JOURNAL OF SOLID STATE CHEMISTRY 105, 588–594 (1993)

BRIEF COMMUNICATIONS

Microwave Decomposition of Solid Crystalline Ammonium Paratungstate and Ammonium Metatungstate

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Received September 18, 1992; in revised form November 13, 1992; accepted December 7, 1992

The potential for microwave decomposition of solid crystalline ammonium paratungstate (APT) and ammonium metatungstate (AMT) was investigated. It was observed that APT and AMT interact with 2.45-GHz microwave radiation. Samples of ammonium paratungstate (20–50 g) were successfully converted into WO_{3-x} ($0 \le x \le 0.2$). A wide variety of morphological parameters were found. The interaction of AMT with the 2.45-GHz microwave radiation resulted in the partial loss of crystalline water and the partial dissolution of the sample in the released water.

1. Introduction

Thermal decomposition of APT, $(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 4H_2O$, and AMT, $(NH_4)_6[H_2W_{12}O_{40}] \cdot xH_2O$ (where $x \ge 2$), is a fairly well known process widely used in the tungsten industry (*1*, *2*). The decomposition of APT carried out under a reductive atmosphere results in nonstochiometric tungsten oxides with a composition depending on the reduction parameters (*3–5*). The morphology, crystallite size, and size distribution of the derived oxide product are closely related to the primary APT; however, solid state processes, heat conduction in the powder-like solid phase, and evolution and outlet of the gas phase products influence the morphology on a wide scale (*6*).

An alternative method of promoting reactions which require heat is to use microwave heating instead of conventional thermal heating. A key feature of microwave processing is that the energy is directly transmitted into the load material, so that samples are heated from inside out, in contrast to the traditional heat transfer process controlled by sample shape and dimension in conventional furnaces (*7*). Therefore the study of the microwave decomposition of APT and AMT may help to provide a deeper understanding of the conventional reduction or calcination process and may result in new structural features of the derived oxides. The receptivity of tungsten oxide, WO_3, to microwave heating has already been reported (*8*); but according to our knowledge, the receptivity of APT and AMT has not been reported. The aim of this paper is to give experimental evidence of the interaction of APT and AMT with microwave radiation and to report on experimental conditions resulting in the decomposition of APT.

Experimental

A home installed reactor with a 3-kW, 2.45-GHz magnetron and a gas inlet system was used for the decomposition of APT. The microwave reactor system is schemati-

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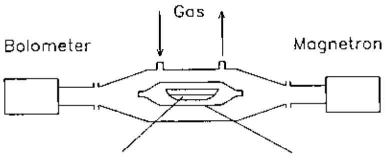

FIG. 1. Experimental setup for microwave treatment of APT.

cally shown in Fig. 1. Microwave power is transmitted through a rectangular waveguide to the work chamber. A closing element, together with a power indicating bolometer, serves for power homogenization. A silica boat surrounded by a silica tube (cylinder) is placed in the work chamber. Samples of APT powder (20–50 g) of grain size 10–100 μm were treated at maximum power under N_2, under 5% H_2 containing N_2 (forming) gas, or under air. The duration of the treatment was about 5–20 min, depending on experimental conditions.

AMT was treated in a commercial 500-W, 2.45-GHz microwave oven equipped with gas inlet. Standing silica test tubes with various diameters containing 20–100 g samples of AMT were placed under a forming gas stream or under ambient air. The samples were treated at nominal 500-W for 1–10 min.

APT mixed with tungsten blue oxide, TBO (50 g APT + 50 g TBO mixture), was also treated in standing test tubes at 500-W for 5–20 min in the commercial microwave oven.

APT used for the experiments was from Wolfram Bergbau- und Hüttengesellschaft m.b.h., Bergla, Austria; AMT was prepared from ammonium tungstate solution by electrodialysis (*9*) in our laboratory. AMT crystallized in 3–4 mm grain size crystallites. Samples of these large crystallites and of milled powder were used for the experiments. TBO was prepared by thermal decomposition of APT at 420°C in N_2 plus H_2.

The decomposed powders resulting were investigated under a scanning electron microscope. Oxygen index analysis (*10*) and ignition residue determination were performed, and powder diffraction patterns were recorded by a Guinier focusing camera and a Hilger diffractometer. The ammonia content was determined by Kjeldal's method.

