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BRIEF COMMUNICATIONS

On the Mechanism of Oxidation of {103}-*CS* Structure in the W–O System

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The reduction of tungsten trioxide crystals by the gaseous buffer equilibration technique and the structural transformations involved have recently been studied by high-resolution transmission electron microscopy (HREM) at this laboratory (*1–3*). During reduction of WO_3 crystals at about 1270 K, in the interval of oxygen partial pressures from 1.0×10^{-2} to 2.7×10^{-6} Pa, {102} crystallographic shear (*CS*) structures are formed with compositions in the range WO_{3-x}, $0 < x \leq 0.07$. Further reduction gives rise to the intergrowth of {102}-*CS* and {103}-*CS* structures (1,4), while pure {103}-*CS* structures in the composition interval of $0.07 \leq x \leq 0.01$ are formed at oxygen partial pressures of 4.0×10^{-7} to 6.0×10^{-8} Pa. References (*5, 6*) are recent reviews of the studies of the W–O system at this laboratory. In light of these results, it was considered of interest to use the HREM imaging technique to study the reoxidation mechanism of {103}-*CS* structures.

Some previous results pertinent to this problem should be mentioned. Observing selected diffraction lines with the aid of high-temperature X-ray diffractometry, Gado (*7*) found that the mechanism of reduction of tungsten trioxide crystals to $W_{20}O_{58}$ ("beta-oxide," {103}-*CS* structure, Ref. (*8*)) differs from that of the oxidation of $W_{20}O_{58}$ to WO_3. During reduction, he found a continuous transformation in the structure and degree of perfection; from "disordered tungsten trioxide," now known as {102}-*CS* structure (*9*), through disordered "beta-oxide," to the "perfectly ordered" $W_{20}O_{58}$ phase. He further suggested that upon oxidation of $W_{20}O_{58}$, the vacancies (relative to tungsten trioxide) are directly filled by oxygen, with subsequent reshearing to form the WO_3-type structure.

During an HREM study of specimens with {103}-*CS* structure, Sundberg (*10*) observed the intergrowth of apparently pure WO_3 domains and {103}-*CS* of composition $WO_{2.917}$($W_{24}O_{70}$ phase). The average compositions of the intergrown crystals were reported to lie in the range $WO_{2.93}$ to $WO_{2.96}$. The intergrowth was interpreted as a local reoxidation of the {103}-*CS* structure occurring as the equilibrium shifts with decreasing temperature during sample preparation.

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TABLE I

THE SAMPLE PREPARATION CONDITIONS AND FINAL RESULTS

Experimental conditions				Results	
Sample No.	$p(O_2)$/Pa	T/K	Time/hr	Oxidation of $W_{18}O_{52}$	Reduction of WO_3
1	7.2×10^{-6}	1280	12	The oxidation has affected only certain fragments. Figures 1 and 2 are typical illustrations of these partially oxidized fragments	Most of the observed fragments are WO_3-type. Some well-developed {102}-*CS* planes are observed, however
2	5.4×10^{-6}	1281	24		
3	1.1×10^{-6}	1281	46	In these samples, WO_3-type, {102}-*CS* and {103}-*CS* structure are observed. The oxidation was not complete. The fragments which show WO_3-type lattice images are very sensitive to the electron beam, and a {102}-*CS* structure develops very rapidly upon irradiation	The samples resemble in all respects previously observed ones (*1*, *16*). The reduction is complete
4	2.0×10^{-4}	1287	50		
5	2.1×10^{-5}	1281	51		
6	1.2×10^{-3}	1287	72	The oxidized and reduced samples are basically identical. The fragment shown in Fig. 3 is from the oxidized sample, but is also typical of the reduced sample.	

Previous redox (thermodynamical) measurements (*11–14*) of the W–O system have also shown that the system, particularly the CS structure region, exhibits pronounced hysteresis. The present study concerns the nature of the structural transformations upon oxidation of crystals having {103}-*CS* structure, and the cause of the hysteresis effect.

From yellowish WO_3 crystals, grown by chemical transportation with water vapor (*1*), a sample with {103}-*CS* structure was prepared by gas/solid equilibration at about 1270 K for 48 hr, with an oxygen partial pressure of 6.87×10^{-8} Pa. A part of this sample was checked by HREM, and 31 crystal fragments gave an average sample composition of $WO_{2.892\pm0.007}$, as evaluated statistically from the electron micrographs (*1*, *15*). This is in complete agreement with what could be expected from the previous study (*1*). All the fragments were of the {103}-*CS* structure type, but 28 of them were shown by electron diffraction to consist of the ordered *CS*-phase $W_{18}O_{52}$ in the homologous series W_nO_{3n-2} described by Magnéli (*8*).

