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THERMOANALYTICAL STUDY OF THE COMPOSITION OF β-TUNGSTEN

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Abstract

The aim of the present work was to provide arguments to the almost 'hystorical' problem of what β-tungsten is.

WO_3 was reduced in dry H_2 gas atmosphere in order to examine, whether β-tungsten formed in such a way contains oxygen as part of the lattice described as W_xO (e.g. $W_{20}O$) or is a pure metallic phase of tungsten.

As a result of thermoanalytical measurements and of chemical analysis for oxygen, the assumption is supported that in the 600–800°C temperature range of metal formation not the W_xO (β-W)→W(α-W) transformation but the β-W→α-W structural rearrangement of materials with identical chemical composition is the most probable process.

The earlier opinion that the formation of the β-W structure requires the presence of oxygen atoms was not verified by our results.

Keywords: oxygen indexes, structure, thermoanalysis, β-tungsten, WO_3 reduction

Introduction

Tungsten is known in the β-W and α-W metallic modifications. Both have cubic lattice with parameters given in Table 1 [1, 2].

Table 1 Lattice parameters of α- and β-W

Modification	Type off cell	Space group	Lattice param. Å	Content of cell	Lit.
α-W	A2	lm3m O_h^9	a=3.165	2	[1]
β-W	A15	Pm3n-O_h	a=5.046	8	[2]

β-W was first prepared by Hartmann [3] and Fink [4] by electrochemical deposition from the melt of tungstates.

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The X-ray characterization of the material was also carried out by Hartmann *et al.* [5], who supposed the presence of lattice-forming oxygen atoms [5, 6]. They proposed a composition corresponding to the W_3O formula. According to Vasko [7] *this is not surprising, considering the difficulties associated with the* electrochemical formation of pure metallic tungsten. But in such a structure not only the lattice-forming role of oxygen has to be explained, but also its formation in the course of powder metallurgical reduction.

A certain ambivalence can be observed with the problem of pure, metallic β-W or its oxygenated variations. Several authors generally accept the W_3O formula [8, 16], while other [17–19] do not even mention the possible oxygen content of the β-structure.

Many authors [20–24] studied the reduction of WO_3 by thermogravimetry and did not find the TG step corresponding to the W_3O composition. On this basis its existence should be excluded also.

Millner et al. [22] reported in 1957 the formula of $WO_{0.066}$, and $WO_{0.042}$ for the β- and α-W, which are based partly on theoretical consideration because that time the sensitivity and accuracy of thermal analysis was not good enough.

For β-tungstens made by powder metallurgical reduction, the formula $WO_{0.05}$ is most frequently used [22], which appears sometimes as $W_{20}O$ [21]. Millner [25] reports a slightly different composition for β-W, with the formula $WO_{0.1}$. Wider ranges between $W_{14}O$ – $W_{20}O$ can also be found [26]. The latter authors claim a stabilizing effect of the oxygen either as a lattice component or as a species adsorbed on the surface.

A quite impressive assumption is the tungsten-tungstide [$W_3{}^*W$] structure [18, 19, 22, 28], containing tungsten ions of different oxidation states in the lattice. *It can be formally described as a slightly oxidized tungsten with no real oxygen content*, and also as an allotropic modification of α-W [20, 22, 27, 28].

The most recently published works [29–31] do not provide a clear statement either. Nowadays, too, the question of whether β-W is a low temperature modification of α-W, or a suboxide [29] e.g. W_3O, $W_{20}O$ etc. is still discussed. This was the reason, which mainly motivated the present work.

Experimental and results

Thermoanalytical examinations

High purity $WO_3 \cdot H_2O$ was heat treated for 2 h at 300°C and the obtained dehydrated material was powdered in an agate mortar to a particle size of 1–2 μm. The examinations were carried out with a Mettler T-WR thermobalance.