TABLE I

DATA ON MICROWAVE DECOMPOSITION OF AMMONIUM PARATUNGSTATE

Sample	Experimental conditions				Results of chemical analysis			
Weight (g)	Sample holder	Ambient gas	MW power at, 2.45 GHz (W)	Time (min)	Color of product	Ignition residue	Oxygen index	NH_3 content (w%)
R6: APT, 20 g	silica boat	N_2	3000	10	violet-blue	101.47	2.7898	0.03
R7: APT, 20 g	silica boat	5% H_2 + N_2	3000	3	violet-blue	101.53	2.8140	0.07
R25; APT + TBO 50% mixture 100 g	standing silica test tube	5% H_2 + N_2	500	20	blue	100.84	2.9256	0.04
R26*: APT + TBO 50% mixture 95 g	standing silica test tube	air	500	30	blue	100.43	2.9320	0.07
R27*: APT + TBO 50% mixture 95 g	standing silica test tube	air	500	30	yellow	100.02	3.0000	0.01

Note. R26* and R27* samples are from one test tube of decomposed powder mixture: R27 is yellow from the upper part of the test tube, R26 is dark blue from the lower part of the test tube.

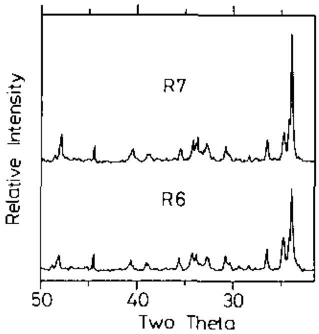

FIG. 2. X-ray powder diffraction patterns of the microwave decomposed products R6 and R7 of APT. The shadowed peak is an effect of the sample holder).

Results and Discussion

Results of microwave decomposition of APT are shown in Table I. APT powder placed in a silica boat was treated in the 2.45-GHz/3000-W microwave reactor. The APT powder decomposed into a violet-blue-colored reaction product with simultaneous evolution of H_2O and NH_3. With the help of ignition residue, NH_3 content, and oxygen index measurements the decomposition product was determined to be a tungsten oxide compound with a formula close to $WO_{2.8}$. X-ray powder diffraction (Fig. 2) shows that the product is not a single phase. Two crystalline phases were assigned to γ-oxide, $W_{18}O_{49}$ (J. C. Powder Diffraction Standard Data File (PDF) 36-101) and β-oxide, $W_{20}O_{58}$ (PDF 5-0386). Only weak reflections were indicative of an ammonium and/or hydrogen bronze phase. (The reflection data of Kiss *et al.* (*11*) were used to identify the ATB phase.) The weak reflections seem to be in agreement with the low NH_3 content of the product, which has about 5–20% of the NH_3 content of the commercial, mainly ATB-containing, TBO. The coexistence of the dominant $W_{20}O_{58}$ and minor ATB phases can be fitted into the process of phase variation during calcination observed by Zhiqiang *et al.* (*12*) if we consider that, at the large bed height of the microwave treated powder in the test tube, nascent NH_3 and its cracking products are the reductive agents with a maximum-shaped concentration-time curve, while the temperature increases continuously (but not uniformly) in disagreement with the standard industrial and laboratory practice. The presence of the $W_{18}O_{49}$ phase and the lack of the WO_3 phase indicate that the temperature should have been higher than 600°C, the upper limit of temperature used for calcination by Zhiqiang. (The temperature was not measured in this experiment, but a dark red glow of the product was observed.)

Experiments carried out with the same amount of APT in the same silica boat, for a similar or not much longer time, but in the 2.45-GHz/500-W commercial microwave oven, resulted in insufficient increase of the sample temperature. However, treatments of powder mixtures using APT and TBO in the 500 W commercial oven met expectations. A mixture (50 w%) of APT and TBO was placed in a standing silica test tube. After 5 min of treatment NH_3 evolution indicated decomposition. In 20–40 min the whole amount of the powder mixture converted into a gray-blue-colored product.

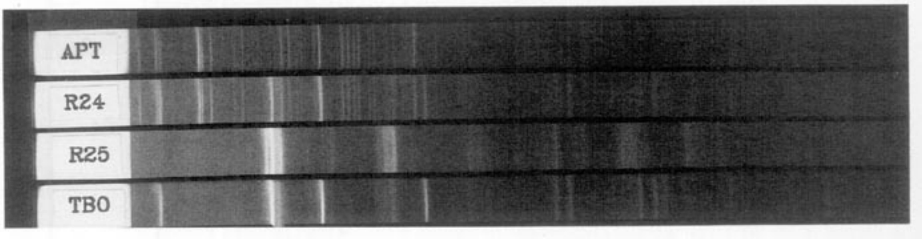

FIG. 3. Guinier patterns for APT, TBO, R24 (mixed powder of 50 w% APT and 50 w% TBO), and R25 (microwave decomposed product of sample R24).