Parts of this sample were reoxidized by further treatment in gaseous buffers of selected oxygen activity for various periods of time together with original tungsten trioxide crystals. The sample of WO_3 and $W_{18}O_{52}$ were kept separately but very close together in platinum crucibles, enabling comparison of the oxidation and reduction processes. The oxygen partial pressure was now within the interval for formation of {102}-*CS* structure. After the heat treatment the crystals were crushed in a mortar and the fragments studied in a Siemens ELMISKOP 102 with the technique described earlier (*3*). Typical results are summarized in Table I.

Figure 1 shows a typical example of a fragment obtained in samples oxidized for 12 hr under conditions known to give rise to the formation of {102}-*CS* structure (*1*, *15*, *16*). The micrograph shows three distinct regions, labeled A, B, and C, respectively, from the edge of the fragment. At A, the image approximates a WO_3-type lattice, and this part thus appears to be fully oxidized. At B, the region looks considerably strained or disturbed. It is possible that the oxidation has not gone completely through the crystal along the projection axis and

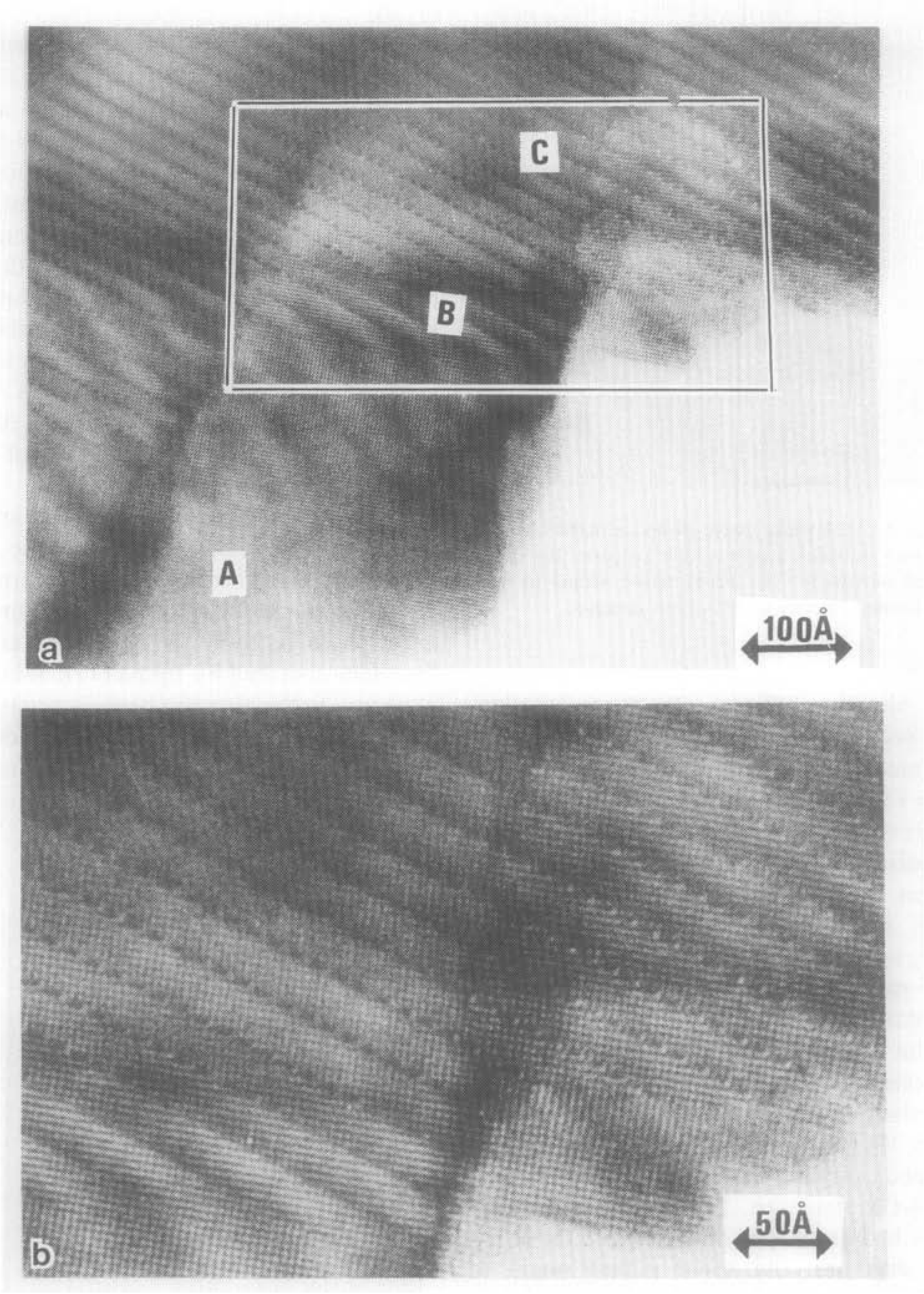

FIG. 1. (a) An HREM image of a fragment, from 12 hr oxidation. The micrograph shows three different regions; WO_3-type (A), {103}-*CS* structure (C), and a region with wavy contrast in between (B). (b) Higher magnification of the indicated area.

