Hydrogen Reduction of Tungsten Oxides: Alkali Additions and Their Interaction on the Metal Nucleation Process

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Abstract

It is known that the addition of alkali compounds influences W particle growth during the reduction of tungsten oxide using hydrogen. Literature exists but the mechanism and mode of interaction remain unclear. To improve understanding of the reduction process, lithium, sodium and potassium compounds were added to a highly pure tungsten oxide prior to reduction, and interrupted reduction experiments were carried out at 750 °C. The resulting powders were investigated by metallographic and chemical means, X-ray diffraction, SEM and EDX analysis.

The experiments showed that intermediately formed tungsten bronzes play an important role in the early stages of reduction. In addition it is demonstrated that the kinetics of the reduction sequence differs significantly between doped and undoped tungsten oxide powders, as demonstrated by the on-line measurement of reaction water in the hydrogen process gas.

The results help to understand how the presence of alkali compounds effects the reduction of tungsten oxides.

Keywords

reduction, tungsten oxide, alkali compounds, hydrogen, nucleation, mechanism

Introduction

Hydrogen reduction of tungsten oxides is an important and well established industrial process for the manufacturing of high quality tungsten powder [1].

The overall reduction can be summarized by the chemical Eq. (1) given below.

\[
\text{WO}_3 + 3 \text{H}_2 \leftrightarrow \text{W} + 3 \text{H}_2 \text{O}
\]  

(1)

However, as shown in earlier investigations [2-7], a series of oxides is formed intermediately during reduction and a chemical vapour transport process (CVT) takes place. The intermediate phase
transformations are $\text{WO}_3 \rightarrow \text{WO}_{2.9} \rightarrow \text{WO}_{2.72} \rightarrow \text{WO}_2 \rightarrow \text{W}$. The CVT process is based on the formation of a volatile tungsten oxide, $\text{WO}_2(\text{OH})_2$, which forms with the water produced during reduction. Thus, a certain vapour pressure of this compound prevails during the reduction sequence which determines the morphology of the reaction products, in particular of the metal powder particles formed [2]. Each transition stage during reduction has, therefore, to be considered from two viewpoints: phase nucleation, and phase growth. Whereas the first stage can be considered to occur always on the surface of the reacting species (e.g. $\text{WO}_2$) in the form of a vapour/solid reaction, the growth stage can take place via the volatile tungsten compound. These two stages are shown in the Eq. (2)-(4) for the formation of tungsten metal:

\[
\text{WO}_2 + 2 \text{H}_2 \leftrightarrow \text{W} + 2 \text{H}_2\text{O} \quad \text{(tungsten nucleation),} \tag{2}
\]

\[
\text{WO}_2 + 2 \text{H}_2\text{O} \leftrightarrow \text{WO}_2(\text{OH})_2 + \text{H}_2 \quad \text{(formation of volatile tungsten compound)} \tag{3}
\]

\[
\text{WO}_2(\text{OH})_2 + 3 \text{H}_2 \leftrightarrow \text{W} + 4 \text{H}_2\text{O} \quad \text{(tungsten growth by CVT)} \tag{4}
\]

It was demonstrated by Schubert et al. [6] that in the case of pure tungsten oxide the nucleation of the metal phase becomes possible only at significantly lower hydrogen humidity, as expected from thermodynamic data. This gap between the theoretically and kinetically possible areas of tungsten metal formation at a given temperature is a result of the nucleation work which has to be done when $\text{WO}_2$ is transformed into $\text{W}$ metal. However, if the nucleation process is facilitated by a “nucleation aid” formation of tungsten metal becomes possible even at this higher humidity because the moment a tungsten nucleus is formed further growth of tungsten can readily occur via the vapour phase. The higher the humidity within the powder bed, the more $\text{WO}_2(\text{OH})_2$ is available, and the faster is the particle growth.

Investigating the role of potassium on the reduction of so-called non sagging tungsten, used in the lighting industries, Neugebauer [8] observed the early formation of tungsten metal out of potassium tungsten bronzes ($\text{K}_x\text{WO}_3$) than out of $\text{WO}_2$. In later investigations [6], several ternary tungsten compounds (tungstates, tungsten bronzes) and even metal powder particles (Mo, Co, Ni, Cu) were able to act as nuclei for tungsten deposition by CVT [9].