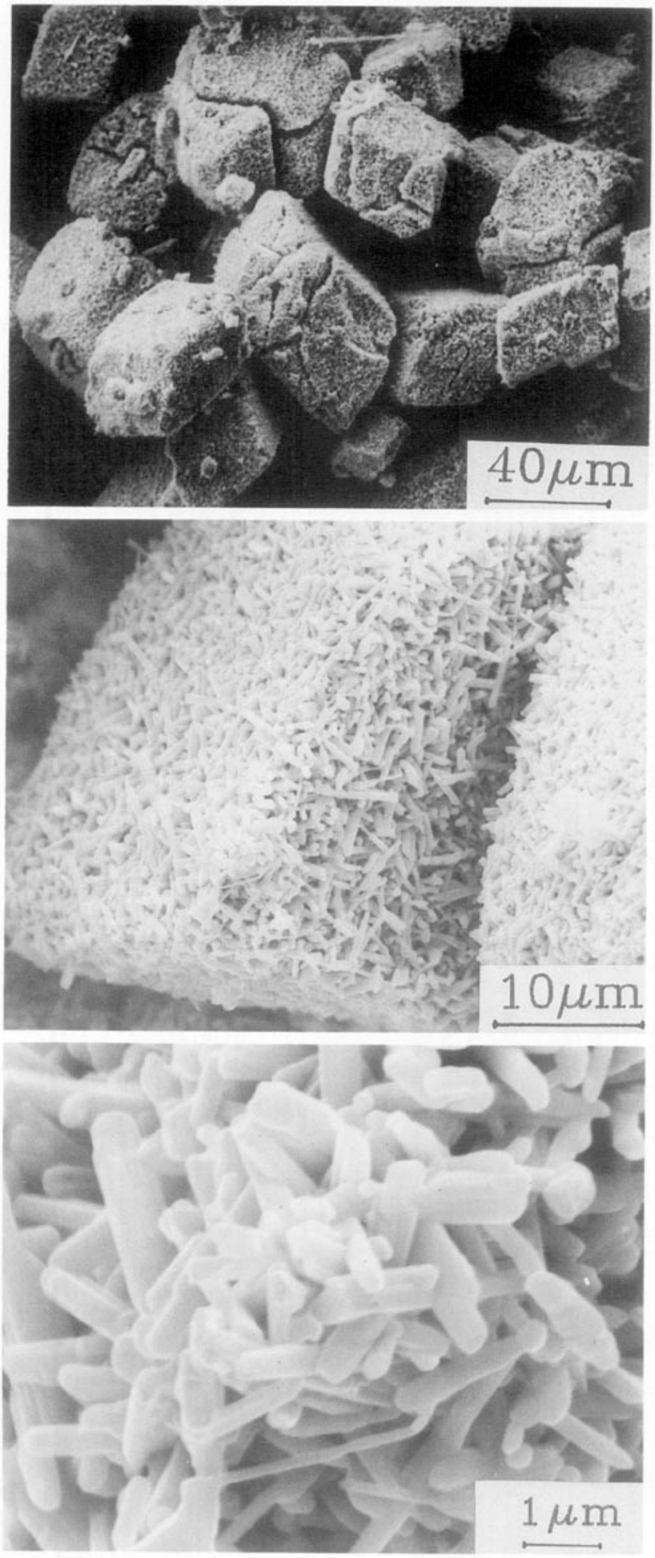

FIG. 4. Scanning electron micrograph of microwave decomposed product R6 with composition $WO_{2.79}$.

