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Growth and morphology of $W_{18}O_{49}$ crystals produced by microwave decomposition of ammonium paratungstate

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Abstract

By microwave irradiation of ammonium paratungstate (APT, $(NH_4)_{10}H_2W_{12}O_{42} \cdot 4H_2O$), needle crystals of $W_{18}O_{49}$ with a wide variety of size and morphology were formed. Their sizes and morphologies varied depending on various facets of individual APT pseudomorphous particles on which whiskers were grown, and among neighbouring decomposed APT pseudomorphous particles. Based on scanning electron and transmission electron-microscopic observations, it has been concluded that individual whiskers were monocrystalline and grew by a root growth mechanism from a nucleus formed in the amorphous layer, and that a rapid leader-like whisker growth in length was followed by a subsequent slower growth in thickness. Any evidence supporting a screw dislocation mechanism or tip growth by vapour–liquid–solid have not been detected.

1. Introduction

The monoclinic $W_{18}O_{49}$, ($WO_{2.72}$), one of the tungsten suboxides, is an important intermediate reduction product of tungsten trioxide, WO_3 , influencing significantly the morphology of the tungsten powder end-product [1]. $W_{18}O_{49}$ crystallises in needles and agglomerates of needle-like crystallites [2]. This is true for the formation by vapour transport [3], in oxidative [4], and reductive [5] atmospheres and for the transformation in the solid phase [6]. There are several other ways to prepare $W_{18}O_{49}$; from solid constituents [7], in situ in the electron microscope

[4,8–10]; however, the main interest has been focused on its formation by gas phase reduction of higher oxides: WO_3 or WO_{3-x} using H_2 [11], or CO [12], as reductive agents.

Needles were found to be formed during the gas phase reduction process in the presence of H_2O [5,8,13] whether H_2O was a product of the H_2 reduction, or it was deliberately added to the gas phase containing CO as reductive agent [12]. Interpreting the role of H_2O , vapour transport of tungsten oxide [14,8] is required in the formation of $W_{18}O_{49}$ needles [6]. The kinetics of the expected CVD growth have been investigated [15,16]. The ranges of temperature, water partial pressure and gas flow rate favourable to the formation of $W_{18}O_{49}$ needles, or excluding it, have been established [15].

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The observations of Berglund and Sahle [6] indicate that $W_{18}O_{49}$ forms incoherently with a highly distinct phase boundary from the precursor higher oxide. A formation process of nucleation and subsequent growth of the oxide, with an amorphous tungsten oxide as an intermediate stage have been proposed [17]. The occurrence of an amorphous phase during the formation of $W_{18}O_{49}$ has been reported by several investigators [8,10,17]. However, little is known about the mechanism of the growth of $W_{18}O_{49}$ needles. Hashimoto suggested tip growth for extremely thin oxide needles forming on heated preoxidised tungsten filaments in the electron microscope. These needle crystallites were found to be bundles of individual needles less than 15 nm in thickness [4].

This paper deals with further observations on growth peculiarities of $W_{18}O_{49}$, formed under microwave decomposition of APT, $(NH_4)_{10}H_2W_{12}O_{42} \cdot 4H_2O$ [18,19].

Microwave decomposition of APT has several advantages for studying the morphological features and the growth mechanism of $W_{18}O_{49}$. At the beginning of the microwave irradiation process, the temperature of APT rises slowly in the microwave reactor, but later a very rapid thermal run-away, and a rapid decomposition of APT takes place [20,21]. NH_3 released by APT itself appears to play the role of reductive agent [22] and the reduction of WO_3 comes to an end after the escape of NH_3 . Released water of hydration causes large H_2O pressure peaks in the gas phase confined in the pores of the tungsten oxide powder [23].

Since conditions during microwave decomposition of APT have been found favourable to the growth of $W_{18}O_{49}$ whiskers, it was expected that further information on the morphology of the resulted $W_{18}O_{49}$ would clarify the mechanism of whisker growth of tungsten oxide compounds.

