Processes of Reductive Decomposition of APT above 400°C; Transformation of APT → KTB → β–W in the Presence of K

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ABSTRACT

Ammonium-tungsten-oxide bronzes (ATB) are formed in the course of thermal decomposition of ammonium paratungstate (APT). The formation of a hexagonal ATB between 400 and 600°C was known. It has now been found, by continuous measurement of the NH_3 evolved, and by X-ray analysis, that a tetragonal ATB can also be detected in a reductive decomposition, as well as the known HTB (hydrogen-TB). The subsequent appearance of the three oxide bronzes and a specific ATB–KTB transformation in the presence of potassium is shown.

INTRODUCTION

Ammonium-tungsten-oxide bronzes (ATB) are formed in the course of thermal decomposition of ammonium paratungstate (APT) that is going through several intermediate phases, like, e.g., $WO_{2.9}$. The applied atmosphere is generally of a reductive character. The final product of the reduction process is α-W, which is formed from WO_2, sometimes passing through the phase β-W. In the presence of K-containing additives (which is common in the case of manufacture of so-called "doped tungsten" for incandescent filaments) potassium-tungsten bronzes (KTB) appear after the evolution of ammonia. In addition to the well-known tetragonal KTB, hexagonal KTB can also be formed, which transforms in every case into β-W. To the best of our knowledge, there is no ATB isomorphic with the tetragonal KTB. Nevertheless, in addition to the already mentioned hexagonal KTB, two other bronzes, an ammonium and a hydrogen bronze, exist, the role of which in the formation of β-W (without K) and in the incorporation of K has not yet been described. We observed the subsequent appearance of the three different ATB versions and a specific ATB→KTB transformation in a single decomposition process.

EXPERIMENTS

The decomposition of APT and/or reduction of blue oxide (BO) was followed by continuous NH_3 measurement of the exhaust gases using the equipment shown in Fig. 1.

The furnace consists of four quartz tubes placed within one another. The reaction was carried out in a quartz boat located in the tube of smallest diameter. The second tube is the holder of the heat filaments. The third one is covered with a thin gold layer and serves for heat reflection. The fourth one is for heat insulation (the space between the third and fourth tubes is evacuated). The furnace has a long enough platform (130 mm) with constant temperature (±1°C at 650°C). The length of the platform is adjustable by alteration of the coil spacing of the heating filaments. The reducing gas was a mixture of hydrogen (20%) and nitrogen (80%) that was used at the same time as a diluting gas for NH_3, evaluated during the process. The NH_3 content was measured by a portable gas analyzer (Miran 104) at a path length of 10.5 m and wavelength of 10.4 μm. The gas analyzer is equipped with a pump, which permits (continuous) measurements. The maximum allowable concentration of NH_3 in the analyzed gas is approximately 50 ppm, which makes dilution necessary.

Fig. 1: Equipment used for decomposition and/or reduction: 1. Furnace, 2. Recorder, 3. Infrared gas analyzer, 4. Temperature controller.

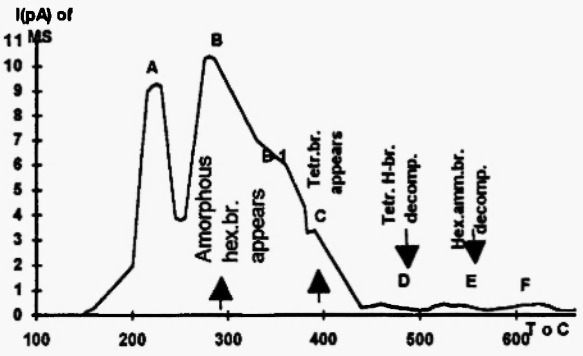

Fig. 2: MS diagram of decomposition of APT in H_2.

Peaks on the curves, generated with the registration of NH_3 content of the exhaust gases, were compared with the curves from our previous measurement by mass-spectrometry (Fig. 2), TG and DTA /5/. It was found that the two small peaks (D, E) in the temperature range 400-600°C are very informative.

X-ray diffractograms were made at the same time on the intermediate products.

The decomposition curves of APTs below 400°C were not informative enough and additionally the large amount of NH_3 caused difficulties in the measurement. Therefore, it is more convenient to carry out the tests with partly decomposed APTs, when the greater part of the NH_3 content has already evolved (at peaks A and B in Fig. 2). This is the case with the industrially produced BO and therefore we concentrated on examination of BO samples. Some typical examines of the measurement series are shown in Figs. 3 and 4.

It can be seen quite well from these figures how high the sensitivity of the measuring method is.

The shape of the curves and their reproducibility depend significantly on the temperature diagram of decomposition; the most suitable interval is between 420 and 560°C.

The NH_3 content of the BO samples can be characterized by two numerical values (Fig. 3 a-d) corresponding to peaks D and E, respectively in Fig. 2. The two peaks at 460°C and 530°C can be distinguished very well.

For incandescent filament purposes, the BO is doped with compounds of Al, K, Si (AKS-doping). In the case of doped BO, peak E almost disappears (Fig. 4) because of chemical reactions taking place in the doping process (e.g., the remaining NH_3 is driven out by the potassium dopant).

