometry of the boundaries concerned is always the same. It would thus appear that of the two, elastic strain energy is more important. Iguchi (*10*) has shown that the strain in the rutile matrix between (121) *CS* planes is always less than that between (132) *CS* planes, but that the relaxation energy of the ions within the *CS* planes themselves is greater for (121) *CS* planes than for (132) planes for n values of 7 and greater in the formula M_nO_{2n-1}. As a minimum energy situation is preferred, the difference in behavior between TiO_2 and VO_2 may be attributable to the relaxation of the ions within the *CS* planes.

Another significant difference between TiO_2 and VO_2 is the behavior of the crystals upon reaction with M^{3+} ions. In the TiO_2 system, complex *CS* or intergrowth phases often form. In the analogous situation with VO_2 no complex *CS* phases at all appear. Perhaps the most obvious difference between TiO_2 and VO_2 lies in the fact that vanadium has a higher valency available to it, the V^{5+} state, whereas titanium has only the Ti^{4+} state. Thus substitution of M^{3+} ions into the octahedral sites of TiO_2 needs a mechanism whereby the crystal can lose oxygen to maintain neutrality. On the other hand, a VO_2 crystal doped with M^{3+} can retain charge neutrality by simply incorporating into the crystal an equivalent number of V^{5+} ions, a process involving only electron shifts. Other reasons, however, may be important and to clarify the differences between the binary and ternary vanadium oxides with those of titanium, it would be of interest to compare the behavior of mixed Ti, V dioxides with that of the parents.

Besides a comparison with the titanium oxides it is of interest to compare both TiO_2 and VO_2 with NbO_2. In this latter oxide, no *CS* planes at all are formed upon reduction (*15*). The reason why this should be so is not known with certainty and a number of factors probably play a part. For example, a cationic preference for octahedral coordination seems important. In addition, (121) and (132) *CS* planes can be regarded as lamellae of a corundum-type oxide coherently intergrown in the parent oxide matrix. As in the niobium–oxygen system no corundum oxide appears to form, and in the next lower oxide, NbO, the cations are not octahedrally coordinated, it suggests that *CS* plane formation in NbO_2 would be inherently less likely than in VO_2 or TiO_2. However, these crystal–chemical arguments do not answer the question entirely, as β-Ga_2O_3 forms *CS* structures with TiO_2 although it does not possess the corundum structure and contains some cations in tetrahedral rather than octahedral coordination (*6*).

It is therefore necessary to consider features of the structures other than simple crystal–chemical aspects. It has been pointed out that an empirical correlation exists between defect structure and dielectric constant, and that materials with high static dielectric constants are more likely to support *CS* formation (*16*). It was tentatively suggested that this may be related to the lattice dynamics of the structure and in particular to the stability of the low-frequency soft modes. From this point of view the trend from TiO_2 to NbO_2 via VO_2 seems consistent. TiO_2 is an insulator with a high dielectric constant. NbO_2 is a metal and would not be expected to support *CS* on this basis. VO_2, with its well-known metal-insulator transition appears to be intermediate between TiO_2 and NbO_2. It would be of interest to compare the dielectric behavior and the lattice dynamics of these three materials carefully in order to determine the extent to which the suggestions briefly mentioned above are responsible for the change in defect structure in these and other rutile structure materials.

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