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# Ion exchange adsorption processes on the surface of ammonium tungsten oxide bronze in aqueous media

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A possible chemical model for the doping of tungsten metal was studied using technological blue oxide [$(NH_4)_xWO_3$]. Applying potassium-42 and rubidium-86 radioactive isotopes as tracers Langmuir–Hückel type isotherms were determined. The constants of the isotherms led to conclusions on how the ion-exchange capacity of blue oxide and the solubility of the adsorbate varied as a function of composition of the solutions. The results show the conclusions that: (1) primarily the acidic protons of the OH-groups from the dissociative adsorption of water, and not the ions of the crystal lattice ($NH_4^+$) which can be exchanged for ions of the liquid phase, and consequently (2) there is a certain possibility for controlling the ratio of the adsorbed potassium-, aluminium-, and silicate-doping ions.

## 1. Introduction

For a number of years in the tungsten research of the incandescent lamp industry, the nature of how the traces of foreign elements in concentrations of $10^{-4}$ to $10^{-3}$ wt % raise the temperature of recrystallization, what kinds of particle-effects result in a macrocrystalline structure and in the so-called non-sag character [1] have been of great interest. The most recent investigations attempt to clarify the characteristic physicochemical effects of the foreign atoms appearing during powder metallurgical reduction [2]. These effects may induce the desired properties of the metal in different ways. There are several procedures for getting the additives into the starting material of tungsten production (the so-called technological blue oxide). One of these procedures developed earlier by us [3] has its basis in a chemical model [4] according to which cations (e.g. $K^+$ and $Al^{3+}$) are bound on the oxide surface by ion-exchange, the anions (e.g. $SiO_3^{2-}$) on the other hand are fixed in a cation-induced, specific adsorption process.

We have reported recently [5] that the reaction of sodium tungsten oxide bronzes of general formula $Na_xWO_3$, $x$ being a stoichiometric number in the range $0.35 < x < 0.75$ in appropriately chosen aqueous solutions can be conveniently studied by the ratioactive tracer method. In the present study the target of our investigations was $(NH_4)_{0.114}WO_{2.96} \cdot 0.068\,H_2O$, a tungsten oxide bronze (ATOB), available in sufficient quantities for extensive investigations.

## 2. Experimental method and results

It was mentioned already that in the powder metallurgical production of tungsten metal certain additives are applied to produce the desired crystal structure, and macroscopic properties. In our earlier investigations, following Meel and Verheijen [6] and Neugebauer [7] we studied the doping of the yellow $H_2WO_4$ ($= WO_3 \cdot H_2O$), and later the blue ($WO_{2.87}$) tungsten oxide. Our results were in agreement with the idea that potassium ions are bonded on the surface of tungsten oxides by ion-exchange, and these chemically bound additive ions may produce the known "additive-effects" during powder metallurgical reduction. The primary ion-exchange equilibria could be correctly described by Langmuir–Hückel type isotherms [8] the parameters of which, i.e $Z$ and $c_0$, served as the basis of meaningful conclusions. The isotherm was used in the form:

$$\frac{100 - f}{vf} = \frac{1}{Z}(c_e + c_0) \qquad (1)$$

where $f$ is the amount of ions (%) bonded on the surface of a given amount of oxide, $v$ is the volume of the liquid phase ($dm^3$), $Z$ the maximum capacity of the given amount of oxide for ion-exchange, $c_e$ the equilibrium ion concentration, and $c_0$ a characteristic concentration for the adsorbate (both in mol $dm^{-3}$). The equilibrium concentration and the starting concentration ($c$) in the solution are related by:

$$c_e = \frac{100 - f}{100}c \qquad (2)$$

Rubidium-86 and potassium-42 isotopes were used as tracers, and the half-lives (18.6 day and 12.4 h, respectively) allowed a double tracing, i.e. the study of the simultaneous adsorption of the two ions directly. Following the complete decay of the potassium-42 isotope, the radioactivity of the reference solutions and that of the reaction mixtures (taking 2 ml samples

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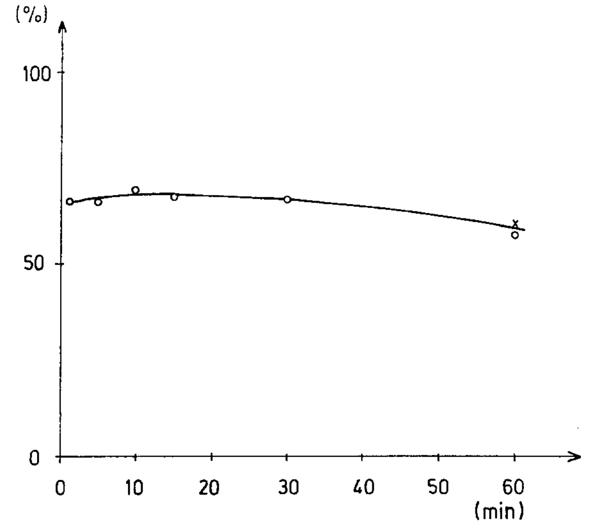

*Figure 1* Ion-exchange adsorption time curve (50 mg ATOB in 25 cm$^3$, 5.37 × $10^{-5}$ M RbCl solution at 25° C) (×) repeated.