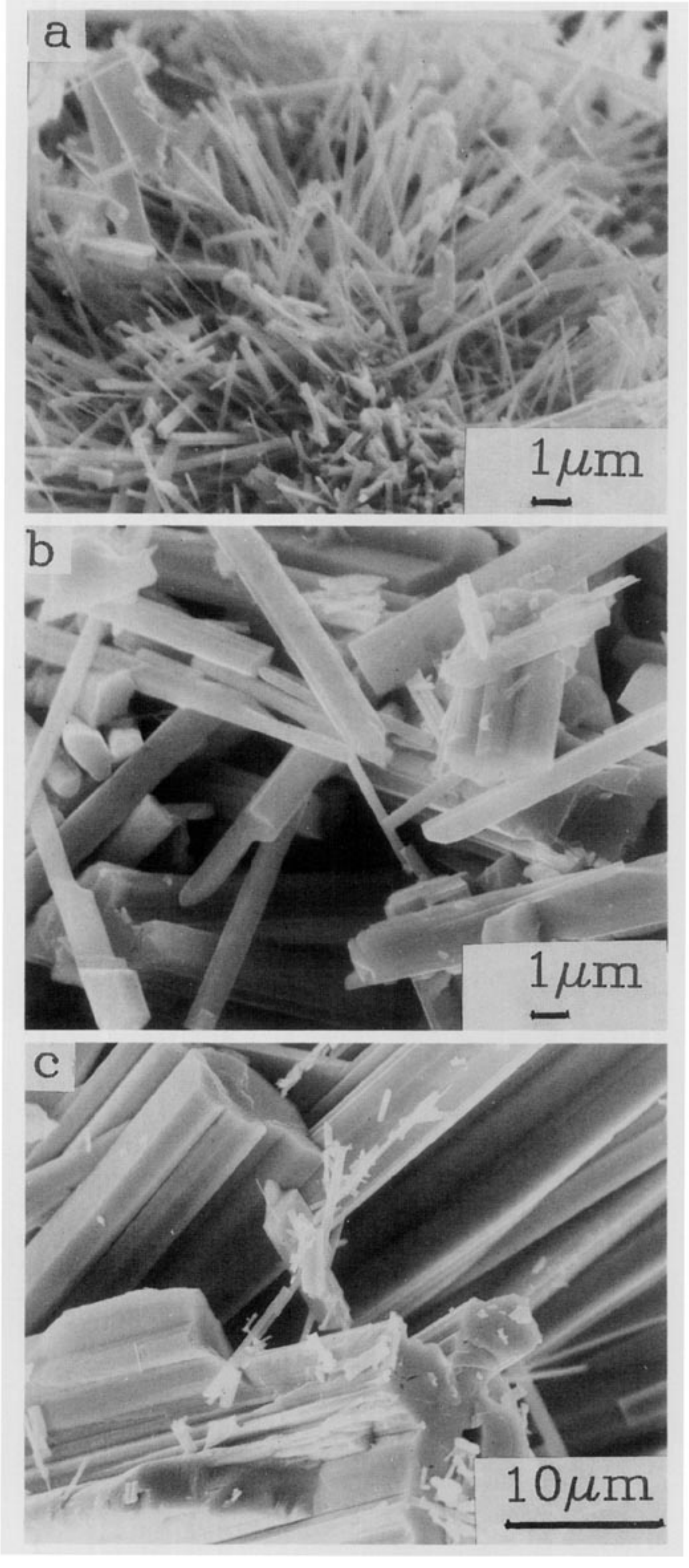

FIG. 5. Needle crystals with composition $WO_{2.79}$. (a), (b), and (c) are from different parts of the same sample.

According to the Guinier patterns (Fig. 3) the product differs from the APT and also from the TBO used. According to the chemical composition, the product can be considered to be WO_{3-x}, where x is about 0.07–0.08. Decomposition under air in the standing test tube resulted in a yellow-colored upper layer with chemical composition WO_3, while the lower part of the powder column was blue-colored with composition $WO_{2.93}$. X-ray powder diffraction of the blue-colored product showed a mixture of crystalline phases, assigned to $W_{20}O_{58}$ and monoclinic WO_3 (PDF 24-747). $W_{18}O_{49}$ and ATB phases were not found.

The microwave-treated decomposed powder product remained macroscopically pseudomorphic to the starting APT (Fig. 4). However, gas phase processes rebuilding the outer shell of the crystallite (as shown in Fig. 4) during the evolution of H_2O and NH_3 can become dominant and can create a fabric of needle crystals with a large variation in diameter (Fig. 5). A similar fabric of needle crystals grown in a "fast" reduction process was shown in a recent work (*6*).

Experiments with ammonium metatungstate were carried out in the 500-W commercial oven. Interaction was observed between microwave radiation and AMT in the form not only of large crystallites but also of fine powder. Treatment of 100 g AMT powder (500-W for 2 min) increased the temperature of the sample from room temperature to 90°C, while a similar treatment of a similar amount of APT resulted in only a 4°C increase of temperature. Following the treatment of the AMT, formation of water droplets was observed. As the sample began to dehydrate a partial dissolution in the formed water took place, and the product was no longer powder-like but cemented. Longer microwave treatment of this intermediate decomposition product caused only a slight increase in temperature. NH_3 evolution and the completion of the decomposition were not observed.

The present results on APT and AMT microwave decomposition characteristics indicate that processes in which the decomposition products H_2O, NH_3, and reduced WO_3 take part play a significant role during the interaction of tungsten oxide compounds with microwave radiation. Further work is necessary to establish the mechanisms of the observed interaction, which produces nontypical coexistence of reduced tungsten oxide phases.

Acknowledgments

The authors express thanks to Dr. M. Spross, director, Wolfram Bergbau- und Hüttengesellschaft, Bergla, Austria, for supporting this work and Professor E. Lassner for stimulating ideas and providing ammonium paratungstate. They also thank Professor L. Bartha and Professor J. Neugebauer for encouragement and valuable discussions, P. Arató and F. Wéber for performing X-ray investigations, and A. Tichy-Rács for participating in experiments with the 3000-W magnetron.

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