JOURNAL OF MATERIALS SCIENCE 17 (1982) 1955–1962

Some new aspects of the phase diagram of the NH_4^+/H^+–W–O system

A. B. KISS, Gy. GYARMATHY
Tungsram Company, Budapest, Hungary

T. NÉMETH, L. BARTHA
Research Institute for Technical Physics of the Hungarian Academy of Science, Budapest, Hungary

The phase composition of partially-reduced products of ammonium paratungstate (APT) was investigated. The samples were prepared by reducing the APT in a $H_2 + N_2$/1:29 volume ratio/atomosphere in the temperature range 610 to 860 K, and studied by means of chemical analysis, by X-ray diffraction analysis and by thermoanalytical methods. The reduction products can be described by the general formula of $M_xWO_{3-y+x/2}$ where M can be either H^+ and/or NH_4^+. Products considered as tungsten bronzes (TB) can be formed in a fairly narrow temperature range. Another product, the so-called decomposed APT (DAPT) is a mixture of bronzes and of some other compounds characterized by $y < x/2$ and considered as some intermediate phases between TB and tungstates.

1. Introduction

Ammonium paratungstate (APT) is a generally accepted base material for tungsten powder production. During the reduction of APT $[(NH_4)_{10}(W_{12}O_{40}(OH)_2)\cdot 4H_2O]$, decomposed APT (DAPT) develops transitionally and is doped with K, Al, Si if non-sag (NS) tungsten wire is to be produced. It has been clarified in recent years that the ion exchange ability of DAPT plays an important role in the doping [1–8]. For the understanding of this solid–liquid interaction, the chemical and structural properties of the DAPT have to be known [9].

2. Experimental procedure

2.1. Preparation of samples

APT samples, each of 10 g, were reduced by annealing in a gas mixture, of $H_2 + N_2$ at a 1:29 volume ratio, in a tube furnace for 45 min at a temperature between 610 and 850 K. Having cooled the samples to room temperature in the same atmosphere they were stored in pure argon until required for investigation.

2.2. Chemical analysis

The O/W atomic ratio of the samples (the so-called oxygen index, $I_O = 3 - y$) was determined by means of the Kiss–Tisza method [10], while the ammonium content of the samples was measured by a micro-Kjeldahl method.

2.3. Phase analysis

The phases were identified on the basis of Guinier-type X-ray diffraction patterns (using Cu$K\alpha$ radiation and KCl as the interior standard). The ASTM file numbers 5-532, 23-1448, 5-386 and 5-393 were used for the identification of the ammonium- and hydrogen-bronzes, of $W_{20}O_{58}$ and of $W_{18}O_{49}$.

2.4. Thermal analysis

The quantities of the volatile components were measured by a Chevenard-type thermobalance with a special inlet tube [11] using samples of 2 g each. The applied atomosphere was a high purity argon flow (100 $l\,h^{-1}$) and the heating rate was 300 $K\,h^{-1}$.

2.5. Calculation of the chemical composition

By re-oxidizing the intermediate reduction products of APT to WO_3 in air, weight-changes can be

0022–2461/82/071955–08$03.46/0 © *1982 Chapman and Hall Ltd.*

measured. These changes consist of a weight loss, Δm_1, due to the evaporation of NH_3 and/or H_2O and of a weight gain, Δm_2, due to the oxygen uptake processes. The sum of the weight changes, Δm, can be described as follows:

$$\Delta m = -\Delta m_1 + \Delta m_2, \quad (1)$$

where Δm, Δm_1 and Δm_2 are expressed as per cent weight changes. Δm_1 and Δm_2 can be calculated from the following relationships [10]:

$$-\Delta m_1 = [100 - (W + O)], \quad (2)$$

where W and O are the O and W contents of the products (wt%) and

$$+\Delta m_2 = (3.00 - I_O). \quad (3)$$

The expanded equation can be formulated as

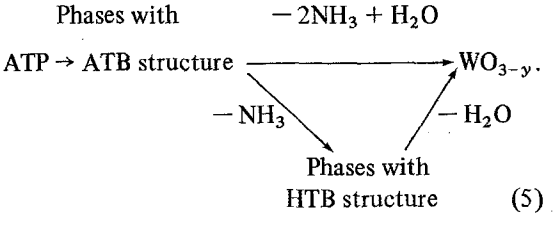
$$\pm \Delta m = -[100 - (K/M_W + I_O M_O)] + [K(3.00 - I_O)M_O], \quad (4)$$

where $\pm \Delta m$ is the sum weight-change in per cent, K is the ratio of the WO_3 content (in per cent) of the reduced product to that of the WO_3 molecular weight ($WO_3\%/M_{WO_3}$), M_W is the atomic weight of tungsten, M_O is the atomic weight of oxygen and I_O is the oxygen index ($= 3.00 - y$).

3. Results

Table I summarizes the chemical analysis results of the reduction products formed between 610 and 850 K. The X-ray diffraction analysis data, given in Table II, prove the presence of a tetragonal phase found earlier [12] and described [9] as hydrogen tungsten bronze (THTB). This phase appears parallel with the decomposition of the hexagonal ammonium tungsten bronze (HATB). The X-ray results are in agreement with the data of Table I, as the amount of H_2O developed during the re-oxidation of the samples increases with decreasing NH_3 content, which is quite natural in case of a material of higher H^+-ion content.

On the basis of these results, the two following ways for the formation of lower oxides from ATB-type material can be given:



(5)

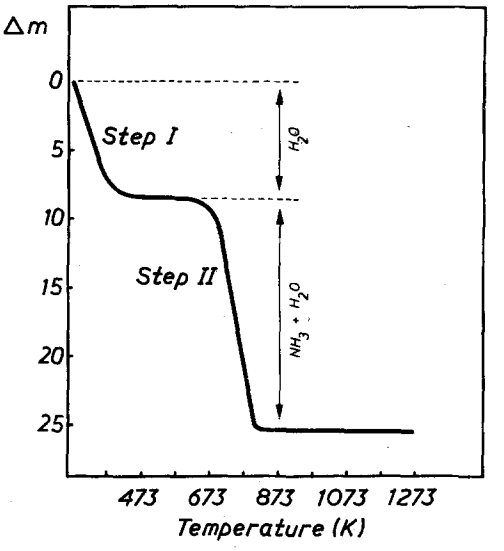


Figure 1 Thermogravimetric curve of a typical product formed at 380° C in argon atmosphere.

The quantity of HTB phases can be calculated on the basis of thermoanalytical results, as shown in Fig. 1. The curve is typical of those of the partially-reduced APT products.

The mass decrease in Step I equals the H_2O bound loosely, probably by adsorptive forces, to the solid surfaces, while that in Step II equals the NH_3 and H_2O quantities evolved during the thermal decomposition of materials with the ATB and HTB structures. As no other process can lead to the water evolution, one can assume that the water evolved in Step II originates from the components of the bronze structures. It is worth mentioning that the process

$$NH_3 + WO_3 \rightarrow WO_{3-y} + y \cdot H_2O + y/6 \cdot N_2, \quad (6)$$

can be excluded because nitrogen was not detected. Using the data for NH_3 content and taking into account the composition of the $(NH_4)_2O$-group, the H^+-ion quantity bound in the bronze structure can be estimated by subtracting from the total number of H_2O moles those equivalent to the NH_3 (see Fig. 2 and Table III).

