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The Transformation between Hexagonal Potassium Tungsten Bronze and Polytungstate

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The oxidation of hexagonal potassium tungsten bronze to polytungstate in air or oxygen and the corresponding reduction of polytungstate in vacuum or argon atmosphere has been studied. Despite the close structural relationship between these phases the results show that the reaction is not a simple continuous and coherent transformation but has a more complicated mechanism involving the nucleation and growth of new phases.

Introduction

It has recently been shown (*1*, *2*) that certain potassium polytungstates are structurally closely related to the hexagonal tungsten bronzes. It has also been known for some time that these polytungstates can be reduced to tungsten bronze and, reversibly, hexagonal tungsten bronze can be oxidized to polytungstate (*3*). In view of the structural similarity the mechanism of these reactions is of particular interest. In connection with studies on these phases we have made a preliminary investigation of this transformation, the results of which are presented below.

The tungsten bronzes are reduced compounds with the general formula M_xWO_3. Several structure types exist, but we shall here be concerned only with the hexagonal phase, HTB, which forms with the heavier alkali metals, M = K, Rb, and Cs, for $0.19 \leq x \leq 0.33$ (*4*). Its structure (Fig. 1) can be considered as build of WO_6 octahedra sharing corners to form a three-dimensional framework of composition WO_3, with rather wide hexagonal tunnels in which the alkali atoms are located. The maximum alkali content, $x = \frac{1}{3}$, is obtained with all available tunnel positions filled. Small displacements of the tungsten atoms in the (001) plane give rise to a doubling of the c axis, which then corresponds to the height of two octahedra (*5*). The unit cell dimensions for potassium HTB (prepared at 850°C) are: a = 7.385 Å (practically inde-

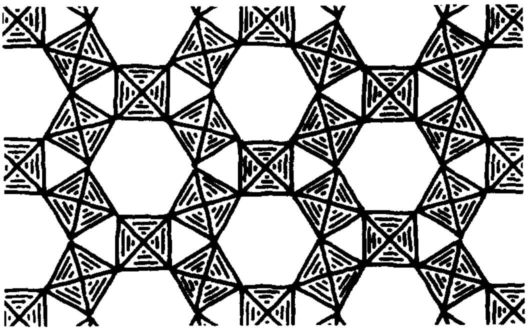

FIG. 1. The framework of WO_6 octahedra occurring in the structures of hexagonal tungsten bronze and potassium hexa- and octatungstate. The octahedra share corners along the direction of projection, [001].

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pendent of x) and $c = 7.503$–7.534 Å for $x = 0.20$–0.33 (*4*).

The general formula for the polytungstates can be written $M_xWO_{3+x/2}$. In the potassium polytungstate system stoichiometric phases are known for $x = 2, 1, \frac{2}{3}$, and $\frac{1}{2}$. In addition to these there is a phase (or "pseudophase") with a homogeneity range extending from $x = 0.33$ (hexatungstate composition) to $x = 0.25$ (octatungstate composition). The crystal structure of this pseudophase is basically the same as that of HTB, but within the range there are two different superstructures of the orthohexagonal unit: one which forms for compositions close to the hexatungstate, $x \geq 0.32$, and the other for lower x values, including the octatungstate composition. They are clearly revealed in single crystal diffractographs by characteristic multiplicities of the hexagonal a axis in one direction; fourfold in the "hexatungstate" and fivefold in the "octatungstate" (*2*). The sizes of the orthorhombic unit cells are

$$\begin{aligned} \text{hexatungstate:}\quad & a = 7.305\ \text{Å}, \\ & b = 25.41\ \text{Å}, \\ & c = 7.631\ \text{Å}; \\ \text{octatungstate:}\quad & a = 7.302\ \text{Å}, \\ & b = 63.56\ \text{Å}, \\ & c = 7.627\ \text{Å}. \end{aligned}$$

As in the HTB structure there is a superstructure also in the c direction, but here the odd layer lines in the X-ray diffraction patterns are weak and contain only streaks, which indicates disorder (*2*). The powder patterns of the two superstructure phases are very similar but can be distinguished mainly by some of the weak reflections with low θ (*2*). The detailed structures have not been determined, but it may readily be assumed that the additional oxygen atoms (compared to HTB) are located in the tunnels together with the potassium atoms. It is likely that the superstructures result both from small displacements of the tungsten atoms and from ordering of the potassium and oxygen atoms in and between the tunnels (*1*, *2*). A model for such an ordering which is consistent with electron diffraction data for the "hexatungstate" has recently been suggested by Goodman (*1*).