2. Experiment

Samples were prepared by decomposition of APT (analytical grade, from Wolfram Bergbau- und Hüttengesellschaft m.b.h., Bergla, Austria) under a neutral gas ambient in a 2.45 GHz home-installed microwave reactor at nominally 3000 W. The experimental setup, results of chemical analysis and X-ray powder diffraction of the samples have been de-

scribed previously [18,19]. Quantitative X-ray powder diffraction [24] was used in an attempt to obtain information on the amorphous fraction and on the crystalline phases. The morphology was studied by scanning electron microscopy (JEOL JSM 25, and Cambridge Stereoscan 600) as well as by transmission electron microscopy (Philips CM20). For investigation by TEM the material was ground in an agate mortar, and a large number of small fragments were dispersed on carbon-coated specimen grids. Crystal structure of individual needles was established by electron diffraction. Attempts were made to reveal growth features and crystal defects by chemical etching of the samples using HF, ammonia water or K_3FeCN_6 based etchants. Growth features were examined before and after chemical etching.

3. Results

The decomposed products of the originally loose granulate of APT crystallites in the sample holder were found to be tightly textured lumps. X-ray diffraction data have shown that the product contains WO_3 , $W_{20}O_{58}$, $W_{18}O_{49}$ and amorphous phases. A lump looks as if it developed in the following way: needles extending from the oxide particles cling to one another fixing the parent oxide particles to each other. Needle-covered particles surrounding individual micropores can be studied under the electron microscope in the position they occupied during the growth of the needles. In Fig. 1 the micropores are surrounded by particles which are covered with nee-

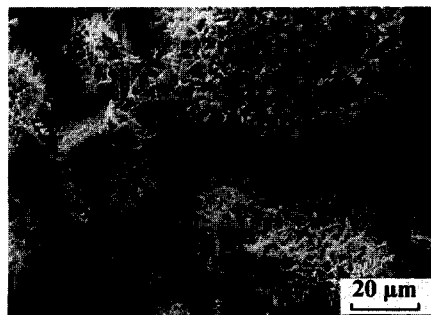


Fig. 1. Detail of a lump of microwave decomposition product of APT, where neighbouring particles are fixed to each other by contacting needles. The micropore in the middle of the micrograph is surrounded by APT pseudomorph particles covered by $W_{18}O_{49}$ needles differing in size.

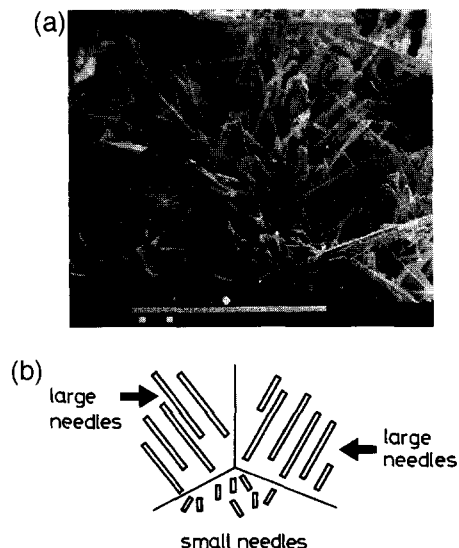


Fig. 2. (a) SEM photograph and (b) schematic drawing of the corner of an APT pseudomorph particle with whiskers grown on vicinal faces considerably differing in dimension; scale bar represents 10 μm .

dle crystallites. The needles extending from the neighbouring parent particles are very different in length and thickness. Needles that are similar in length have been found very different in thickness and morphology.

Another feature of the morphology, on corners of the parent oxide crystallites, the vicinal faces are covered by needle bushes differing in dimension (Fig. 2).

Individual needles were also found to be very different in micromorphology. In Fig. 3a and Fig. 3b two extremities having the same outer dimensions are shown. During our examination of the tips with

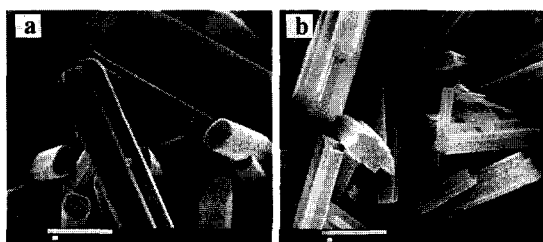


Fig. 3. Tips of two types of $\text{W}_{18}\text{O}_{49}$ needles (a,b); bar = 1 μm ; note the marked differences in the texture and intergrowth features. Needle roots are supported by lower level needles giving much darker contrast features than bright upper level needles.