TABLE I Isotherm constants obtained by rubidium-86 tracer method

| Salt | Medium | $Z \times 10^5$ (mol g$^{-1}$) | $c_0 \times 10^5$ (mol dm$^{-3}$) |
|---|---|---|---|
| RbCl | water | 3.54 | 1.80 |
| $RbCl:NH_4Cl$ | water | 3.02 | 1.96 |
| RbCl : HCl | water | 2.43 | 1.33 |
| RbCl | $1 \times 10^{-2}$ M HCl | 1.76 | 3.38 |
| $RbCl:\frac{1}{3}AlCl_3$ | $1 \times 10^{-2}$ M HCl | 1.01 | 0.72 |
| RbCl : KCl* | water | 2.28 ($Rb^+$)<br>1.02 ($K^+$) | 1.50<br>1.78 |

*Data of the double-tracing.

of the liquid phase) were measured through several days and the ratio of potassium and rubidium was determined from the decay curves.

All the materials used were of highest purity, and the ultrapure ATOB "adsorbent" was kindly supplied by TUNGSRAM Co. Hungary. Crystal fractions of the size 80 to 100 $\mu$m were used in most of the experiments if not stated otherwise.

The solutions were usually made by gradual dilution of stock solutions (accompanied by applying the tracers), the stocks being prepared by weighing. For example a solution of potassium silicate was prepared by soaking silicic acid in water followed by reaction with solid KOH in small excess and dissolving the resulting salt in a small amount of water. The solutions for the experiments were then prepared by dilution to the desired concentration.

All the experiments were carried out at 25 ± 0.1° C (except those to establish a temperature dependence of the process). The desired proportion of the mass of adsorbent and the volume of solution, as well as the time required to reach the primary equilibrium were determined in preliminary experiments. It can be seen from Fig. 1 that equilibrium is reached quickly, and the gradual fall of the curve exceeding experimental error (maximum ±2%) can only be observed over a longer period. This latter phenomenon can be attributed to the building back into the bronze of $NH_4^+$ ions previously released into the solution.

It is worth mentioning that the solubility of oxide bronzes is $\sim 10^{-5}$ M, somewhat depending on the actual composition of bronze.

According to our earlier experience, the isotherm 1 describes correctly the sorption equilibrium in the solubility range from the solubility of the adsorbent to about $1 \times 10^{-3}$ M. Taking into account the $^{86}$Rb concentration in its carrier (RbCl) and the requirements for the radioactivity measurements of the desired accuracy, the lowest concentration of the solutions studied could be set at $5.37 \times 10^{-5}$ M.

## 2.1. Isotherms with RbCl

For the isotherm determinations 50 mg oxide bronze was stirred in 10 ml solution for 10 min at 300 r.p.m. in a test-tube like reactor. The phases were separated on a 0.40 to 0.80 $\mu$m Sartorius membrane filter and samples of 2 ml volume were withdrawn from the liquid phase, the radioactivity of which were compared to that of the initial solutions. Usually two parallel measurements were done, in case of unexpected values, however, the experiments were repeated as many times as required to arrive at consistent data.

The isotherm constants were first determined using pure aqueous solutions. In the case of foreign ions a 1 : 1 concentration ratio (1 : mol/charge, in the case of multivalent ions) was used to study the changes in the parameters of the rubidium isotherms.

It was of interest to investigate (by addition of $NH_4Cl$) how much the added $NH_4^+$ represses the ion-exchange equilibrium, and whether there was any exchange of the $NH_4^+$ ions of the oxide bronze for $Rb^+$ from the solution?

The reason for double tracing with $^{42}K^+$ and $^{86}Rb^+$ was to clarify the participation of $Rb^+$ and $K^+$ ions in a simultaneous adsorption and to check the reality of the data obtained with other foreign ions. Table I contains the parameters of the $Rb^+$ exchange isotherms in solutions of different composition. It can be seen, that HCl is not able to replace all the doping ions completely even in the case of concentrations an order of magnitude higher than those of the other solutions. An HCl concentration of $1 \times 10^{-2}$ M was also required to prevent hydrolysis of $Al^{3+}$, i.e. to keep all the aluminium in solution as $Al(H_2O)_6^{3+}$.

