Thermochimica Acta, 103 (1986) 175—180
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMOGRAVIMETRIC STUDIES OF THE HYDROGEN REDUCTION OF NICKEL TUNGSTATE

J.N. ALBISTON and F.R. SALE
Department of Metallurgy and Materials Science
University of Manchester/UMIST
Grosvenor Street, Manchester M1 7HS

ABSTRACT

Thermogravimetry, using a C.I. Electronics thermobalance, has been incorporated with X-ray diffraction analysis to study the mechanism of the hydrogen reduction of nickel tungstate, over the temperature range 200-900°C. Nickel tungstate was prepared in a hydrated form by precipitation from aqueous solution. Both the hydrated precipitate and the anhydrous salt were reduced so that results could be compared. The reduction behaviour of the nickel tungstate was shown to be similar to that of cobalt tungstate as predicted from the relative thermochemical stabilities.

INTRODUCTION

During studies on the preparation of silver-tungsten electrical contact materials by the hydrogen reduction of silver tungstate (ref.1) it was found to be necessary to add nickel as a sintering aid. One possible method to achieve this was to use the co-precipitation of nickel and silver tungstates followed by their concomitant reduction. As such the reduction mechanism of nickel tungstate needed to be known especially at low temperatures of the order of 200-500°C. Guerassimov (ref. 2) had indicated that the reduction of nickel tungstate would proceed via the formation of nickel oxide and tungsten oxide during the early stages of reduction followed by further reduction of the oxides. Also as intermetallic phases exist in the Ni-W binary phase diagram, the formation of intermetallic compounds may be expected during the final stages of reduction of nickel tungstate.

EXPERIMENTAL PROCEDURE

Material Preparation

The nickel tungstate was prepared by precipitation via the following route:

$$Ni(NO_3)_{2(aq)} + Na_2WO_4.2H_2O_{(aq)} \rightarrow NiWO_{4(s)} + 2NaNO_{3(aq)} + 2H_2O_{(l)}$$

After precipitation the nickel tungstate was washed with distilled water before filtering and drying at 80°C for 10 hours. X-ray diffraction analysis of the precipitate did not yield a diffraction pattern with any observable peaks.

0040-6031/86/$03.50

This indicates either that the precipitate was below the minimum particle size required for X-ray diffraction or that the precipitate was amorphous. Fig.1a shows a scanning electron micrograph of the powder and suggests that the particle size is approximately 0.02µm in size. This is in fact very close to the 0.01µm detection limit of the X-ray diffractometer. Using the C.I. balance the precipitated nickel tungstate was found to be hydrated in the form $NiWO_4.xH_2O$ with the value of x between 2 and 3.

The anhydrous nickel tungstate was produced by heating the hydrate in air at 800°C for 2 hours. During dehydration, the nickel tungstate changed colour, from green to a yellow/brown, and a weight loss of 10.85%, which corresponds to a value of x equal to 2.1, was recorded. The variability in the weight losses associated with the dehydration may be explained by the hygroscopic nature of the hydrated tungstate. The anhydrous tungstate was found to produce an X-ray diffraction pattern almost identical to the ASTM index card for nickel tungstate. A photomicrograph of the anhydrous nickel tungstate is shown in Fig.1.

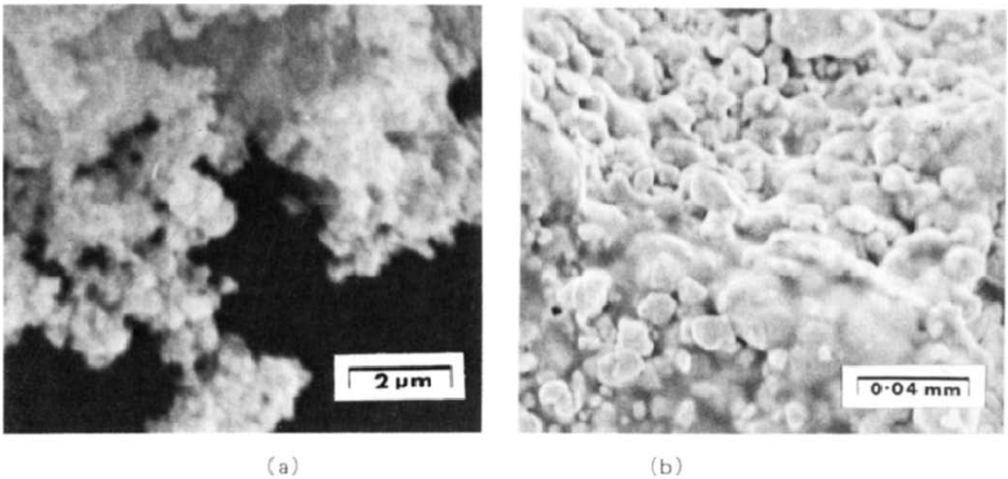

Figure 1. Scanning electron micrographs of nickel tungstate (a) Hydrated (b) Anhydrous.