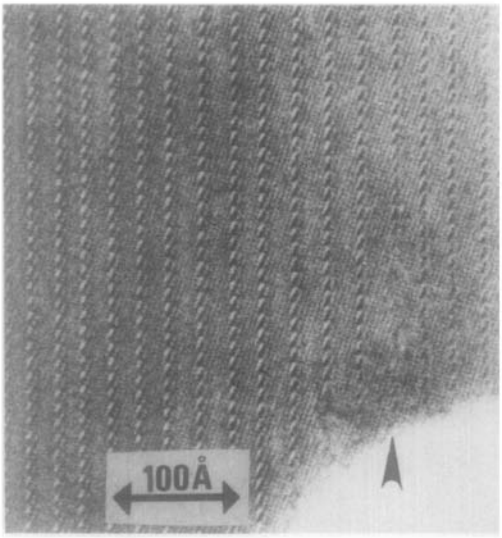

FIG. 2. An HREM image of an oxidized {103}-*CS* structure in which a part of one *CS*-plane has disappeared (arrowed). The *CS*-structure seems to have transformed directly to WO_3-type structure.

that slightly different structures overlap. The region marked C and the interior of the fragment are the initial $W_{18}O_{52}$ structure.

In Fig. 2 showing a part of another crystal from the same batch, only one *CS*-plane has disappeared over a part of its length and seems to have been partially oxidized to WO_3 structure (arrowed). This suggests that, in this particular case, the oxidation has proceeded predominantly along the projection axis.

The twinning observed in the {102}-*CS* regions formed by oxidation (Fig. 3) is characteristic for this structure when formed from WO_3, and is hard to explain if it is formed directly from the well-ordered {103}-*CS* structure. If the {102}-*CS* structures had developed directly from the {103}-*CS* structure, the shear planes ought to have been parallel to each other; and in the images such as those shown in Figs. 1 and 2, intergrowth of the two *CS*-structures ought to have been observed somewhere. Such intergrowth is frequently observed in samples reduced under proper conditions (*1*, *4*).

In the present case, a WO_3-type structure seems to form directly from the {103}-*CS* structure upon oxidation. This is in agreement with the results of Gado (*7*) and Sundberg (*10*) and suggests a reason for the hysteresis effect observed as mentioned above. It can be imagined that during the oxidation of {103}-*CS* structure, the six edge-sharing octahedra at the *CS*-planes are changed to corner-sharing, thereby forming a WO_3-type structure which is subsequently transformed to a {102}-*CS* structure as equilibrium conditions develop. This would explain the occurrence of twinning of {102}-*CS* shown in Fig. 3.

When tungsten trioxide crystals are observed in the electron microscope, *CS*-planes can sometimes be seen to form and grow due to reduction in the beam. Initially a "wrinkle pattern" is observed, as was first demonstrated by Iijima (*17*). When the exposure to the electron beam is prolonged, the wrinkles develop into well defined *CS*-planes. We have noticed that the rate of *CS*-plane formation depends very much on the thermal history of the samples. When

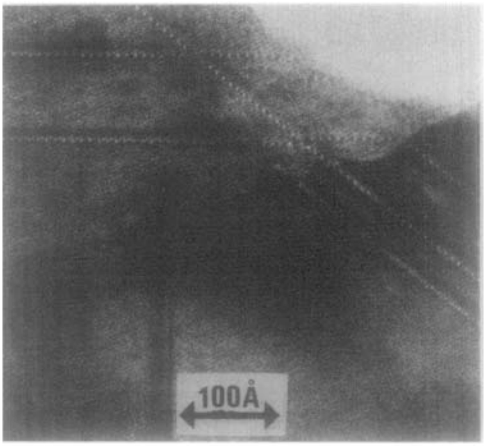

FIG. 3. Disordered {102}-*CS* structure (sample 6) formed by complete oxidation of ordered {103}-*CS* structure.

the initial crystals are stoichiometric (yellow) WO_3 or fragments of a slightly reduced sample already containing *CS*-planes, new *CS*-planes grow rapidly only when a part of the fragment is rather thick or when the condenser aperture is removed, and the heating effect is thus increased.

In contrast to this, the WO_3-type flakes that are formed by short-time oxidation of $W_{18}O_{52}$ are very unstable in the electron beam, and the *CS*-plane growth rate is very fast even when the crystal is thin. Fragments which give a WO_3 electron diffraction pattern at very low beam intensity thus transform very quickly to a {102}-*CS* structure upon a slight increase of the beam brightness. These observations suggest that, in "WO_3"-type crystals obtained by oxidation, there may be certain defects, not revealed either by HREM imaging or electron diffraction, which need only slight heating to rearrange into *CS* planes. It seems likely, however, that these point defects are associated with an oxygen deficiency, and they may thus be oxygen vacancies or metal/oxygen interstitials.

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