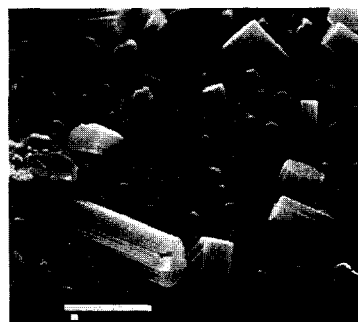


Fig. 4. Needle roots on amorphous-like substrate and parallel aligned individual fibres forming the needles; bar = 1 μm .

or without chemical etching we have never been able to find anything indicating to droplets or screw dislocations. Tips are generally flat while the surfaces of the needles were found either smooth or rather structured showing steps and fibres (Figs. 3a and 3b). Roots seem to stand loosely bound to the cauliflower-like surface of the parent particle (Fig. 4) or are supported by a lower level needle bush (Figs. 3a and 3b). Needles supported by another one can easily be distinguished on the SEM pictures giving a brighter contrast than others better contacted with the conductive substrate.

TEM investigations revealed further details on the texture of the individual needles. A TEM micrograph of a fragment is shown in Fig. 5. The needle-like crystals could be identified by means of electron

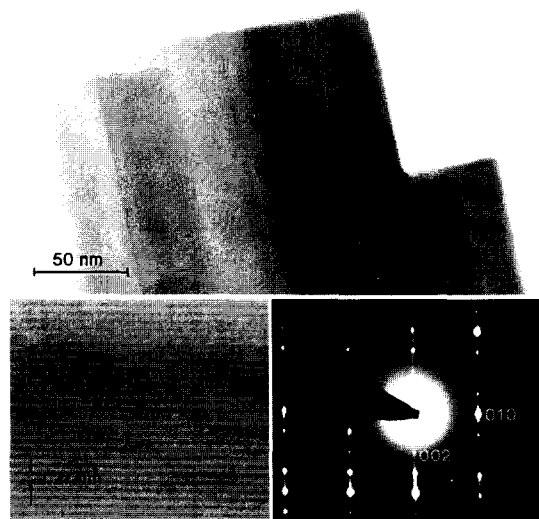


Fig. 5. Lattice images (top and bottom left) and electron diffraction pattern (bottom right) from a $\text{W}_{18}\text{O}_{49}$ fragment.

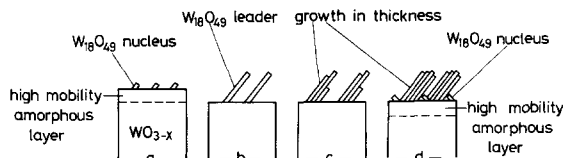


Fig. 6. Schematic representation of the proposed growth mechanism of $W_{18}O_{49}$ needle bush. (a) Formation of a high mobility surface layer and development of $W_{18}O_{49}$ nuclei. (b) Root growth of $W_{18}O_{49}$ leader whisker. (c) Growth in thickness by root growth of secondary needles parallel to the primary whisker combined with chemical vapour deposition of $W_{18}O_{49}$ filling gaps among closely grown whiskers. (d) Growth in thickness continues; repetitive formation of a high mobility layer and new nuclei.

diffraction patterns as $W_{18}O_{49}$ phase (J.C. Powder Diffraction Standard Data File (PDF) 36-101) with their [010] directions parallel to the long axis of the needle; (the needles elongate parallel to the b -axis of the cell). Their diameters were found to range from 35 to 200 nm. Some of the needles were found to be grown to each other on their superficies; epitaxy between the superficies has not been observed under transmission electron microscope.