Deschanvres *et al.* (*3*) observed that samples within the hexa-octatungstate range could be reduced to HTB by heating in vacuum at 550°C and, conversely, the bronze could be oxidized to tungstate in air at 700°C. With the structural relationship between the two phases established, the question arises whether this transformation is a topochemical reaction by which oxygen atoms enter or escape through the tunnels in a more or less unchanged HTB framework, or if a reconstruction of the structure takes place.

Goodman has recently touched upon this problem in connection with electron diffraction studies of a tungstate of the composition $K_{0.27}WO_{3.135}$ (potassium content determined by microprobe analysis) (*1*). The diffraction patterns revealed a four-fold superstructure for this phase as observed by Klug for the hexatungstate (*2*). Klug never obtained the fourfold superstructure for such a low potassium content. This discrepancy may be due to the differences in preparation conditions used (*2*), or, alternatively, Goodman's analysis may be too low. Goodman suggests a structure model based on ordering of the potassium ions in the tunnels and small displacements of the tungsten atoms in the octahedra. He mentions that reduction and oxidation can be performed at 600–700°C in vacuum and air, respectively, with the external faces of the crystals intact. Based on electron diffraction evidence he also proposes a model for this process as far as the ordering of the potassium ions is concerned.

Experimental Details

Hexagonal potassium tungsten bronze (HTB) of compositions within the range $0.19 \leq x \leq 0.33$ and potassium hexa-octatungstate were prepared as described previously (*2*, *6*). The potassium content was checked by atomic absorption analysis in some cases (*7*) and was always found to be in agreement with the values expected from the preparation.

Oxidation of HTB was carried out in air or oxygen. Some samples were simply kept in open silica, platinum, or gold tubes in a muffle furnace, but experiments were also made with a TGA equipment (with a Cahn RG electrobalance).

Polytungstates were reduced either in tubes of silica, evacuated by means of an ordinary rotary pump and sealed off, or in argon gas of atmospheric pressure. In the TGA apparatus high grade Ar was used without purification and the oxygen partial pressure was measured by means of an "Oxymètre" (Hermann-Moritz, Paris).

Oxidation and reduction of crystals were also observed in a microscope equipped with a heating stage and gas cell (*8*). In this case the oxidation was made in oxygen and the argon gas used for the reduction was purified from oxygen by passing over copper metal at 500°C. The remaining oxygen activity was measured by means of a stabilized zirconia cell.

X-ray powder diffraction patterns were recorded in a Guinier–Hägg focusing camera using Cu$K\alpha_1$ radiation. Single crystal diffractographs were taken in a Weissenberg camera using Cu$K\alpha$ radiation.

Most scanning electron micrographs were taken in a Cambridge Stereoscan Mark IIA instrument with gold deposited on the specimens.

Oxidation

From TGA runs it was found that oxidation of hexagonal potassium tungsten bronzes in air starts already at 400–425°C. It is completed after 3–4 hr at 560–600°C for crystals of 10–20-μm size, but larger crystals require longer heating time or higher temperature to be fully oxidized. X-ray powder patterns of the oxidized products showed that the hexatungstate structure is always formed in this process irrespective of the initial composition of the bronze. For $x < 0.32$ some tungsten trioxide is also formed, which indicates that the hexatungstate probably has a normal composition (x = 0.32–0.33). Scanning electron micrographs of the oxidized products show that the HTB crystals (Fig. 2) have been transformed into aggregates of needles, partly fused together and mostly oriented roughly parallel to the hexagonal axis, thereby more or less retaining the external shape of the parent HTB crystal (Fig. 3). The needle crystals are of different length which, together with their general appearance, indicates that they have grown during the transformation process and are not just fragments of the original crystal. The pictures give the impression that a liquid phase has been involved in the growth. This is particularly true in the images of crystals oxidized at 700°C and higher.