Thermogravimetry

A "C.I. Electronics 2CT5" thermobalance with vacuum head and universal attachment was used for this study with sample weights of 500mg and a full scale deflection of 200mg. Flow rates of 250 ml min^{-1} and 350 ml min^{-1} were used for hydrogen and nitrogen respectively. During reduction the reactions could be interrupted at any period by removing the furnace and flushing with nitrogen. X-ray diffraction studies were conducted on a Philips diffractometer fitted with a P.W. 1710 diffractometer control system which allowed the d-spacings of the diffraction peaks to be printed directly onto the chart recording. Cukα radiation was used in all cases.

RESULTS AND DISCUSSION

Reduction of Hydrated Nickel Tungstate

The % reduction-time curves for the reduction of the hydrated nickel tungstate at temperatures between 200 and 900°C are shown in Fig. 2.

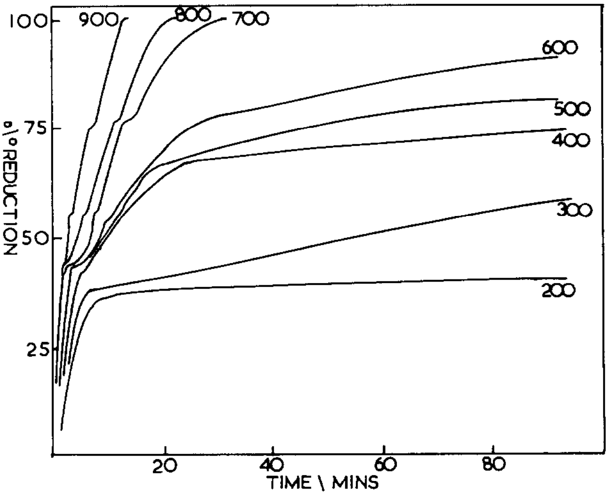

Figure 2. Relationship betwen % reduction and time for reduction of hydrated nickel tungstate

Initial observation of these curves indicates the presence of various stages in the reduction process which yield changes in slope of the curves at different % reductions. At 200°C the total reduction achieved was 35%. This is below the theoretical value for the removal of all the associated water. However, at 300°C a change in slope occurred in the curve at a value in excess of 35% and the sample then underwent a steady weight loss after dehydration. This indicates that some chemically combined water is removed at a temperature between 200 and 300°C, a result which was confirmed by differential thermal analysis. This weight loss after dehydration could be due to one or more of the following three reactions; the reduction of $NiWO_4$ to either metallic nickel and $W_{20}O_{58}$ or nickel oxide and $W_{20}O_{58}$ with the additional possibility that β-tungsten and nickel oxide could be formed. The latter reaction is least likely because during the reduction of silver tungstate (ref. 3), under the same conditions, no β-tungsten was observed. X-ray diffraction studies failed to identify a crystalline product of reaction at 200°C, whilst only one broad, low intensity peak was present, around the d-spacing where nickel oxide might be expected, in the product at 300°C. This suggests the formation of nickel oxide and $W_{20}O_{58}$ at 300°C.

At 400°C, there was a rapid dehydration of the sample, followed by a rapid reduction which produced a change in reaction rate at 41% reduction, the theoretical value for the production of $W_{20}O_{58}$ and nickel oxide. After this, the reaction continued with a gradual loss in weight which was due to two competing reduction reactions, namely, nickel oxide to nickel and $W_{20}O_{58}$ to β-tungsten. X-ray diffraction analyses of the products confirm these observations. An additional interesting observation is that the metallic nickel detected at this stage of the reduction process decreased in concentration at later stages of reduction although no new nickel-containing phases were detected. In addition WO_2 was also identified as a product. This is contrary to work on the reduction of pure tungsten trioxide in dry hydrogen at this temperature (ref. 4-6), and seems likely to have occurred because of the retention of excess water vapour in the reactor after the dehydration process.

Reduction at 500°C produced the same rapid dehydration as at 400°C. However, an extra change in slope was evident in the curve at 59% reduction, which is close to the theoretical value for the production of nickel and $W_{18}O_{49}$ although this oxide was not detected. After this point the reduction proceeded slowly with $W_{20}O_{58}$ giving WO_2 (whilst water vapour was present) and any residual $W_{20}O_{58}$ giving β-W directly (once the water vapour was removed from the reactor). X-ray diffraction analysis supported such possibilities, however, neither metallic nickel, nor any other nickel-containing phase, was detected. This situation is similar to that observed during the hydrogen reduction of cobalt tungstate (ref. 7, 8). Braconni and Dufour (ref. 7) suggested that an amorphous Co-W-containing phase designated ϕ formed at temperatures below 700°C whilst French and Sale (ref. 8) postulated the presence of an amorphous Co-W phase containing oxygen and suggested that its stability was controlled by the residual oxygen potential. The similarity between nickel and cobalt tungstates indicates that on reduction nickel may be present in an amorphous Ni-W-O phase until a critical oxygen potential is reached. An alternative explanation for the failure to detect nickel is that it was too finely disseminated to yield a diffraction pattern. However, no electron metallographic evidence was ever found for this explanation.