Alkali additions to tungsten oxides prior to their hydrogen reduction are known to influence significantly the properties of resulting metal powders, in particular their particle size; e. g. additions are used industrially to produce tungsten metal powder with mean particle sizes well above 10 $\mu$m [1].

Two different mechanisms have been proposed up to now to explain the interaction of the additives on the reduction process:

- The catalytic action of liquid alkali compounds upon the reaction with water vapour forming the volatile oxide hydrate [9]. Equimolar concentrations of Li, Na and K have about the same effect on particle coarsening, which supports this theory.
- the occurrence of tungsten bronzes, and their effect on the metal nucleation process [10-11].

It is the aim of the present work to find experimental evidence to support one or other of these mechanisms for alkali additions.
The term *tungsten bronze* was used for the first time by F. Wöhler [12] because of the compounds’ metallic lustre as well as their interesting electrical properties. Their chemical structure is commonly written as \( \text{Me}_x\text{WO}_3 \) (Me...metal, with \( 0<x<1 \)). Depending on the \( x \)-value they may form hexagonal, triclinic, tetragonal or cubic structures. They are non-stoichiometric compounds and are known for their shiny colourations (purple, violet, blue, red or golden).

**Experimental**

**Starting Materials**

High purity tungsten yellow oxide was provided by Wolfram Bergbau- und Hütten AG. Alkali additions to the tungsten oxide were made in the form of potassium carbonate, sodium carbonate and lithium hydroxide, all of analytical quality (Sigma-Aldrich).

Different experiments were made to study the effect of the alkali compounds during the hydrogen reduction process.

**Interrupted Reduction Experiments**

Firstly a powder mixture was prepared by blending 1 kg \( \text{WO}_3 \) with an equivalent of 2 g of alkali metal. In this case the distribution of the compound was not uniform, and alkali compound “islands” remained within the powder bed (*non-uniform dopant addition*). This facilitated direct observation of the compounds formed (due to their characteristic colours as compared to the surrounding non-doped matrix) and how they affected the reduction process.

This mixture was then filled into a reduction boat to a layer height of 2 mm. The boat was then pushed into the heating zone of a tube furnace (Figure 1(a)) at 750 °C under dry hydrogen (6L/min). The reduction sequence was interrupted after 5 and 30 min by pulling the boat into the cooling zone.

Further reduction experiments were carried out with a powder layer height of 25 mm. In this case the interruption was made after 120 min to investigate the reduction sequence under very humid conditions. The powder mixture was then partly infiltrated with resin and cut vertically to prepare a cross section through the whole powder bed. This permitted investigation of the whole layer from top to bottom, without any mixing of interlayers.

**Humidity Measurement of the Reaction Water**

In this case the respective alkali compounds were added in the form of an aqueous solution in equimolar amounts (14 mmol/kg) to the tungsten oxide to achieve a *uniform dopant distribution*. The powders were filled in reduction boats and reduced in a tube furnace with dry hydrogen at 750°C and 900°C, in the same way as described above.

Measurement of the of reaction water produced over time was carried out by a thermal conductivity measurement unit (Figure 1(b)) capable of following the water formation over the whole reduction sequence. It thus provides data on the kinetics of the reduction process.
Analysis

The analysis of the powders included optical microscopy, scanning electron microscopy (FEI Quanta 200), equipped with an energy dispersive analysing system (EDAX Genesis), X-ray diffraction (Philips X’Pert PRO, Generator PW 3040/60, Goniometer PW 3050/60, copper anode), chemical analysis (ICP-OES) and metallographic investigations of the resin-embedded powders.

In case of lithium compounds no chemical analysis could be performed by X-ray emission analysis (EDAX).