If x denotes the quantity of cations (NH_4^+, H^+ or both) bound after the reduction, while y denotes the reduction degree in the same product of WO_{3-y} composition, then the change of the phase-composition will be as shown in Figs 3 and 4. In Figs 3 and 4 the straight lines represent the composition of bronzes according to the strict criterion of $y = x/2$ [13, 14]. The curves of Fig. 3 obtained from the chemical analysis are in full

TABLE I The chemical composition of the phases

Measured values				Calculated values							Structure type
(°C)	I_O	WO_3(%)	NH_3(%)	± Δm(%)	$NH_3 + H_2O$(%)	H_2O(%)	NH_3/WO_3, x	H_2O/WO_3	$y = 3.00 - I_O$	$y \lessgtr x/2$	
340	2.998	97.94	1.127	−2.06	2.073	0.946	0.1569	0.1209	0.002	$\ll$	hexagonal bronze
360	2.995	98.10	0.877	−1.90	1.929	1.052	0.1211	0.1382	0.005	$\ll$	
380	2.993	98.31	0.590	−1.69	1.737	1.146	0.0819	0.1502	0.007	$\ll$	
400	2.990	98.45	0.432	−1.55	1.613	1.180	0.0599	0.1545	0.010	$<$	hexagonal + tetragonal bronze
420	2.988	98.56	0.325	−1.42	1.501	1.176	0.0449	0.1538	0.012	$<$	
440	2.985	99.06	0.196	−0.94	1.039	0.843	0.0269	0.1097	0.015	$>$	
460	2.983	99.66	0.065	−0.34	0.456	0.391	0.0089	0.0505	0.017	$>$	
480	2.979	99.82	0.018	−0.18	0.324	0.306	0.0024	0.0395	0.021	$>$	tetragonal bronze
500	2.972	99.92	0.007	−0.08	0.273	0.265	0.0009	0.0341	0.028	$>$	
520	2.962	100.10	0.0	+0.10	0.162	0.162	0.0	0.0208	0.038	$\gg$	tetragonal + β-oxide
540	2.950	100.30	0.0	+0.30	0.040	0.040	0.0	0.0051	0.050	$\gg$	β-oxide
560	2.904	100.66	0.0	+0.66	0.0	0.0	0.0	0.0	0.096	$\gg$	β- + γ-oxides
580	2.780	101.54	0.0	+1.54	0.0	0.0	0.0	0.0	0.220	$\gg$	γ-oxide

TABLE II The results of the qualitative X-ray diffraction pattern evaluation

Temperature (°C)	Structural types			
	Hexagonal bronze	Tetragonal bronze	Reduced oxides	
340	NH_4–W-bronze	–	–	–
360	NH_4–W-bronze	–	–	–
380	NH_4–W-bronze	–	–	–
400	NH_4–W-bronze	H-bronze (a)	–	–
420	NH_4–W-bronze	+ H-bronze	–	–
440	(a)	+ H-bronze	–	–
460	(b)	+ H-bronze	–	–
480	(b)	+ H-bronze	–	–
500	(c)	+ H-bronze	–	–
520	–	H-bronze	+ $W_{20}O_{58}$ (a)	–
540	–	–	$W_{20}O_{58}$	–
560	–	–	$W_{20}O_{58}$	+ $W_{18}O_{49}$ (a)
580	–	–	–	$W_{18}O_{49}$

(a) Small quantity.
(b) Very small quantity.
(c) Traces

agreement with the identifications based on the qualitative X-ray analysis, and are shown in Table II. The H^+-ion content bound in the reduction products increases with decreasing NH_4^+-ion content, as expected. A similar decomposition mechanism takes place in the APT crystal during low-temperature decomposition, as found earlier [15, 16].

4. Discussion

4.1. Chemical considerations

In tungsten bronzes, with general formula M_xWO_3, as described by Dickens and Whittingham [17], the quantitiy of M electropositive atoms can vary in the range of $0 < x < 1$. Though the value of x defines correctly the reduction grade of the tungsten oxide it seems to be more descriptive to express the bronze character of the product using such a formula which contains the real reduction degree, y directly. The two quantities x and y are rigorously interdependent. An intermediate compound can be considered as a bronze only if the values of x and y fulfill certain requirements. However, it seems to be more favourable to use the general chemical formula for bronzes proposed by Neugebauer [13]:

$$M_xWO_3 = M_xO_{x/2}WO_{3-y} = (M_2O)_{x/2}WO_{3-y} = M_xWO_{3-y+x/2}, \quad (7)$$

where $y = x/2$.