It can be seen from the curves of Fig. 1 that in dry hydrogen the sequence of the reduction follows the $WO_3 \rightarrow W_{20}O_{58} \rightarrow W$ scheme, as it was established by Neugebauer *et al.* [32]. It must be mentioned at this point that the possible size and the shape of the Mettler crucible limit the optimal quantity of the sample to 100 mg (layer thickness 2 mm) which could lead to the curves of Fig. 1. Higher layer thickness could initiate undesired reactions (e.g. the formation of WO_2) due to the humidity in the powder bed. This fact was also mentioned by other authors [20, 22, 27, 28].

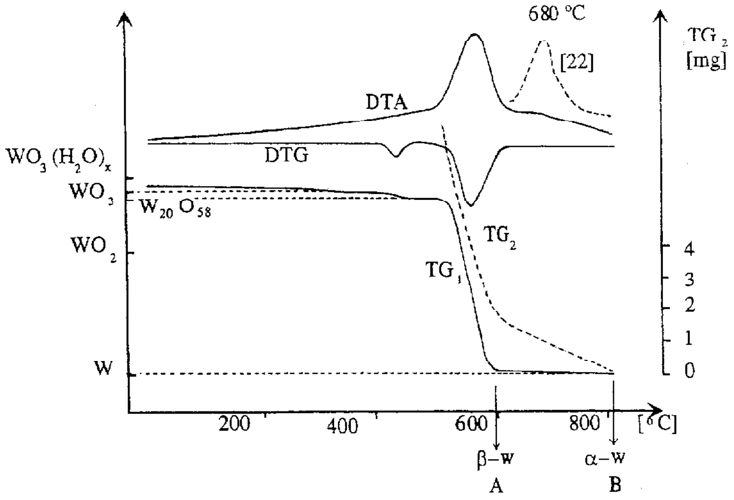

Fig. 1 Thermoanalytical curves obtained in the reduction of WO_3, heating rate: 4°C min^{-1}, stream velocity: 60 dm^3 h^{-1}, reducing gas: H_2 containing<10 ppm H_2O, ($pH_2O<5.5$ Pa.), TG_1: 1 mg/division, TG_2: 0.1 mg/division, DTG: 5 mg min^{-1}, DTA: 20 μV, sample mass: 100.8 mg

Because the DTA effect between 600–800°C was very slight, to avoid the low sensitivity of the heat measurements resulting from the small samples, the DTA curve was taken from the literature. This curve was independently measured in a DTA instrument under similar conditions, but using much larger samples [22]. Consequently, it is justified to use the results. Let us now examine the curves obtained at 600–800°C. The DTA curve shows characteristic changes, the TG_1, TG_2 and DTG curves remain practically unchanged. This means that the conversion between the A and B phases is only of physical and not of chemical nature between various chemical compositions. The latter should result in TG steps and DTG minima. Our curves prove that in the given temperature range only W→W structural conversion occurs and not a WO_x→W chemical transformation.

In order to obtain an easier representation, we took Millner's formula [25] of $WO_{0.1}$ for β-W, and drew the corresponding TG_2 curves (mass-curve of tenfold sensitivity) as shown in Fig. 2. The above curve or at least a small step would be obtained in this section of the TG_2 curve, if β-W were an oxide.

Since this kind of conversion could not be detected in Fig. 1 at all, we concluded that in the course of the reduction with dry H_2 gas both β- and α-tungsten

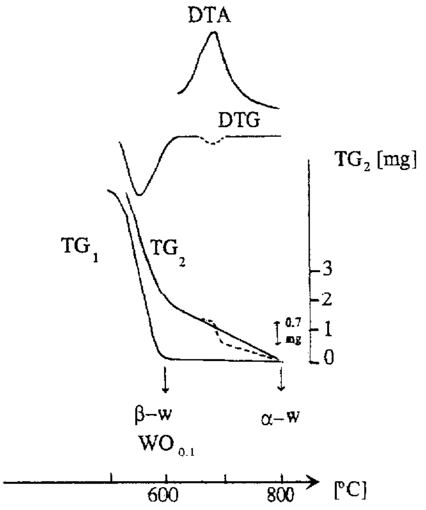

Fig. 2 Assumed characters of the TG curve for the β-W $WO_{0.1}$ composition; — measured curves; - - constructed curves

are formed as metallic tungsten. (The characters of TG_2 curves, whithout DTA suggest this conclusion.) In contrast to earlier ideas this means that the ordering of the β-W crystal in H_2 gas does not require the presence of stabilizing oxygen atoms. This may be considered as an evidence of the pure metallic phase.