At 600°C the reduction was similar to that conducted at 500°C. However, a greater ultimate % reduction was obtained and $W_{20}O_{58}$ was transformed to $W_{18}O_{49}$ and WO_2. In addition some WO_2 was reduced to α-tungsten and this step appeared to become rate controlling. Some β-W was, however, still detected at this temperature. Again complete reduction was not achieved in the time scale of the experiments. X-ray diffraction analysis confirmed the presence of the W-containing phases however there was again the absence of any peaks corresponding to nickel or any of its compounds.

At 700°C and above the reduction reached completion with the full sequence of $W_{20}O_{58} \rightarrow W_{18}O_{49} \rightarrow WO_2 \rightarrow \alpha$-tungsten taking place without the formation of any β-W. X-ray diffraction of the final products at these temperatures also indicated that an intermetallic compound, Ni_4W, was formed. As indicated earlier, this behaviour is similar to that observed for the reduction of cobalt tungstate and indicates that full reduction of nickel tungstate is necessary before the intermetallic compound is precipitated from a ternary amorphous phase. Conversely, it may be that such elevated temperatures are required for the finely dispersed metallic nickel to react with the tungsten to produce the compound.

Reduction of Anhydrous Nickel Tungstate

Two series of experiments were conducted over the temperature range 400 to 900°C to investigate how water vapour, produced from the dehydration process, affected the overall reduction sequence. In the first of these the hydrogen flow rate over the sample was increased from 250 ml min^{-1} to 425 ml min^{-1} in an attempt to remove the water vapour from the reactor in a short period of time. Whilst in the second set of experiments anhydrous nickel tungstate was used. Both types of experiments showed that there was no effect on the sequences of phases detected at reduction temperatures of above 500°C. However, at 500°C neither $W_{18}O_{49}$ nor WO_2 were detected as products of partial reduction. This confirms the earlier proposal that water vapour stabilized WO_2 at this temperature. In addition it is evident that β-W is only produced by direct reduction of $W_{20}O_{58}$ at the lower temperatures.

CONCLUSIONS

(1) At low temperatures the reduction of hydrated nickel tungstate may be complicated because the increased partial pressure of water which results from dehydration may stabilize the oxides $W_{18}O_{49}$ and WO_2 at temperatures where they are not normally seen.

(2) Using either an increased hydrogen flow rate or the anhydrous form of nickel tungstate the reduction process can be summarised by the following equations:

Below 400°C

$$NiWO_4 \rightarrow NiO + W_{20}O_{58}$$

400°C

$$NiWO_4 \rightarrow NiO + W_{20}O_{58} \rightarrow Ni + W_{20}O_{58} + (\phi) \quad + \beta\text{-W}$$

500°C

$$NiWO_4 \rightarrow \phi + W_{20}O_{58} \rightarrow \phi + \beta\text{-W}$$

600--900°C

$$\mathrm{NiWO_4} \rightarrow \phi + \mathrm{W_{20}O_{58}} \rightarrow \phi + \mathrm{W_{18}O_{49}} \rightarrow \phi + \mathrm{WO_2} \rightarrow \mathrm{Ni_4W} + \alpha\text{-}\mathrm{W}$$

(where ϕ represents an amorphous nickel containing phase).

REFERENCES

1. P. Walkden, J.N. Albiston and F.R. Sale, Powder Metallurgy, 28 (1985) 36-42.
2 J. Guerassimov, Proc. 16th IUPAC Int. Congress of Pure and Appl. Chem., Paris (Butterworth, London 1957) 227-235.
3 J.N. Albiston, M.Sc. thesis, Manchester University, 1983.
4 A.K. Basu and F.R. Sale, Trans. Inst. Min. Metall., Sect. C, 86 (1977) 134-139.
5 T.R. Wilken, W.R. Morcom, C.A. Wert and J.B. Woodhouse, Metall. Trans. B, 7 (1976) 589-597.
6 A. Taskinen, P. Taskinen, S. Vuorinen and M.H. Tikkanen, Scand. J. Metall., 6 (1977) 223-237.
7 P. Braconni and L.C. Dufour, Metall. Trans. B, 7 (1976) 321-332.
8 G.J. French and F.R. Sale, J. Materials Science, 20 (1985) 1291-1300.