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Copper-tungsten composite powders by the hydrogen reduction of copper tungstate

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The reduction of two different samples of copper tungstate at 500, 600 and 700° C has been studied using thermogravimetry, X-ray diffraction analysis and electron optical techniques. The morphologies of the resultant Cu–W powders have been related to the morphologies of the original tungstate samples and to the time and temperatures of reduction. The reduction mechanism of the tungstate has been shown to be equivalent to the reduction of pure tungsten oxides once the initial metallic copper phase has been produced. The end products of reduction are mixtures of β-W and Cu at 500° C and α-W and Cu at 600 and 700° C.

1. Introduction

Tungsten–copper composite material has been used as electrical contacts for many years. The standard production technique is to infiltrate tungsten powder compacts with liquid copper such that the green strength tungsten compact generally determines the overall tungsten distribution in the completed contact. The present work, which has been carried out as part of a larger study of the chemical control of particulate morphology of tungsten, tungsten alloy and tungsten compounds, has investigated the direct manufacture of tungsten–copper material of unusual morphologies from copper tungstate. Earlier work by the present authors has shown that the particle morphology of tungsten metal produced by the hydrogen reduction of blue oxide may be changed dramatically by control of temperature and/or the water vapour partial pressure in the gas atmosphere [1, 2]. Consequently, if the reduction of the tungstate occurs via the formation of the various tungsten oxides the particle morphologies described in the earlier work may possibly be obtained for the tungsten component of the tungsten–copper composite material.

The reduction processes of various metal tungstates have been discussed and classified by Guerassimov [3] according to two extreme types of behaviour which may be summarized as:

$$MWO_4 + 3H_2 \rightarrow MO + W + 3H_2O \qquad (1)$$

and

$$MWO_4 + (4-x)H_2 \rightarrow M + WO_x + (4-x)H_2O \qquad (2)$$

In the former situation tungsten and metal oxide (MO) may be obtained on reduction of the metal tungstate. In the latter situation the metal may be produced along with one of the tungsten oxides, which is subsequently reduced to yield tungsten metal. The reduction of magnesium, calcium, strontium, barium and maganese tungstates has been predicted to occur according to Equation 1 whilst the hydrogen reduction of copper, cadmium and lead tungstates should occur according to Reaction 2. Intermediate behaviour between the two extremes given in Equations 1 and 2 may occur when either mixtures of tungsten alloys and tungsten or tungsten alloys and tungsten oxides are produced. Iron, cobalt and nickel have been predicted to behave according to these intermediate schemes [3], and work by Bracconi and Dufour [4, 5] has considered the production of Co_3W and tungsten metal from cobalt tungstate. This paper presents results obtained on the kinetics of reduction of copper tungstate in dry hydrogen at various temperatures. Complete reduction has been attempted in these experiments. The product phases have been characterized to determined the mechanism of reduction of the tungstate and to determine any morphological changes that occur during reduction.

2. Experimental procedure

2.1. Materials

Hydrated copper tungstate was precipitated at room temperature by the addition of $CuSO_4 \cdot 5H_2O$ to a solution of normal sodium tungstate which was prepared by the dissolution of tungstic acid in sodium hydroxide. The precipitate was filtered and washed with distilled water. On drying in air at 50° C the dihydrate, $CuWO_4 \cdot 2H_2O$, was obtained as a light-green powder. Anhydrous copper tungstate was produced by heating an intimate mixture of equimolar proportions of cupric oxide and tungsten trioxide at 700 and 800° C for periods of three hours. At 700° C the tungstate was obtained as a loose brown powder. A brown sintered agglomerate occurred at 800° C; however, this was friable and could easily be broken down to yield a powder. All chemicals used in both preparations were "AnalaR" grade materials.

The dehydration reaction of the precipitated copper tungstate was investigated at temperatures of 500, 600 and 700° C in a glass spring thermobalance to ensure that fully anhydrous samples were used in subsequent reduction experiments. Standard scanning thermogravimetric determinations of the dehydration behaviour were also carried out using a Stanton–Redcroft T.G-750 unit.