It should be mentioned at this place that although both $c_0$ and $Z$ were calculated by the method of least squares, $c_0$ may carry a substantially larger error than $Z$.

## 2.2. Isotherms with KCl

Since $^{42}K^+$ has a much shorter half-life than $^{86}Rb^+$, it was possible to determine the constants of the isotherms even in the case where all three doping ions were present; $K^+$, $Al^{3+}$ and $SiO_3^{2-}$. The relevant figures are contained in Table II.

## 2.3. The effect of temperature on the exchange of $Rb^+$

Previous investigations [9] have revealed that the parameters of the isotherms were usually temperature dependent. The results of this study with respect to the temperature effect are shown in Table III.

TABLE II Isotherm constants obtained by potassium-42 tracer method

| Salt | Medium | $Z \times 10^5$ (mol g$^{-1}$) | $c_0 \times 10^5$ (mol dm$^{-3}$) |
|---|---|---|---|
| KCl | water | 2.99 | 3.44 |
| KCl + $K_2SiO_3$* | water | 4.17 | 3.08 |
| KCl | $1 \times 10^{-2}$ M HCl | 1.66 | 13.50 |
| KCl : $\frac{1}{3}AlCl_3$ | $1 \times 10^{-2}$ M HCl | 1.27 | 7.55 |
| KCl + $K_2SiO_3$ : $\frac{1}{3}AlCl_3$* | $1 \times 10^{-2}$ M HCl | 1.13 | 6.63 |
| KCl : RbCl† | water | 2.28 ($Rb^+$) | 1.50 |
|  |  | 1.02 ($K^+$) | 1.78 |

*In addition to the $K^+$ originating from the KCl carrier, $K_2SiO_3$ was also added up to the required concentration of $K^+$. The stock $K_2SiO_3$ solution was neutralized (pH = 7) with 1.0 M HCl, and was diluted until a concentration of $[K^+] = 1 \times 10^{-3}$ M, and $[SiO_3^{2-}] = 3.69 \times 10^{-4}$ M was attained. This diluted solution was used for obtaining appropriate $K^+$ concentration in the samples.

†Data of the double-tracing.

### 2.4. The effect of the particle size of ATOB samples on $Rb^+$ isotherms

The effect of particle size on the adsorption of doping ions is a very important practical factor. In a RbCl solution of $3.037 \times 10^{-4}$ M (10 ml solution, 50 mg oxide bronze) we have found an unexpected nonlinear change of the adsorption capacity with the surface area of the bronze (Table IV), therefore complete isotherms were also determined (Table V).

## 3. Discussion

The results of this study confirm our earlier assumptions that Langmuir–Hückel type isotherms 1 are suitable to describe the behaviour of doping ions in small concentrations.

Analysis of $Z$ values presented in Table I reveals that $NH_4^+$ is less able to replace $Rb^+$ on the surface than $K^+$ and $H^+$. This seems to confirm that those are not the bronze-forming ions which directly participate in exchange processes [5, 10]. (This conclusion is in accordance with Spicin and Castanov's statement that $1.5 \times 10^{-5}$ mol $H_2O$ m$^{-2}$ bound on the surface of the oxide bronzes, and this water evaporates only at 300° C.)

It is striking that hydrogen ions are not able to completely replace the tracer ion on the surface even in a concentration two orders of magnitude higher than that of the tracer, however, even under such circumstances, $Al^{3+}$ replaces $K^+$ or $Rb^+$.

The data of Table II are in agreement with the previously mentioned model of doping, i.e. with the hypothesis of a secondary adsorption of $K^+$, as a result of cation induced fixation of $SiO_3^{2-}$, since in the presence of $SiO_3^{2-}$ considerably higher $Z$ values were determined for the adsorption of $K^+$.

It is worth mentioning that (under practically the same conditions) more $Rb^+$ than $K^+$ can be bound on the surface of the oxide bronze. We attribute this finding to the more positive character of rubidium.

It has been already pointed out, that the $c_0$ parameter of the isotherm can be determined less accurately than $Z$, the parameter characterizing the ion-exchange capacity, however, in this case $c_0$ varies so obviously with the composition of the solutions that it should be interpreted as showing a considerable change in the solubility of the adsorbate (Table II).