It is evident that compounds can be called bronzes only if their chemical compositions strictly satisfy the terms expressed by the straight line in Fig. 5. As more material is reduced, more bronze forming atoms should be present in the lattice. By

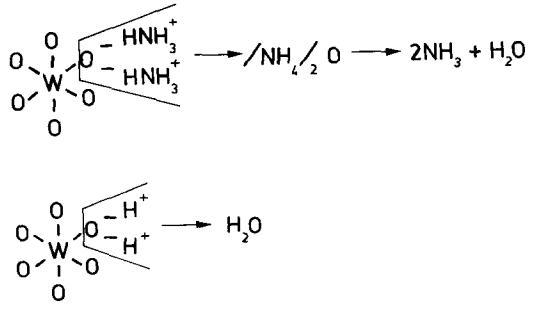


Figure 2 Schematic illustration of the evolution of NH_3 and H_2O gas products from the crystal lattice.

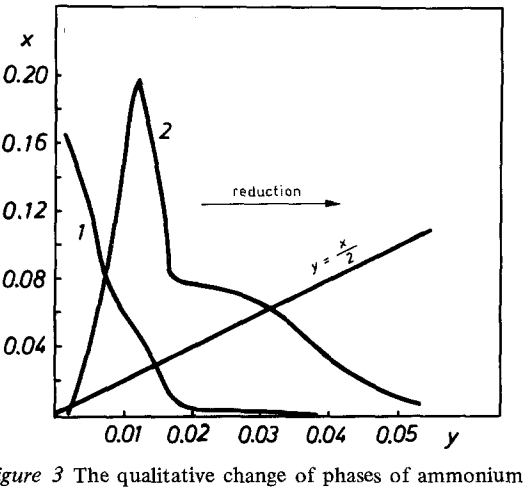


Figure 3 The qualitative change of phases of ammonium and hydrogen bronze structures dependent on the reduction degree. 1, NH_4^+/WO_3; 2, H^+/WO_3.

TABLE III Composition data calculated from the analytical "H_2O" content of the phases

Temperature (°C)	H_2O/WO_3 (see Table I)	Loosely-bound		H_2O/WO_3 bound by chemical forces			H/WO_3 bound in the H-bronze structures
		Measured H_2O (%)	Calculated H_2O/WO_3	Measured	In the form of $(NH_4)_2O$, x (see Table I)	In the H-bronze structures	
340	0.1209	0.380	0.0499	0.0709	0.0784	~ 0.0	0.0
360	0.1382	0.430	0.0564	0.0817	0.0605	0.0211	0.0422
380	0.1502	0.460	0.0609	0.0891	0.0409	0.0481	0.0962
400	0.1545	0.380	0.0499	0.1042	0.0299	0.0742	0.1484
420	0.1534	0.250	0.0331	0.1205	0.0224	0.0980	0.1960
440	0.1097	0.160	0.0208	0.0889	0.0134	0.0754	0.1508
460	0.0505	0.050	0.0064	0.0441	0.0044	0.0396	0.0792
480	0.0395	0.0	–	0.0395	0.0012	0.0383	0.0766
500	0.0341	0.0	–	0.0341	0.0004	0.0336	0.0672
520	0.0208	0.0	–	0.0208	0.0	0.0208	0.0416
540	0.0051	0.0	–	0.0051	0.0	0.0051	0.0102
560	0.0	–	–	–	–	–	–
580	0.0	–	–	–	–	–	–