2.2. Reduction experiments

The dry hydrogen (dew point −60° C) reduction of both the dehydrated precipitated tungstate and the anhydrous tungstate prepared from the separate oxides was carried out in the glass spring balance used for the dehydration studies. The balance and its operation have been described elsewhere [6]. A hydrogen flow rate of approximately $250\,ml\,min^{-1}$ was used for all experiments, preliminary tests having shown that this flow rate ensured that the rate of reduction was not controlled by the supply of hydrogen in the bulk gas phase but the flow was not large enough to cause detectable cooling of the specimen. In the initial experiments sample weights of approximately 0.5 g were contained on shallow nickel pans; however, these were replaced by a zirconia pan because the copper reduction product was found to dissolve in the nickel pans (as discussed later).

2.3. Characterization of materials

A "Cambridge Stereoscan 180" scanning electron microscope has been used to study the particle morphologies before and after reduction. The microscope was filled with a "Kevex" energy dispersive detector for electron-probe microanalysis of the separate components of the product phases. X-ray diffraction analysis with a "Siemens Kristalloflex" diffractometer and CuKα radiation was also used to characterize all the materials used in the study. Solutions which were produced by the leaching of samples in hydrochloric acid were analysed by atomic absorption spectrophotometry to check on the impurity levels of the precipitated samples and the copper–tungsten ratios in the reduced samples. The precipitated sample was found to contain some 0.06 to 0.08 wt% sodium which was not removed in the washing sequence.

3. Results and discussion

3.1. Dehydration and characterization of copper tungstate

3.1.1. Kinetics of dehydration

The experimental data from the Stanton-Redcroft unit showed that the precipitated hydrate began to lose weight on heating in air at 50° C. The weight loss continued up to temperatures of about 450° C, after which the weight remained constant up to 850° C. This extended temperature range for the dehydration is unexpected and is quite different from that which occurs for many other hydrated tungstates, for example, the water of crystallization of sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) is removed on heating over the temperature range 80 to 120° C. Because the dehydration occurred over such a large temperature range during the scanning thermogravimetric experiments, isothermal weight loss measurements were made using the glass spring balance as the dehydrated samples were prepared. The results of these measurements are shown in Fig. 1 where the weight loss after 30 min at temperatures of 125, 225, 300 and 450° C is plotted as a function of temperature. The theoretical weight loss associated with the dehydration of $CuWO_4 \cdot 2H_2O$ is 10.4%, which is in reasonable agreement with all the experimental data. This data gives values ranging from 2.0 to 2.4 for the molecules of water associated with the tungstate, and indicates that a minimum temperature of 450 to 500° C is required to produce anhydrous copper tungstate

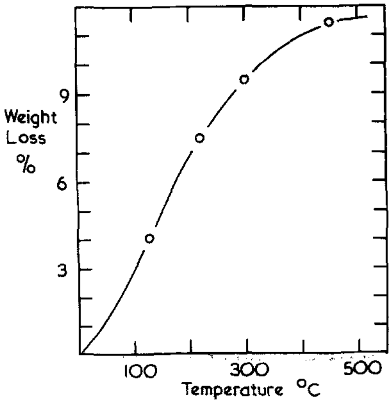

Figure 1 Relationship between per cent weight loss (after 30 min) and temperature for the dehydration of the precipitated copper tungstate.

from the precipitated material. Consequently dehydrated samples were prepared at temperatures of 500, 600 and 700° C prior to hydrogen reduction.

3.1.2. X-ray diffraction anaylsis

The diffraction data obtained for the hydrated precipitate is presented in Table I. There is no standard ASTM index data with which to compare the experimental results. The diffraction patterns obtained for the precipitated material after dehydration at 500, 600 and 700° C, which are presented in Table II, agreed with the data found for the tungstate samples produced by heating mixtures of CuO and WO_3 (Table III) and agreed substantially with the standard data given in the ASTM index for $CuWO_4$. It is thus apparent that the different samples of anhydrous copper tungstate are structurally identical and cannot be differentiated by X-ray diffraction alone although the relative intensities of lines do vary from sample to sample.