The surprising dependence of the isotherm parameters on temperature (Table III) is a consequence of the competition of ammonium ions (arising from dissolution of the oxide bronze), hydrogen ions (participating directly in the exchange process), and potassium and rubidium ions, since the free enthalpy belonging to the exchange of these four ions may be different.

The complex effect of the three doping components can surface not only in solubility changes but also in the powder metallurgical reduction of doped ATOB. Our results show that all the three doping ions can be fixed on the oxide bronze through the primary and secondary processes. The practical consequence of ion-exchange doping is in that the raw material of reduction can be regarded as an [(ATOB) K, $SiO_3$Al] complex molecule. On the other hand, when the additives are fixed on the bronze by evaporation of a strong HCl solution, they are left behind mainly as salts, and the resulting solid phase can be characterized as a mixture of an [ATOB–KCl–$AlCl_3$–$SiO_2 \cdot H_2O$] composition. According to recent findings, traces of foreign compounds of different forms have different influences during powder metallurgy and in the metallic state.

TABLE III Isotherm constants obtained at different temperatures by rubidium-86 tracing

| (° C) | $Z \times 10^5$ (mol g$^{-1}$) | $c_0 \times 10^5$ (mol dm$^{-3}$) |
|---|---|---|
| 25 | 3.54 | 1.80 |
| 30 | 3.26 | 1.77 |
| 35 | 3.36 | 1.78 |
| 40 | 3.01 | 2.41 |

TABLE IV Values of the rubidium bound on ATOB of different particle sizes (50 mg ATOB, 10 cm$^3$ RbCl solution of $3.037 \times 10^{-4}$ M starting concentration)

| The range of particle size (μm) | Individual (%) | Average values (%) |
|---|---|---|
| 45–63 | 46.18 | 44.52 (?) |
|  | 42.87 |  |
|  | 46.52 (repeated) |  |
| 63–80 | 48.95 | 47.70 |
|  | 46.46 |  |
| 80–100 | 45.83 | 45.58 |
|  | 45.33 |  |
| 100–160 | 47.44 | 47.15 |
|  | 46.86 |  |
| 160 < | 49.09 | 50.49 (?) |
|  | 51.89 |  |
|  | 46.56 (repeated) |  |

TABLE V Isotherm constants obtained using ATOB of different particle sizes ($^{86}$Rb tracer)

| The range of particle size ($\mu$m) | $Z \times 10^5$ (mol g$^{-1}$) | $c_0 \times 10^5$ (mol dm$^{-3}$) |
|---|---|---|
| 45–63 | 3.22 | 1.56 |
| 80–100 | 3.54 | 1.80 |
| 100–160 | 3.12 | 1.05 |
| 160 < | 3.43 | 1.44 |

Different chemical forms of additives influence the kinetics of reduction, the particle size of the tungsten powder and its distribution, moreover, depending on the doping process, very characteristic, individual physico-chemical effects can be observed. From this respect, doping by ion-exchange results in a surface composition, the reduction of which reveals very favourable effects of the additives [11].

The equivocal relation observed between the particle size of ATOB and the parameters of the isotherms require special considerations. In our previous studies on the ion-exchange processes of ammonium hydrogen tungsten oxide bronzes it was established that despite the ion exchange being a surface process, there was no linear correlation with the BET surface area. There may even be an antiparallel change in the ion-exchange capacity and specific surface [12]. Since the bronzes are nonstoichiometric compounds there is a possibility during crystallization for forming surfaces with different defect structure, that is the "active centres" are not necessarily evenly distributed, as a result of which the actual number of these centres does not necessarily increase together with an increase in the specific surface or in the particle size.

According to the well known Ostwald–Thomson equation (e.g. [13–15]) the solubility is greater the smaller the particles and the increase in the concentration of self-ions may make up for the effect of the increase in specific surface area. (The expelling effect of the self-ions may exceed – or compensate – the increase in ion-exchange capacity as a result of increase in specific surface area.)

## 4. Conclusion

In the early stage of tungsten production for the incandescent lamp industry, potassium-, aluminium- and silicium-compounds are added to the tungsten oxide to give rise to the so-called non-sag characteristics. It has for a long time been an open question how the additives ($K^+$, $Al^{3+}$, and $SiO_3^{2-}$) are bound to the surface of tungsten oxide, and how the surface complexes arising by this doping influence the course of reduction and the further processing of the oxide and metal. Doping by ion-exchange is based on a possible chemical model, in which the additives are introduced in appropriate amounts and ratios through ion-exchange adsorption.

The results presented in this paper give support to this chemical model. By appropriately changing the composition of the doping system surface complexes of required composition can be produced, and these complexes influence the particle size and distribution of tungsten powder and the quality of the end product.

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