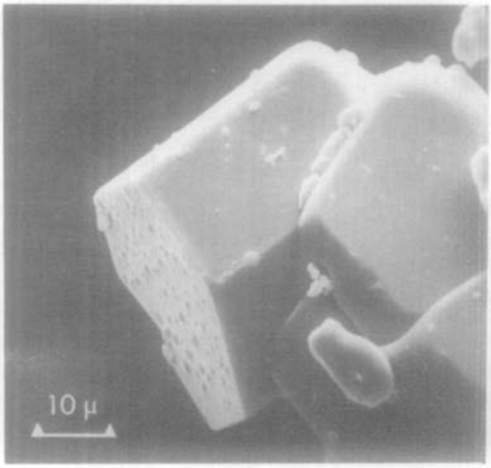

FIG. 2. Scanning electron micrograph of HTB crystals formed by complete reduction of octatungstate in an evacuated, sealed tube at 800°C.

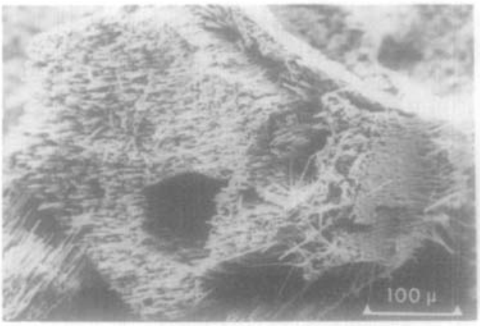

FIG. 3. Typical appearance of an HTB crystal which has been oxidized in air or oxygen.

By continuous observation of the oxidation process in the heating stage optical microscope at gradually increasing temperature it was seen that the crystals began "sweating" at around 700°C. When the oxidation was completed the liquid drops on the surface of the crystals had disappeared. This can be explained if one assumes a melting point minimum below 700°C in the system K_xWO_3–$K_xWO_{3+x/2}$. A detailed investigation of the melting behavior in this ternary system has not been made, however. This requires delicate DTA measurements with the samples kept in sealed ampoules at various pressures. It will be the topic of a separate study.

"Single crystal" X-ray diffraction photographs of the aggregates show only very diffuse spots of an HTB-type pattern. The relatively strong odd-*l* layer lines characteristic for the bronze have disappeared after oxidation at 600°C for 1 day, but no tungstate superstructure in the *ab* plane can be seen. Only after prolonged heating at 750°C or higher do very weak and diffuse superstructure spots from a four-fold (hexatungstate) lattice become visible.

Reduction

Hexa- and octatungstate behave somewhat differently on reduction. This may partly be due to the different sizes of the crystals: the hexatungstate forms long thin needles, generally of a thickness around 1 μm, while the characteristic shape of the octatungstate crystal is an elongated plate with a width of 20–60 μm and a thickness of 5–20 μm.

Hexatungstate

By heating in evacuated, sealed silica tubes hexatungstate was completely reduced to HTB after 3 days at 750 and 850°C, while a sample heated at 600°C was a two-phase mixture of hexatungstate and HTB as indicated by powder patterns. Although the reaction took place in sealed tubes the calculated increase in oxygen pressure inside the tubes by complete reduction is not excessive: in the order of 0.1–0.2 atm (10–20 kPa) at the reaction temperature. SEM images of crystals from the 750 and 850° samples (Fig. 4) show that transformation to hexagonal morphology has taken place. This is particularly clear in the 750° sample where the crystals have grown considerably compared to the original hexatungstate crystals.

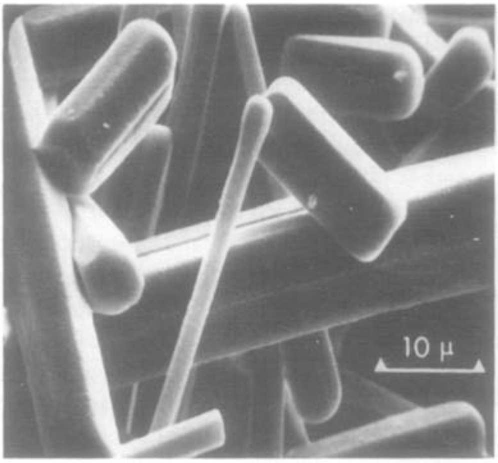

FIG. 4. Crystals formed by reduction of hexatungstate in a sealed tube for 3 days at 750°C.

A TGA run of hexatungstate in Ar ($P[O_2] \approx 10^{-4}$ atm) showed that measurable reduction under these conditions does not start below 690°C and that it proceeds rather slowly. The temperature was raised by ~ 50°C/hr to 850°C and only after being kept at this value for 5 hr was the sample completely reduced, as determined from the weight loss.