Determination of oxygen indexes

For the analytical determination of the O/W mole ratio in metallic phases the Kiss-Tisza [33] and the Kiss-Csuhaj [34] method was used with the slight modification that instead of $1.999\cdot10^{-2}$ mol l^{-1}, $0.999\cdot10^{-2}$ mol l^{-1} $KMnO_4$ was used for titration. The oxygen index (O_I) was calculated by the following equation:

$$O_I=O/W=3-\frac{Af4\times10^{-4}M_{(WO_3)}}{M_{(Ox)}m_{(WO_3)}}$$

where A is the volume of consumed $KMnO_4$ solution in cm^3, f the factor of the titrant, $M_{(WO_3)}$ and $M_{(Ox)}$ the molecular and atomic masses of WO_3 and O, respectively; $m_{(WO_3)}$ the mass of the WO_3 equivalent to the actual sample size (~0.02 g), which was obtained by a 2 h ignition in air of an other portion of the material.

In order to check the suitability of the method, a thin piece of tungsten wire was analysed. The sample was previously cleaned from oxides in hot 20% KOH solution, water, followed by 10% HCl, then water, and finally dried. In addition, an α-W sample, formed at 800°C according to the process of Fig. 1, and also an-other α-W sample, prepared by the reduction of ammonium-tungsten-oxide-bronze (ATOB) at 900°C, were analysed.

In both cases the W powder samples were cooled to room temperature in a stream of dry H_2. To avoid any surface oxidation, attention was paid to the rapid (1–2 min) transfer of the samples into the $K_3[Fe(CN)_6]$+KOH solution. The analytical results are presented in Table 2.

Table 2 Initial oxygen indexes of a tungsten wire and W powders of α-structure

Type of error	No.	W wire	α-W from ATOB	α-W from WO_3
	1	3–2.9950=0.0050	3–3.0083=–0.0083	3–2.9663= 0.0337
	2	3–2.9972=0.0028	3–2.9842= 0.0158	3–2.9906= 0.0094
	3	3–3.0050=–0.0050	3–2.9884= 0.0116	3–3.0030=–0.0030
	4	3–3.0010=–0.0010	3–3.0038=–0.0038	3–3.0320=–0.0320
	5	3–2.9900=0.0100	3–3.0078=–0.0078	3–3.0000= 0.0000
Mean value	O/W	0.0023	0.0075	0.0016
Standard deviation ±δ		0.0057	0.0132	0.0207
Standard error of the mean ±Δ=		0.0025	0.0059	0.0092

Since the mean values in Table 2 only slightly differ from zero, it can be stated that both the wire and the powders consist of pure metal and practically have no oxygen index.

It can be concluded from the previous evaluation of the themroanalytical curves of Fig. 1 and also from the analytical results of Table 2 that β-W behaves

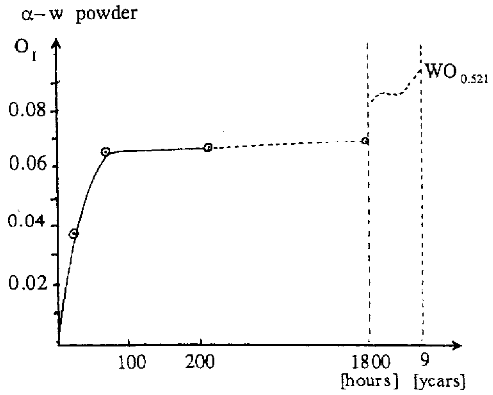

Fig. 3 Change of the O/W oxygen index in air for a whole block of pure α-W

as a pure, oxygen-free metal, just like α-W. The two different examination methods exclude the $W_xO \rightarrow W$ phase transformation.

The slight, but steady loss of mass in the 600–800°C range will be explained later. It merely should be noted that neither the TG curves nor the DTA curve indicate any $W_xO \rightarrow W$ chemical conversion.