TABLE I *d*-spacings and intensities of the major lines for $CuWO_4 \cdot 2H_2O$.

d-spacing (A)	I/I_1
4.42	13
3.99	86
3.95	90
3.90	90
3.79	16
2.99	66
2.52	100
2.51	100
1.76	47
1.75	53
1.71	56
1.46	38
1.45	38
1.44	20
1.43	20

3.1.3. Particle morphologies

Figs. 2 and 3 show representative micrographs of the hydrated precipitated tungstate and the

TABLE II *d*-spacings and intensities of the major lines for products of dehydration of $CuWO_4 \cdot 2H_2O$

d-spacing (A)	I/I_1 (500° C)	I/I_1 (600° C)	I/I_1 (700° C)
5.80	13	12	33
4.66	50	51	100
3.88	29	42	59
3.77	30	42	45
3.68	30	33	29
3.43	39	60	84
3.11	100	100	98
2.96	70	90	90
2.89	18	33	67
2.82	50	53	65
2.78	50	59	67
2.61	10	9	35
2.52	34	43	75
2.46	24	43	43
2.44	40	54	31
2.33	30	48	53
2.26	11	12	18
2.19	19	21	20
2.10	20	26	31
2.07	3	5	6
2.01	13	22	14
2.00	11	11	6
1.97	7	15	8
1.935	12	19	22
1.93	12	19	27
1.88	55	6	8
1.86	18	26	49
1.83	10	10	16
1.77	12	17	16
1.74	13	6	4
1.72	25	28	49
1.71	22	26	51
1.65	18	15	18
1.62	12	25	16
1.61	13	19	16
1.55	10	10	18
1.52	9	10	10
1.51	9	10	10
1.50	10	11	12
1.48	10	10	10
1.47	10	11	10
1.46	21	23	25
1.43	6	7	16
1.40	21	25	31
1.38	6	6	12

TABLE III *d*-spacings and the intensities of the major lines for $CuWO_4$ prepared from CuO and WO_3

d-spacing (Å)	I/I_1	*d*-spacing (Å)	I/I_1
5.80	10	1.93	12
4.66	60	1.88	10
3.88	40	1.87	25
3.77	35	1.83	10
3.68	26	1.77	18
3.43	50	1.71	25
3.11	100	1.65	18
2.96	80	1.62	12
2.89	25	1.61	13
2.82	60	1.56	12
2.78	60	1.53	8
2.61	20	1.50	12
2.52	55	1.46	21
2.46	25	1.45	5
2.44	36	1.43	6
2.33	50	1.40	18
2.26	15	1.38	6
2.19	20		
2.10	20		
2.07	10		
2.01	15		
2.00	10		
1.97	10		

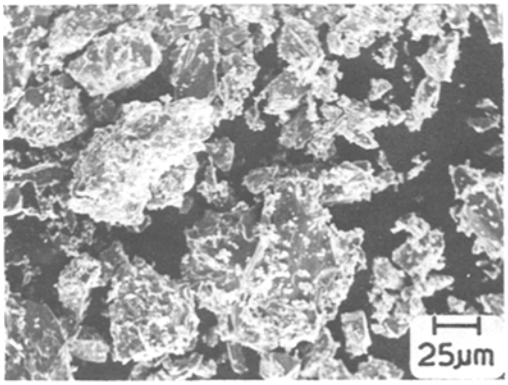

Figure 2 Precipitated hydrated copper tungstate.

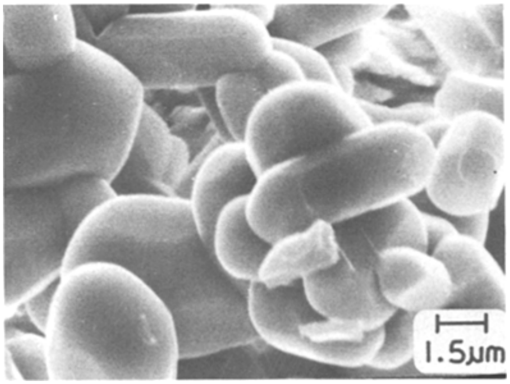

Figure 3 Anhydrous copper tungstate prepared from CuO and WO_3.