Electrical resistance was measured during reduction on samples prepared by pressing of APT and W oxide powders. The contacting wires were pressed into the sample.

The pressed tablets showed semiconductor behavior and, therefore, the temperature coefficient of electrical resistance was very high. This hindered the reliability of the measurement at low temperatures. The electrical resistance decreased above 360°C when oxide bronzes had already formed and exhibited metallic behavior (Fig. 5).

For identification of the phases of intermediate and final products, Guinier and X-ray diffractometry were

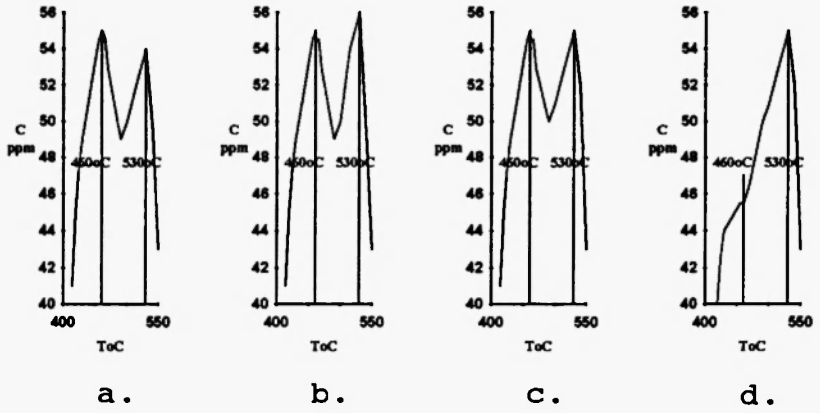

Fig. 3: Evaluation of NH_3 during decomposition of the undoped BOs.

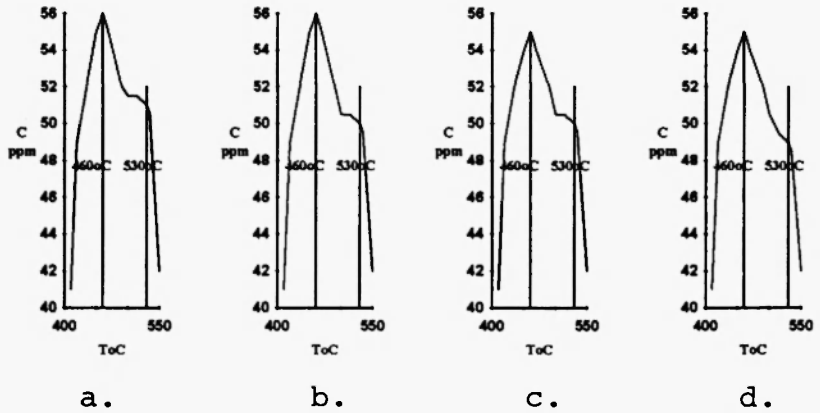

Fig. 4: Evaluation of NH_3 during decomposition of the doped BOs.

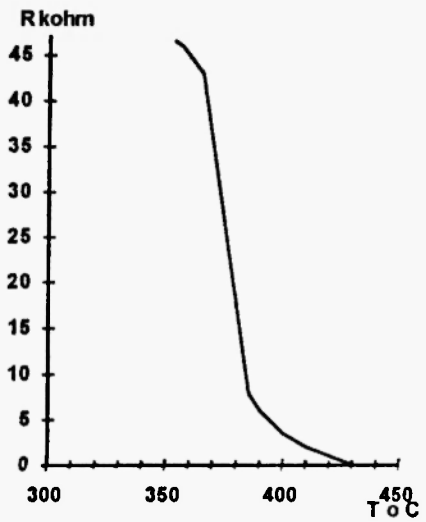

Fig. 5: Alteration of electrical resistance of APT in the reduction process.

used. The type and the main parameters of the X-ray measurement were as follows:

- MPD 1880 Bragg-Brentano automatic focusing powder diffractometer with CuKα monochromatic X-ray source.
- Measurement type: Step Scan
- Pacing [°2θ]: 0.02
- Time of pacing [s]: 1

Evaluation of the results was carried out by using the PC-APD 3.5 program and 1-41 JCPDS data sheets.

DISCUSSION

Curves generated with registration of NH_3 content

of exhaust gases during the thermal decomposition of APT show two small peaks between 400 and 600°C (Fig. 2). These peaks coincide with decomposition of the tetragonal H bronze and the hexagonal NH_3 bronze, respectively (Fig. 6, Table 1). The third small peak (F in Fig. 2) needs further investigation.

Concerning the two peaks revealed at 460°C and 530°C (Fig. 3), the height of the first peak decreases or even disappears, if the APT was exposed previous to heating for a longer period at 400°C, while the second peak is sensitive to the potassium dopant and is significantly smaller after doping (Fig. 4).

The surface under the peaks also signifies the NH_3 content that is measured by the traditional analytical methods, but in our measurements the two NH_3 contents of different bonding energy values are clearly distinguished. Even less specific is the measurement by weight loss, when the volatilization of H_2O causes additional weight loss. Moreover, above 500°C the reduction starts causing another measuring error (Fig. 7).