To obtain further new information, we also examined the variation of the oxygen index of α-W as a function of the time. According to Fig. 3 the surface of the tungsten with initial zero oxygen is expected to get oxidized. In about 22 h time the O/W ratio for the full block will increase to 0.037 due to chemisorption, and later it will stabilize at around 0.065. From here on any further change is minimal. A nine-year old α-W sample, however, which was originally pure metal powder, now showed a value of 0.5 for the oxygen index.

X-ray analysis of the phases

With special regard to the instability of β-W crystals in air, we followed the changes of solid phases characterized by the thermal curve of Fig. 1 and carried out tests in a high temperature X-ray diffraction (HTXRD) chamber and reduced the initial tungsten oxide with a H_2 gas current of the same purity. For the HTXRD investigations a Philips MDP 1880 automatic powder diffractometer with a HTK-16 high temperature attachment was applied. The sample holder is a platinum ribbon which is heated to the required working temperature. The heating rate was 30°C min^{-1}.

The diffractograms justify the phases of the TG curves of Fig. 1. On the basis of Fig. 4 and Table 3, in the horizontal, 500°C section of the curve pure β-oxide ($W_{20}O_{58}$) is formed, which is converted gradually to β-W between 500–600°C. The product at 650°C consists of pure β-W, which rearranges into the pure α-structure at 800°C.

Discussion

Thermoanalytical curves exclude that in the range between 600–800°C any A→B phase conversion takes place, since these curves indicate merely structural changes of chemically identical A→A′ formations. Taking also into consideration that the α-W final product appears to be pure – this is proved by chemical analysis – it follows that also the β-product must be a metal, free of oxygen.

On this basis we think that both α-W and also β-W phases consist only of W components and the $W_{20}O$ formula and others do not coincide with this idea.

Our results suggest the following conclusions:

A: In sufficiently dry H_2 gas atmosphere both the α-W and also the β-W modifications can be regarded as pure metals, provided that they are kept constantly in reducing gas.

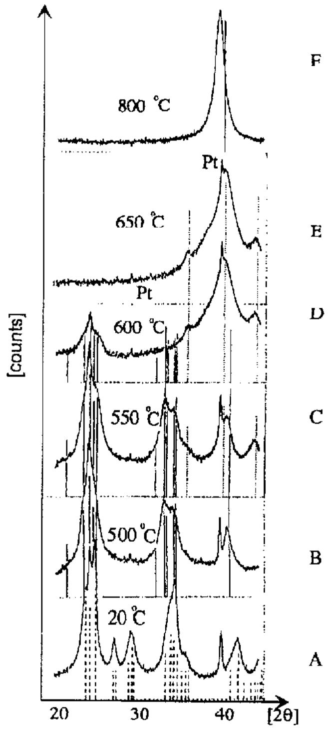

Fig. 4 X-ray diffractograms of phases at various temperatures. Experimental parameters: focusing: Bragg-Brentano. X-ray source: monochromatic CuK_{α}, type of scan: step, scanning steps 2 θ°: 0.02, scan step time s: 1; data base: 1-44 ICDD; software: PC-APD 3.6 g

B: In atmospheric air, however, both the α-W and β-W phases will take up oxygen, thus the mean composition of the whole metal powder could be described as W_xO or WO_x. We have to add, however, that this oxygen does not belong to the lattice, is only present in the adsorption layer.

C: The concept that β-W should be of $W_{20}O$ stoichiometry, as described in several works, should be supervised. The amount of adsorbed oxygen depends on the surface structure, particle size, and specific surface of the metal powders.