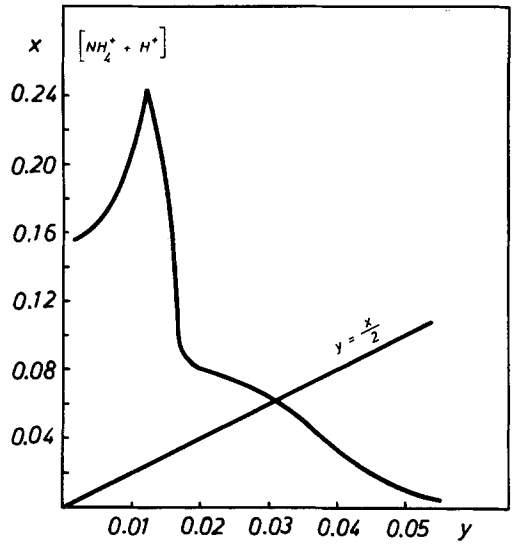


Figure 4 Summary of phase changes formed, consisting of NH_4^+- and H^+-ions, as a function of the reduction degree.

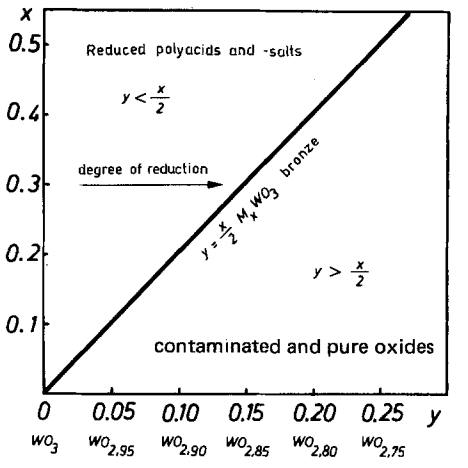


Figure 5 Relation between composition of possible phases in NH_4^+/H^+–W–O system and the reduction degree.

progressive reduction of polytungstates or, alternatively, by progressive contamination of WO_3, compositions with $y \lessgtr x/2$ can be produced with the same probability. Regarding this, with reference to the theoretical phase diagram shown in Fig. 5, the probable compositions can be divided into three parts. Along the $y = x/2$ straight line the bronzes can be formed, while in case of $y < x/2$ the reduced polytungstates are formed and in case of $y > x/2$ contaminated or pure oxides are present.

The diagram of possible phases shown in Fig. 5 seems to be a good base for the explanation of phase-transformations during thermal reductions. Figs 3, 4 and 5 indicate that the compounds formed in the initial stage of the APT reduction where $y \ll x/2$ are polyacids or polysalts, rather than bronzes. This is important from the point of view of their chemical status. In this system, bronzes can only be formed in a really narrow interval of compositions, where the $y = x/2$ straight line intersects the curves. In the vicinity of the straight line the slope of the curve is definitely decreasing (the curve belonging to the H^+-ions tends towards the horizontal) showing that, from thermodynamical and structural points of view, the bronzes are compounds of high stability. It is surprising that the H^+-ion curve intersects the $y = x/2$ straight line twice (see Fig. 3). In the initial stage of reduction a compound forms which already satisfies the bronze composition, while at about $y = 0.03$ a new compound of bronze composition arises through acidic polytungstates (hydrotungstates).

Fig. 6 represents a phase diagram of the NH_4^+/H^+–W–O system in the formation range of DAPT, ending at the γ-tungsten oxide. Ahead of the $y = x/2$ plane of composition, within the given temperature range, the system consists of reduced polytungstates (acids and/or salts), while at the intersections of plane and curves are the NH_4- and H-bronzes and behind the plane the contaminated and/or pure oxides seem to be stable.

It has to be emphasized that such a formation of phases is valid only under the described experimental circumstances. So, the ratio of the compounds can be slightly influenced by the NH_3 and/or H_2O contents of reduction gas. Increasing H_2 content of the gas phase shifts toward lower temperatures. Essential changes can be detected in the process only if the NH_3 and/or H_2O content of the gas changes. Experiments are planned, in order to clarify the effect of the NH_3 partial pressure, p_{NH_3}, and/or the H_2 partial pressure, p_{H_2}.