During the decomposition process, the conductivity of the intermediate products changes remarkably (Fig. 5): up to 350°C semiconductive, over 430°C metallic conductivity.

The X-ray tests show three tungsten bronze intermediate products (Table 1). Their percentage distributions are shown in Fig. 8. These curves have been derived from the 2θ reflections in Fig. 9, where the shift of the peaks can be seen rather clearly in the interval 2θ: 48-50.

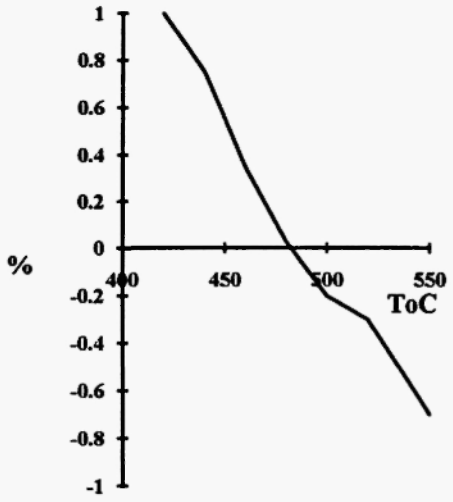

Fig. 7: Weight loss of the intermediate products.

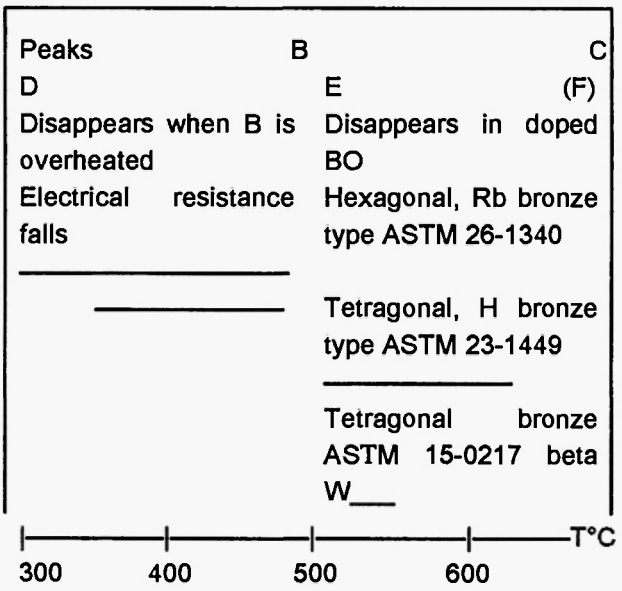

Fig. 6: Meaning of the peaks in Fig. 2-5.

Table 1
d value of oxide bronzes formed during the decomposition of APT ASTM

JCPDS 26-1340 (Rb br.) hexagonal	JCPDS 23-14449 (H br.) tetragonal	JCPDS 15-0217 tetragonal
1	2	3
6.42		3.78
3.78	3.89	
3.69	3.70	3.17
3.25		
3.20	3.12	
2.64	2.68	
2.44	2.62	2.44
2.30		
2.13	2.17	
2.08	2.00	1.90
1.89	1.94	1.84
1.86	1.85	

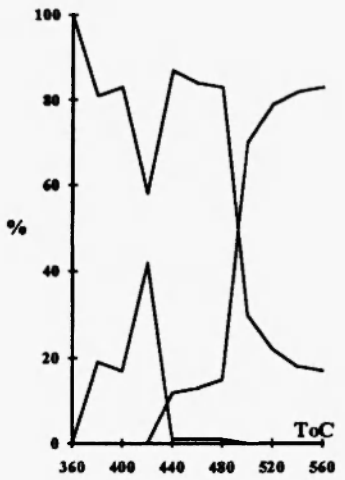

Fig. 8: Percentage distribution of the three tungsten bronze phases (see Table 1).

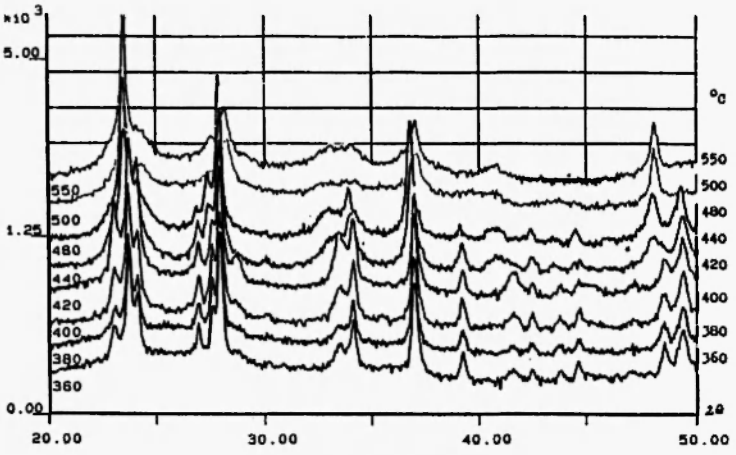

Fig. 9: 2θ reflections.

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