Results

Interrupted Reduction Experiments

Lithium: After 5 min reduction time the layer surface could visually be separated in two zones. The area closer to the hydrogen inlet showed a greyish blue matrix with some grey speckles, while the rest of the surface layer was brown with several steel-blue “islands”. These steel-blue speckles or craters were formed exactly in positions where before reduction the dopant compound had been. Fig. 2(a) shows a picture of the boat (dry hydrogen from left).

Results from examination of points marked 1, 2, 3 and 4 in Fig. 2(a) by SEM and XRD are given in Table I.

Table I: XRD and SEM examination of powder bed after 5 min reduction time in dry hydrogen at 750 °C (lithium addition); APT psm. … APT pseudomorphs.

<table>
<thead>
<tr>
<th>Pos.</th>
<th>Colour</th>
<th>Phases in XRD</th>
<th>Morphology (SEM)</th>
<th>Resumé (XRD + SEM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>grey/blue</td>
<td>WO$_3$-X-related</td>
<td>lumps of cuboids</td>
<td>Li-bronze with monoclinic structure</td>
</tr>
<tr>
<td>2</td>
<td>grey</td>
<td>W, WO$_2$, Li-bronze</td>
<td>APT psm.</td>
<td>tungsten metal already formed</td>
</tr>
</tbody>
</table>
After 30 min reduction time the biggest part of the powder surface was grey with some brown areas. The number of brown areas increased from left to right, as shown in Fig. 2(b). Examination of points 1 to 4 in Fig. 2(b) showed that the amount of tungsten dioxide in the X-ray diffractograms increased from 1 to 4. Two additional phases were detectable: W-metal and lithium tungstate (Li₂WO₄).

**Sodium:** After a reduction time of 5 min (Fig. 3(a)) the surface of the powder bed showed a gradual transition from brown (left side) to dark brown/violet colour. An array of bluish and ruby spots could be seen all over the surface where the sodium compound had been before reduction.

![Figure 3: Reduction boat after (a) 5 min and (b) 30 min reduction time at 750 °C (sodium added). Hydrogen stream from left.](image)

XRD-measurements and SEM-analyses supported the presence of sodium bronzes (see Table II).

**Table II: XRD and SEM examination of powder bed after 5 min reduction time in dry hydrogen at 750 °C (sodium addition).**

<table>
<thead>
<tr>
<th>Pos.</th>
<th>Colour</th>
<th>Phases in XRD</th>
<th>Morphology (SEM)</th>
<th>Resumé (XRD + SEM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>brown</td>
<td>WO₂, Na-bronze (cub)</td>
<td>WO₂, lumps, APT-pseudos</td>
<td>Still no metal formed</td>
</tr>
<tr>
<td>2</td>
<td>blue/ruby</td>
<td>Na-bronze (tet), WO₂</td>
<td>Lumps of needles, WO₂</td>
<td>Na-bronze in tungsten dioxide</td>
</tr>
<tr>
<td>3</td>
<td>blue/ruby</td>
<td>Na-bronze (tet), WO₂</td>
<td>Lumps of needles, WO₂</td>
<td>Na-bronze in tungsten dioxide</td>
</tr>
<tr>
<td>4</td>
<td>brown/violet</td>
<td>WO₂, WO₂,72</td>
<td>APT-pseudomorphs</td>
<td>tungsten brown and violet oxide</td>
</tr>
</tbody>
</table>

After 30 minutes reduction time the surface layer was mainly brown with golden and orange spots along the whole layer length (Fig. 3(b)). Only to the very left tungsten metal has formed. Table III shows the results of XRD and SEM imaging.

**Table III: XRD and SEM examination of powder bed after 30 min reduction time in dry hydrogen at 750 °C (sodium addition).**