4.2. Structural considerations

The termination of phases on the basis of chemical criteria is self evident, while it seems to be more complicated on a structural basis, due to the very slight alterations of structure with composition around the $y = x/2$ straight line. It is well known that the bronzes can exist over a wider range of compositions, with the same basic structures. However, some slight structural changes, for

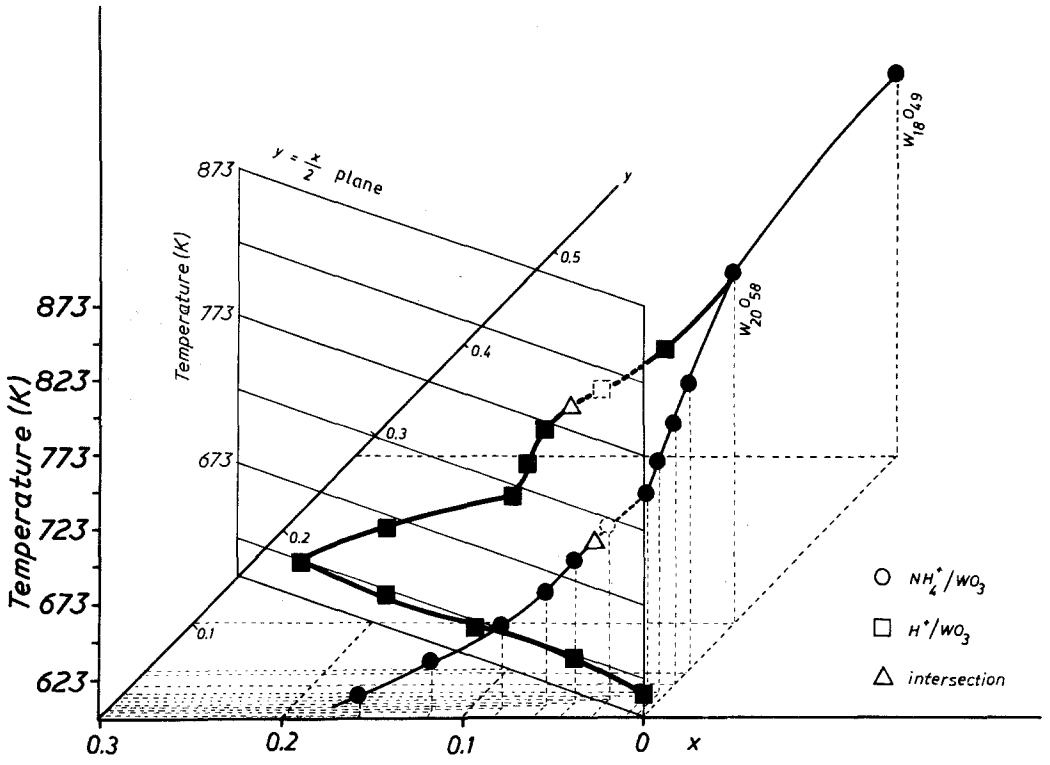


Figure 6 Phase diagram of NH_4^+/H^+–W–O system formed in reduction atmosphere of dry $H_2 + N_2$ gas mixture of 1 : 29 vol ratio.

example, progressive shift of the hexagonal axis ratio [18], show the changes of the reduction degree and/or of the concentration of contaminations compared to the ideal bronze properties. With regard to the reduced NH_4^+- and H^+-polytungstates, especially in their comparison with the true bronze structures, there is unfortunately no information in the literature, in spite of the industrial importance of these compounds; these are clearly materials that should be studied in more detail.