Taking now into consideration the electrical charges it should be analysed what the results would be if the primary β-W ($W_{20}O$), and the secondary β-W $K_{0.1}WO_{0.05}$ formulae, i.e. the O/W=0.05 oxygen-index as described by Neugebauer [21] were accepted. Then the charges could be expressed as follows:

$$W_{20}O=[W_{20}^{0.1+}+O^{2-}]$$

for the *pr.* β-W, whereas for the *sec.* β-W the realistic formula would be

$$0.05/K_2O/[W]$$

Table 3 Detailed phases of the diffractograms as shown in Fig. 4. (The intermittent redrawn and dotted lines mean the lines given by the PDF cards. The lower angular values belonging to higher temperatures are the consequences of increased cell-growth e.g. α-W at 800°C)

Mark on Fig. 4	Compositions of phases	Number of powder diffraction file (PDF)
A	WO_3	20-1323
B	$W_{20}O_{58}$/β-oxid/	5-0386
C	$W_{20}O_{58}$+β-W	5-0386+ 2-1138 41-1230
D	$W_{20}O_{58}$+β-W	5-0386+ 2-1138 41-1230
E	β-W	2-1138+41-1230
F	α-W	4-0866

According to this, the binding energy of oxygen to the K atom is significantly greater than to the W, therefore in the lattice only chargeless W^0 atoms would be present. The above reasoning clearly shows that the representatives of the oxygenated variation contradict their own statement, since the *pr.* β-W would correspond to the oxygenated, whilst the *sec.* β-W to the oxygen-free structure. The latter could be only an adsorption complex.

Naturally these ideas do not exclude the feasibility of the *sec.* β-W→ α-W rearrangement for the efficient inclusion of the doping materials [35].

In our opinion, however, the real nature of *sec.* β-W and its fine structure formed in H_2 gas at high temperatures as well as its chemical structure and assumed bond to potassium, all require further studies.

The small mass loss experienced in a dry H_2 atmosphere between 600–800°C as seen in Fig. 1, observed also by other authors [20] needs further explanation.

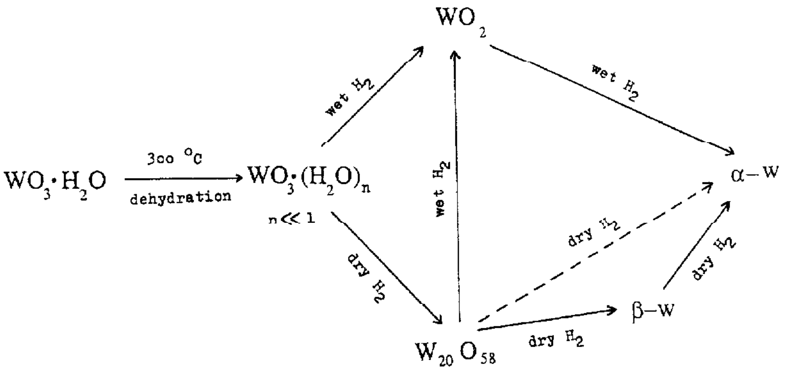

Fig. 5 Scheme of phase-conversions of the WO_3 reduction as a function of the humidity in the H_2 gas

Since in this temperature range the existence of adsorbed oxygen cannot be assumed on the surface of metal grains, therefore the small equal mass loss is explained as follows.

The $W_{20}O_{58}$ can be reduced quite easily up to 600°C, but over this temperature it can be covered with a thick tungsten layer, which hinders the penetration of H_2 molecules. It would also inhibit the diffusion of the H_2O molecules, and the reduction of the traces of the enclosed β-oxide.

Finally, in Fig. 5 a schematic representation of the proposed mechanism of the reduction of WO_3 is shown as a function of humidity of the reducing H_2 gas.

In this system the way of the β-oxide→α-W conversion could be regarded as a kind of 'forbidden transition' since intermediates are formed before the α-W stage is achieved, irrespective of whether dry or wet H_2 was used. Searching for the thermodynamic reason for this, i.e. the change of the free enthalpy ΔG cannot even roughly be estimated, since for the calculation by the $\pm\Delta G = \Delta H - T\Delta S$ equation the thermochemical data are not available. From structural considerations we may only deduce that the difficulties of the β-oxide→α-W conversion may only be overcome by the above intermediate steps. The β-oxide is either reduced via the WO_2 step or the formation of the β-W structure will be the transitional form before the α-W is achieved. Further clarification of the whole complex problem will have to be carried out in the course of future studies.

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