<table>
<thead>
<tr>
<th>Pos.</th>
<th>Colour</th>
<th>Phases in XRD and SEM</th>
<th>Resumé (XRD + SEM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>grey</td>
<td>W, WO₂, Na-bronze (cub)</td>
<td>Tungsten metal formed</td>
</tr>
<tr>
<td>2</td>
<td>golden</td>
<td>Na-bronze (tet), W, β-W, WO₂</td>
<td>Lumps of blocky Na-bronzes, W, cubes of β-W and WO₂</td>
</tr>
<tr>
<td>3</td>
<td>orange</td>
<td>Na-bronze (tet), WO₂, W, β-W</td>
<td>Lumps of Na-bronzes, WO₂, W and cubes of β-W</td>
</tr>
<tr>
<td>4</td>
<td>brown</td>
<td>WO₂, Na-bronze (cub), W</td>
<td>WO₂, lumps of cubic Na-bronzes, W</td>
</tr>
</tbody>
</table>
**Potassium:** The surface of the powder bed after 5 min reduction in hydrogen is shown in Fig. 4(a). The colour changed gradually from brown to violet-brown, with some spots (craters) of dark blue where the potassium compound has been before the reduction. Details of XRD and SEM are listed in Table IV.

![Reduction boat after (a) 5 min and (b) 30 min reduction time at 750 °C (potassium added). Hydrogen stream from left.](image)

After 30 min reduction the powder was grey at the left side of the boat and increasingly brown to the right (Fig. 4(b)). There were eye-catching grey areas with dark violet or ruby spots in the centre, where the potassium compound had been at the start of the reduction. These spots were tetragonal potassium bronzes. The SEM-images additionally revealed that the centres of the craters consisted of needles of potassium bronzes.

**Table IV: XRD and SEM examination of powder bed after 5 min reduction time in dry hydrogen at 750 °C (potassium addition).**

<table>
<thead>
<tr>
<th>Pos.</th>
<th>Colour</th>
<th>Phases in XRD</th>
<th>Morphology (SEM)</th>
<th>Resumé (XRD + SEM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>brown/violet</td>
<td>WO$_{2.72}$</td>
<td>tungsten violet and brown oxide</td>
<td>WO$_{2.72}$ and WO$_2$</td>
</tr>
<tr>
<td>2</td>
<td>blue</td>
<td>K-bronzes (hex, tet), W</td>
<td>intergrown needle bronze structures</td>
<td>W and K-bronzes</td>
</tr>
</tbody>
</table>

**Interrupted Reduction Experiments with High Powder Layers**

The powders used in the experiments described before were also used in this section, but the powder layer height was increased to 25 mm (750°C). For comparison purposes, also an undoped tungsten oxide was used. After 120 min the partly reduced specimens were prepared with an epoxide resin and cut vertically to show the cross section.

**Undoped oxide:** Fig. 5(a) shows the cross section of the powder bed without any alkali addition. It is possible to distinguish three zones: At the top (A) only tungsten metal powder was present (grey zone). The area below (B) consisted of a mixture of brown tungsten oxide and tungsten metal. This area represented the transition WO$_2$ → W. The lowest part (C) of the powder bed contained brown tungsten oxide only. Generally the cross section looked as expected for undoped tungsten oxide powder.
Figure 5: Cross section of (a) the alkali-free and (b) the lithium-doped powder bed after 120 min of reduction at 750 °C in dry hydrogen. Several individual images were set together to show the whole powder bed.

**Lithium addition:** The cross section of the lithium-doped powder bed is shown in Fig. 5(b). The top part of the powder was grey and consisted of tungsten metal. It was sharply separated from the brown oxide. At the positions A and B a ring of tungsten metal surrounded the voids where the lithium compound had been present before reduction. These areas seemed to help the reduction front in moving downwards into the powder bed (i.e. promoting the formation and growth of tungsten at higher humidities).

Below the top grey area brown tungsten oxide containing several grey rings (positions C, D, E, F, Fig. 5(b)) can be found. These rings were lithium-rich inside and tungsten metal-rich outside, shown in Fig. 6(a).

Even in the lower and more humid regions of the powder bed tungsten metal grains could be found close to the formerly lithium-containing voids (Fig. 6(b)).
Sodium addition: The cross section of the powder bed with sodium addition (Fig. 7(a)) contained orange sodium bronzes in the upper part (sodium richer) and orange-red-violet ones in the deeper sections (tungsten richer). The surface already was grey and consisted of tungsten metal powder.

BSE-pictures of the positions A and B (Fig. 8(a) and (b)) show details of the rings surrounding the holes of formerly sodium compound where metallic tungsten was formed. Observations were similar for position C.