4. Discussion

Based on the findings of this study and encouraged by the results of Sarin [8], Schubert [16], Sahle [17] and Hashimoto and co-workers [4,9,10] the following growth mechanism is proposed for $W_{18}O_{49}$ crystals under microwave decomposition of APT (Fig. 6):

(a) APT rapidly loses H_2O and NH_3 [1,23]. Micropores in the powder bed get filled with H_2O and NH_3 gas. In the reductive ambient [22] the oxygen loss of WO_3 begins step by step [6]. At about WO_x ($2.83 > x > 2.72$) the phase becomes amorphous [17]. Simultaneously, with increasing temperature and in the presence of water vapour, a high mobility surface layer develops and the first nuclei of the $W_{18}O_{49}$ phase [17] appear.

Processes of APT decomposition and the oxygen loss have been known for a long time (see key paper of Sahle on nucleation and subsequent growth [17]). SEM and TEM investigations indicative of the presence of an amorphous phase at the base of the

$W_{18}O_{49}$ whiskers in the samples containing $W_{18}O_{49}$ and its parent phase have also been reported [17]. The assumption of the formation of a “high mobility” surface layer previous to the formation of nucleation sites is a new hypothesis suggested in this study. However, a similar mechanism has been put forward for different crystals. An assumption of a liquid phase at the base end of the whiskers of the oxide crystal, $Bi_2Sr_2CaCu_2O_x$ has been recently reported by Matsubara et al. [25]. The authors suggested that the $Bi_2Sr_2CaCu_2O_x$ whiskers appear to grow by continuous precipitation from a thin melt phase at the base end of the whisker. The melt contains a foreign element, Al, which was proved to be an important factor in the growth of $Bi_2Sr_2CaCu_2O_x$ whiskers. Similarly, for the growth of $W_{18}O_{49}$ crystals having needle-like morphology, “wet conditions” are known to be an important factor [6,8]. Under wet conditions, in the presence of free water, a permanent hydrolysis breaks up the W–O–W chains of the amorphous tungsten suboxides resulting in a surface structured with micropores, and with surface hydroxyl groups and physically adsorbed molecular water in the micropores (Pickelmann and Schlotter, [26]). It is easy to assume that atomic movements have “high mobility” in this thin liquid layer in comparison with movements in the bulk of the condensed phase.

(b) After the formation of the nuclei, a very rapid root growth of a “leader” crystal, consuming tungsten oxide from the volume of the high mobility surface layer takes place. The leader crystal can be a monocrystalline whisker, or a bundle of several whiskers.

Root growth of a leading whisker in the growth process of $W_{18}O_{49}$ needles is also a new hypothesis. However, certain experimental observations not only in this study, but those published in the literature, seem to support this hypothesis. Sarin has reported a TEM photomicrograph (figure 9 of Ref. [8]) of initial $W_{18}O_{49}$ whiskers of about 90 nm in diameter formed on a single parent WO_3 particle in the electron microscope.

Another mode of growth – a tip growth via the gas phase – was also reported [4]. Hashimoto’s observation demonstrated tip growth of tungsten oxide needle crystals on the surface of a preliminary oxidised metallic tungsten filament [4]. Growth rates

(0.03–0.04 $\mu\text{m}/\text{min}$) observed in Hashimoto’s experiment are one or two orders of magnitude slower than those of this study. In our opinion, Hashimoto’s observation does not preclude the possibility of root growth. In Hashimoto’s experiment there was a very thin WO_3 phase and no amorphous phase below the whisker roots. The growth rate difference between the two cases and the difference in growth mechanism may be inferred to this difference.

(c) The primary grown needle crystals continue to grow in thickness with a much slower growth rate. Growth in thickness occurs by root growth of secondary needles parallel to the surface of the primary whisker combined with deposition of $\text{W}_{18}\text{O}_{49}$ from vapour transported $\text{WO}_2(\text{OH})_2$ (or a similar hydrate species of a tungsten suboxide) [4,8–10,16] filling gaps among closely grown whiskers.