The hexatungstate crystals referred to above were prepared directly from K_2WO_4 and WO_3 and were too small to be closely observed in the heating stage microscope. As mentioned above, the aggregates formed by oxidation of bronzes always showed the four-fold X-ray superstructure characteristic for the hexatungstate, and a few such "crystals" were reduced in argon atmosphere ($P[O_2] \approx 10^{-12}$) on the heating stage. Also here a rather high temperature had to be used to cause any observable change: at 600°C the aggregates became darker only very slowly, and temperatures of 700–750°C and times of 10 hr or more were required to yield perfectly dark specimens. The "single crystal" patterns of these were still very diffuse, and no HTB odd-layer lines could be seen. Only after heating in Ar for several days at 900°C were these layer lines clearly visible.

In some cases during the reduction of these oxidized-HTB aggregates, bunches of extremely thin needles grew out slowly in various directions at a temperature of 750–800°C. These needles were transparent and could reach a length of about 1 mm. They were thus distinctly different in size from the needles that constitute the oxidized-HTB aggregates (Fig. 3) which would only be seen in the SEM images. They were too thin to give good single crystal X-ray patterns, but spots from an HTB substructure could be seen. The color and shape of these crystals seem to suggest that they were hexatungstate, but it is then remarkable that this phase should grow in a non-oxidizing atmosphere. The true nature of these whisker-like crystals and the conditions for their formation evidently need further exploration.

Octatungstate

The octatungstate crystals (Fig. 5) reduced under vacuum show a more complex behavior. Samples heated for 3 days at 600, 750, and 850°C gave powder patterns which differ slightly from each other and from those of the octatungstate, hexatungstate, and HTB. The general appearance is a gradual shift in the octatungstate lines toward the HTB positions with increasing temperature. Some powder patterns could be interpreted as being due to phase mixtures. For instance, the patterns of several samples heated at 750°C were superpositions of a modified octatungstate pattern and one almost identical with that of HTB. The parameters of the subunit cells of the tungstates differ from those of the HTB cell by 1.5% at most (see above) so the line shifts encountered here are rather small.

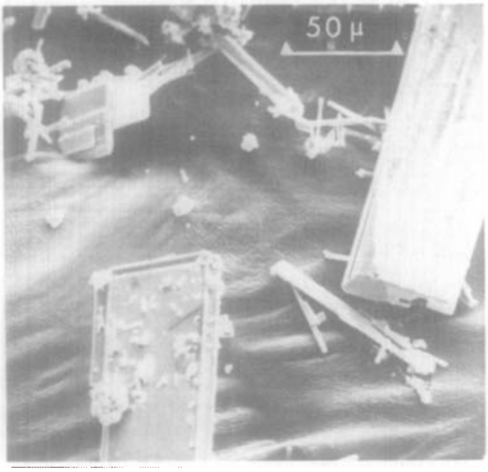

FIG. 5. Typical potassium octatungstate crystals used in the reduction experiments.

The size of the crystals is not important for the product formed: almost identical patterns were obtained with untreated and finely crushed octatungstate crystals. This makes it probable that a state of equilibrium had been reached in these samples. Similar patterns have also been obtained from samples partly reduced in Ar atmosphere in the TGA apparatus up to 800°C. An octatungstate "single crystal" from a sample heated in vacuum for 3 days at 700°C gave a Weissenberg pattern which was a superposition of the octatungstate pattern (with five-fold superstructure) and the HTB pattern. The powder pattern of this sample indicated a phase mixture of modified tungstate and HTB, like those mentioned above. Other samples heated to 750 and 800°C in evacuated tubes gave perfect HTB patterns both from powder and single crystals (Fig. 2). Variations in the initial pressure in the tubes and the volume-to-sample mass ratio with consequent variation in the degree of reduction are probably the reasons for the differences in the end product formed.