In position D in Fig. 8 no tungsten grains but two different sodium bronzes (orange-red and violet) were detected.

EDX analyses of the bronzes in the positions A and D (Fig. 9 (a) and (b)) showed that the amount of sodium in the bronzes increased from the bottom of the powder bed to the top (due to co-detection of other phases the measured analyses could only be regarded as a semiquantitative).
Figure 7: Cross section of (a) the sodium with details of position A and D and (b) the potassium-doped powder bed after 120 min of reduction at 750 °C in dry hydrogen.

Figure 8: BSE image of (a) ring in position A and (b) ring in position B (compare Fig. 7(a) sodium addition). Both pictures show tungsten metal in light grey and the sodium bronze in darker grey.
Potassium addition: Fig. 7(b) depicts the cross section of the potassium-doped powder bed after 120 min of reduction time at 750 °C. There were big voids where the potassium compound was located at the beginning of the reduction. Surrounding these voids in the upper part of the powder bed were rings of tungsten metal.

It appears that the reduction process used potassium-rich areas to advance into the powder bed where without addition only brown oxide was found (Fig. 7(b), position B). In lower regions (position C) only very thin shells of tungsten metal surrounding the voids were observed.

Over the whole of the potassium added powder bed bronzes could be found. The composition of the bronzes were different in the lower (tungsten-rich) and higher (potassium-rich) regions of the powder bed as shown by semiquantitative EDX analyses (Fig. 10(a) and (b)).
Back scattered electron images (Fig. 11(a)-(c)) of the indicated areas in Fig. 7(b) at position B, D and E show that tungsten was nucleated even at most humid conditions in the lower parts of the powder bed.

![Figure 11: BSE pictures of indicated positions in Fig. 7(b); (a) outer rim of position B (left lower corner: brown oxide with few tungsten grains, to the upper right corner: a lot of tungsten grains), (b) detail of position D with tungsten grains and two different bronzes (lighter and darker grey) and (c) tungsten grains embeded in oxidic structures in position E.](image)

**On-line Humidity Measurements during Reduction**

Fig. 12 shows the reaction water formation during reduction of an undoped oxide in comparison to the alkali-doped tungsten oxides at 750°C and 900°C, respectively.

At a first glance the reaction curves seem the same, as they consist of two separate regions which reflect the two main reduction stages; the first gives significantly higher water release during formation of WO₂ from WO₃ (via the violet oxide WO₂.72), the second, a slower but longer, during the formation of tungsten metal (WO₂→W).

A closer look at the humidity curves at 750 °C reveals a characteristic shoulder in case of doped oxides at the end of the first reduction peak which is due to the nucleation and growth of the metal phase even at this early stage (still during the transition of WO₂.72 to WO₂). This shoulder is clear evidence of the presence of a nucleation aid which facilitated metal formation at significantly higher humidities. In all these cases reduction time was significantly decreased. At the end of reduction at 750°C, water formation slowed down in the case of Na- and Li-doped oxides. This can be explained by the reduction of the respective tungstates (Na₂WO₄, Li₂WO₄) which formed in the very late stage of reduction and which could, at 750°C, be reduced only with dry hydrogen (Eq. (5)).

\[
\text{Me}_2\text{WO}_4 + 3 \text{H}_2 \leftrightarrow \text{W} + \text{Me}_2\text{O} + 3 \text{H}_2\text{O} \quad (\text{Me:Li, Na})
\]  

At 900°C, the reduction rate was the same for all dopant variants and the WO₂ to W transition took about 75% of the time taken for undoped oxide. Again, doped transformation occurred at significantly higher humidities. No tail is formed at 900°C because the reduction of the tungstates at this temperature was rapid.
Figure 12: Reaction water curves (kinetic curves) of the reduction of tungsten oxide with hydrogen at (a) 750 °C and (b) 900 °C with different alkali compounds (equimolar additions); compared to pure WO₃ (undoped).