The sketch of “bundle structure of the tungsten oxide needle crystals” (Hashimoto’s figure 2 in Ref. [4]), the micrographs of the recently described acicular crystals of sodium tungsten bronzes [27] as well as electron micrographs of $\text{W}_{18}\text{O}_{49}$ needles ([5,8,11,15,17] and the present study of microwave decomposed APT) seem to be very similar in the outer morphologies of the bundled needles. The growth of secondary needles closely connected parallel to the leading whisker is suggested as a similar or common step in the growth of this bundled structure crystals. Under wet conditions the secondary needles are expected to grow from the root and to stop growing at the end of the leader resulting in a flat tip

end. As the presence of $\text{WO}_2(\text{OH})_2$ in the gas phase was found to be a characteristic common feature at the growth experiments of these needle-like crystals, chemical vapour deposition of $\text{W}_{18}\text{O}_{49}$ on the entire surface is expected to play a definite role in the intergrowth of individual whiskers. Vapour grown material is expected to fill in empty channels among the leader crystal and the later grown needles by a selective high growth rate. The expectation that CVD occurs on the entire surface of the growing crystal has been confirmed by HREM images of crystal edges of $\text{W}_{18}\text{O}_{49}$ needles grown at 1300°C in the absence of water [28], revealing traces of growth on the top surface and superficies as well.

(d) Repeated formation of a high mobility surface layer with the appearance of new nuclei and eventual growth of new leaders consuming the volume of the surface layer. Newly grown crystallites have their roots one level deeper in the parent APT pseudo-morph particle, contacting the previously grown needles generally on their superficies.

So far as first formed $\text{W}_{18}\text{O}_{49}$ needles grow in thickness the decomposition of the parent crystallite continues. The multi-layered needle bush structure of the decomposed parent tungsten oxide crystallite is interpreted by repetitive formation of high mobility surface layers with the appearance of nuclei at deeper levels and repetitive growth of leader whiskers consuming the volume of the high mobility layers at deeper levels. Generally the needle bushes of the different layers are in loose physical connection and

Table 1
Morphologies of $\text{W}_{18}\text{O}_{49}$ crystals formed under various conditions

Ref.	Observed morphology	Growth mechanism as suggested by reference <i>growth mechanism as suggested in this work</i>
Hashimoto [4]	Whiskers	Tip growth by CVD
Hashimoto ([10], Fig. 1)	Needles	Tip growth from droplet
Hashimoto ([10], Fig. 4)	Dendritic crystals	Dendritic growth from liquid phase
Sahle, Berglund [12]	Bundles of needles	Solid state transformation via amorphous phase
Sarin ([8], Fig. 9)	Whiskers	<i>Root growth of leader</i>
Sarin ([8], Figs. 3–4); Haubner [5]; Hellmer [15]; Sahle [17]	Needle bush	<i>Root growth of leader and growth in thickness by secondary root growth and CVD</i>
This work	Bundles of whiskers, needle bush	<i>Root growth of leader and growth in thickness by secondary root growth and CVD</i>

intergrowth of crystallites has also been observed. (Figs. 3a and 3b).

This model of growth mechanism represents the growth of $W_{18}O_{49}$ crystallites during microwave decomposition of APT. The wide variety of sizes and morphologies of $W_{18}O_{49}$ crystallites is due to micro-variation in the temperature of the parent particles and in the composition of the ambient vapour phase surrounding parent particles. For an attempt to generalise the model of growth mechanism of $W_{18}O_{49}$ crystals there are other important formation conditions to be considered. In Table 1 an overview of the observed morphologies of $W_{18}O_{49}$ with proposed growth mechanism is shown. The conditions under which these morphologies are produced are not always well known, but it can be assumed that competing mechanisms produce the variety of morphologies.

5. Conclusion

The results presented in this article demonstrate that the reductive formation of the needle crystals of $W_{18}O_{49}$ occurs as a crystallisation process with the following main steps. (1) Root growth of a leader from a limited volume high mobility layer on the surface of the parent particle. (2) Growth in thickness with root growth of secondary needles parallel to the surface of the primary whisker combined with vapour deposition filling gaps. (3) Repetition of process steps 1 and 2 at deeper and deeper levels in the bulk of the transforming parent particle if conditions for both steps of the crystallisation process remain favourable.

The model is suggested to explain morphologies of $W_{18}O_{49}$ produced not only by microwave decomposition of APT but by reductions under wet conditions reported in the literature.

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