Scanning electron micrographs of the partly reduced crystals which gave modified patterns showed some melt-like features, most pronounced in the 750°C crystals, but showed also many thin flakes grown out from the surface, generally at large angles (Fig. 6). The crystals in the samples which gave good HTB

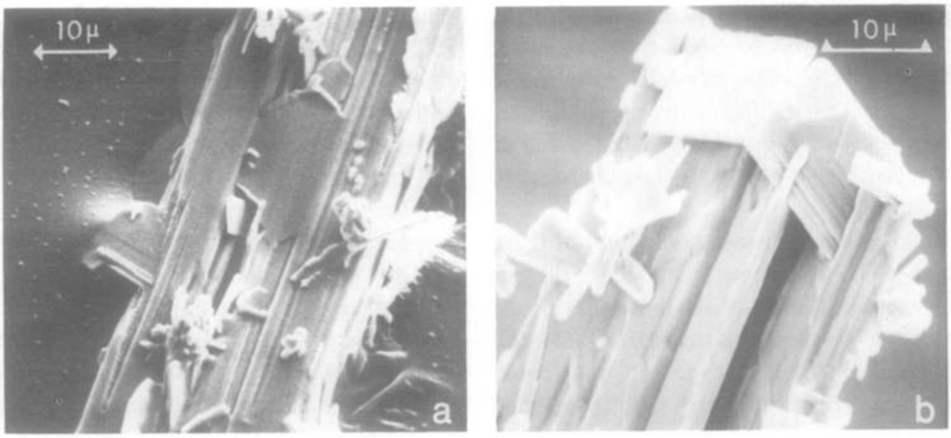

FIG. 6. Crystals from samples of octatungstate reduced in (a) a sealed tube for 3 days at 750°C and (b) in argon gas ($P_{O_2} \approx 10^{-10}$ atm) for 2 days at 750°C.

patterns had the hexagonal rod-like shape characteristic for HTB (Fig. 2).

Discussion

The results presented above indicate that the oxidation–reduction in this system is not a simple uptake and evolution of oxygen with a coherent and gradual transformation of the bronze into the corresponding tungstate and conversely, as has been assumed because of the close similarity between the crystal structures. The results obtained for the oxidation (at 475°C and higher) are consistent with a model in which hexatungstate needles nucleate and grow. At least at higher temperatures this seems to proceed via an intermediate liquid phase.

An essential factor for coherent transformation is the change in lattice dimensions. The lattice parameters for the hexagonal bronze are $a = 7.39$ Å, $c \approx 7.51$ Å (see above) while the corresponding values for the sublattice of the tungstates are $a = 7.32$ Å, $c = 7.63$ Å. An oxidation of the surface of a rod-shaped HTB crystal would thus cause a contraction of the lattice in the *ab* plane which should then result in cracks parallel to *c*, the rod axis. These cracks could make way for rapid oxidation of the interior of the crystal. Although such a process can be part of the mechanism, it can not explain the appearance of the crystals after oxidation, however, especially not the fact that the needle crystals formed have grown longitudinally.

Also the reduction is probably a discontinuous process, at least partly, and intermediate steps may occur. The sharp powder pattern lines from most of the partly reduced specimens, as well as the presence of single crystals giving distinct superposition patterns of the parent phase and the end product, are features not typical for a gradual topochemical reduction proceeding from the surface to the interior of the crystals. The change in appearance of the crystals upon reduction, as revealed in the SEM pictures, indicates that the mechanism involves nucleation and growth of new phases. At what stage of the reaction this takes place is not possible to decide at present.

The observed shifts of the powder pattern lines in the partly reduced samples, on the other hand, suggest that there is likely to be a single phase region with varying oxygen content extending from the octatungstate line of the phase diagram part of the way to the bronze line.

Goodman (*1*) assumes a topochemical mechanism but notes that the oxidation–

reduction is not completely reversible within the whole range from tungstate to bronze. He observed that "after an initial and relatively small oxidation there is a fundamental change in the appearance and hardness of the compound, which is not easily reversed." He also found that this change is associated with the adoption of a $2a \times 2b$ superstructure upon oxidation. This change could correspond to the transformation of the crystals into aggregates of small needles as observed by us. Goodman's reversible range on the high-oxygen side of this border may be the same as the single-phase region that we propose above. The results hardly lend themselves to further comparison, however.

In electron microscopic images of "partly annealed and oxidized" HTB crystals Goodman and McLean (*9*) have observed coherently intergrown regions with and without a fourfold superstructure. Since the composition of these specimens is unknown and since it is not established that the observed crystals had not formed during the oxidation process, these results are not at variance with our observations.

Further experiments are obviously required in order to give a full understanding of this redox process. Phase analysis of the ternary system under carefully controlled oxygen pressure is necessary, and the X-ray diffraction technique should be supplemented by electron diffraction of the products. In this latter case, however, there is always the risk that unintentional reduction takes place in the electron microscope. Investigations along these lines have now been initiated at the Arrhenius Laboratory.

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