**Discussion**

All reduction experiments described in this work have confirmed that ternary alkali compounds (alkali tungsten bronzes, alkalitungstates) are present throughout the reduction sequence. Tungsten bronzes were found to coexist with all other tungsten compounds formed within the powder layer (WO₂.₉, WO₂.₇₂, WO₂, W). At an early reduction stage (i.e. at high humidity within the layer) they form alkali-poor tungsten-rich bronzes whereas with ongoing reduction (lower humidity) alkali-richer bronzes are formed.

These results confirm the thermodynamic considerations of J. Qvick [11], which can be generalised by the Eq. (6) and (7) below.

\[
\text{Me}_x\text{WO}_3 + 3(1 - x/y) \text{H}_2 \leftrightarrow x/y \text{Me}_y\text{WO}_3 + (1 - x/y) \text{W} + 3(1 - x/y) \text{H}_2\text{O} \quad (\text{with } x<y) \tag{6}
\]

\[
\text{Me}_y\text{WO}_3 + (3 - 2y) \text{H}_2 \leftrightarrow y/2 \text{Me}_2\text{WO}_4 + (1 - y/2) \text{W} + (3 - 2y) \text{H}_2\text{O} \tag{7}
\]

Towards the end of reduction alkali tungstates with higher x-values are formed which are themselves reduced if reduced for long times, in dry hydrogen and at high temperatures. Eventually the resulting oxides or hydroxides would be vapourised in accordance with their thermal properties.

Eq. (6) and (7) demonstrate that tungsten metal nucleates from the tungsten bronzes which then act as seeds for the rapid local growth of W particles via CVT. This nucleation of tungsten occurs at significantly higher humidities than from WO₂, as demonstrated by the deep powder layer experiments. Thus, if the alkali-additions are uniformly distributed within the tungsten oxide matrix, W nuclei are formed by the gradual reduction of tungsten bronzes while no nucleation occurs on the surface of the WO₂ particles. Instead, WO₂ reacts with the reaction water present forming the volatile (WO₂)(OH)₂ compound which is then transported to the growing tungsten nuclei.

The three investigated alkali metals lithium, sodium and potassium behave slightly differently. Lithium and potassium bronzes show a stronger effect as a nucleation aid compared with sodium bronzes. Thus, tungsten metal can be formed earlier (i.e. at a higher dynamic humidity) than with sodium additions. Consequently, with Li and K additions the transition of WO₂ to W can take place through larger powder bed depths than with Na. However, with Na additions the depths of reduction are still larger than in
undoped oxide. This means that the influence of humidity on the W nucleation process is less pronounced in the presence of alkali additions and reduction can occur closer to the thermodynamic limit.

Humidity measurements indicate that early nucleation of tungsten metal takes place in all alkali-doped powders at the end of the first reduction step (i.e. shoulder at the end of the first peak in Fig. 12(a)). First nuclei form on the tungsten bronzes and small tungsten crystals start to grow during this period, see Fig. 13 for replicas of tungsten grains on tungsten bronzes after H\textsubscript{2}O\textsubscript{2}-treatment to remove tungsten metal. In contrast, a period of “drying-out” can be seen in case of the undoped oxide suggesting that for complete transition to the metal phase the humidity had to be reduced further still, see Fig. 12(b).

**Conclusion**

This investigation has tried to show how alkali compounds act during the reduction of doped tungsten oxides, making their effects “visible” in XRD and SEM investigations by using both heterogeneous and homogeneous additions. Alkali metals react at the very beginning of reduction with the tungsten oxide matrix to form tungsten-rich alkali bronzes. These bronzes “release” tungsten metal nuclei under comparatively humid reduction conditions which can grow in the humidity gap between that thermodynamically and kinetically possible for tungsten metal formation. Thus, reduction at higher humidities within the reacting layers can be achieved.

During reduction, the bronzes follow a path from tungsten-rich to alkali-rich composition which leads to final evaporation of the alkali compounds at a rate depending on reduction time and temperature. This agrees with some of the available literature [10,11].

Both at 750 °C and 900 °C alkali-doped powders are reduced significantly faster than undoped oxides during the WO\textsubscript{2}→W transition confirming the fact that they are being reduced under more humid conditions.
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