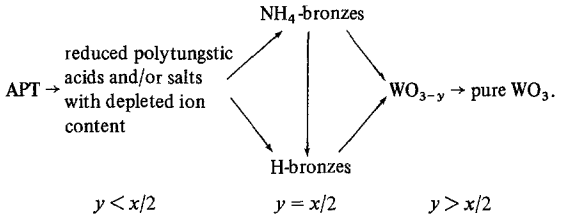
Due to the relative stability of this structural type, the term "bronze" can be more widely used in a crystallographic sense than it can in a chemical one. Accordingly, a structural type can be easily classified as bronze even if it is closer to polytungstate, e.g., from the point of view of its chemical ion exchange ability and other chemical properties. On the basis of new results of ion equilibrium studies, it is hardly questionable that the ion exchange properties of the DAPT are connected to some kind of compounds with acidic and/or salt characteristics [9]. That is, the ion exchange ability has its maximum where phases with composition $y \ll x/2$ [9] exist, and is very small in the vicinity of the bronze composition.

5. Conclusions

The products formed during the partial reduction of APT are called decomposed APT (DAPT) and they are considered as ammonium tungsten bronzes. The phases formed in the initial stage of reduction are blue, shiny crystals, similar to some tungsten bronzes but, on the basis of the bronze definition used in this paper and on that of the experimental results, these reduction products can not be classified as bronzes without some degree of uncertainty. The existence of DAPT and that of HTB established earlier in practice, have been more closly correlated. The idea of designating DAPT should be categorically changed, in the opinion of the authors. From the generalization of the experimental results presented in this paper it should be concluded that the DAPT designates all the compounds partially reduced and characterized by $y < x/2$. These phases can not be considered as tungsten bronzes, in a classical sense, but they are intermediate phases between tungsten bronzes and tungstates. Relying on the chemical properties, these compounds can be called reduced polytungstic acids and/or salts.

In conclusion, the authors suggest some change in the decomposition scheme of APT reduction,

based on the proposed theoretical phase diagram as follows



References

1. F. A. M. M. MEEL and A. W. J. VERHEIJEN, Proceedings of the Spring Meeting of the Metallurgical Society of AIME, Boston, 1972 (AIME, 1972).
2. L. BARTHA, and T. SZALAY, *Acta Techn. Acad. Sci. Hung.* **78** (1964) 309.
3. *Idem, Z. Phys. Chem.* **255** (1974) 974.
4. *Idem, ibid.* **255** (1974) 981.
5. *Idem, Magy. Kém. Foly.* **81** (1975) 67.
6. T. SZALAY, L. BARTHA and T. NÉMETH, *ibid.* **82** (1976) 135.
7. T. SZALAY, L. BARTHA, T. NÉMETH and J. LENGYEL, in "Reactivity of Solids" edited by Y. Wood, O. Lindquist, C. Helgerron and N. G. Vannenberg (Plenum Press, New York, 1977) pp. 449.
8. T. SZALAY, Cand. thesis, Budapest, 1977.
9. L. BARTHA, GY. GYARMATHY, B. A. KISS, T. NÉMETH, A. SALAMON and T. SZALAY, *Acta Chim. Acad. Sci. Hung.* **101** (1979) 127.
10. B. A. KISS and F. TISZA, *Tungsram Technische Mitteilungen* **41** (1979) 1687.
11. J. A. HEGEDÜS, Disszertáció MTA, Budapest. 1972.
12. J. A. HEGEDÜS and B. A. KISS, *Magy. Kém. Foly.* **73** (1967) 41.
13. J. NEUGEBAUER, *MTA MÜFKI Közl.* **0–15** (1974) 23.
14. *Idem, Acta Techn. Acad. Sci. Hung.* **78** (1974) 267.
15. B. A. KISS, P. GADÓ and J. A. HEGEDÜS, *Acta Chim. Acad. Sci. Hung.* **72** (1972) 371.
16. B. A. KISS, T. NÉMETH and E. SZALÁNCZY, *J. Mater. Sci.* **13** (1978) 541.
17. P. G. DICKENS and M. S. WHITTINGHAM, *Quart. Rev.* **22** (1968) 30.
18. B. A. KISS and L. CHUDIK, *Acta Chim. Acad. Sci. Hung.* **78** (1973) 237.

Received 24 June
and accepted 30 November 1981