anhydrous tungstate prepared from the oxide mixture at 800° C respectively. The precipitated sample can be seen to contain a mass of small particles of which the major proportion have been agglomerated to form a cake during the filtration process. The anhydrous sample consists of many quite well-faceted lozenge-shaped particles which range in size from 6 μm in length and 3 μm in width to 2.5 μm in length and 1 μm in width. The anhydrous sample prepared from the individual oxides at 700° C had the same overall particle

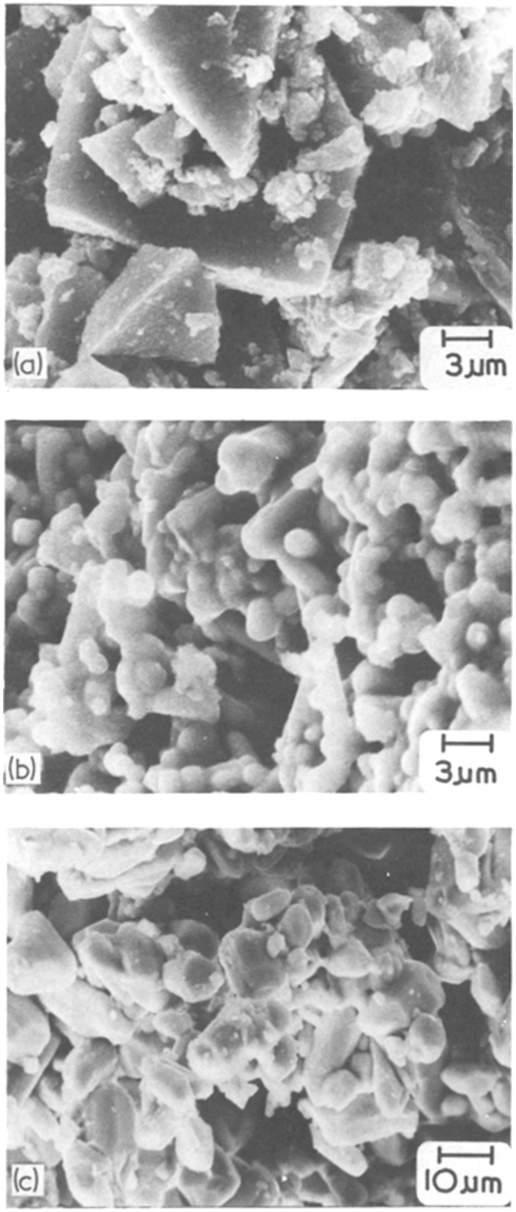

Figure 4 Precipitated copper tungstate dehydrated at (a) 500° C, (b) 600° C, and (c) 700° C.

morphology as that shown in Fig. 4, but the particles tended to be of a slightly smaller size.

Figs. 4a to c show the morphologies of the anhydrous samples produced from the hydrated precipitate at 500, 600 and 700° C. Fig. 4a clearly demonstartes the agglomerated cake-like morphology previously observed for the filtered precipitate; however, the large agglomerates can be seen to consist of very small individual particles of less than 0.5 μm in size. At the higher temperature of 600° C the cake-like agglomerate can be seen to have broken down with the formation of a network of large loosely-sintered particles, some of which are rod-like in appearance. The particle sizes are of the order of 0.5 to 1.0 μm for the small equi-axed particles and up to 5 μm in length and 1.5 μm in width for the rod-like material. At 700° C the anhydrous tungstate particles shown in Fig. 4c take on the same general appearance as the tungstate produced from the individual oxides, with faceted particles ranging in size from approximately 3 to 10 μm. It is thus apparent from Fig. 4 that although the temperature of dehydration has no effect upon the structure of the anhydrous copper tungstate product it has a very marked effect upon the particle size and morphology, with higher temperatures leading to the formation of larger more-faceted crystals.

3.2. Dry hydrogen reduction of copper tungstate

3.2.1. Kinetics and mechanism of reduction

The relationships between weight loss and time for the reduction at temperatures of 500, 600 and 700° C of anhydrous copper tungstate produced from the precipitated tungstate are shown in Fig. 5. The precipitated tungstate was dehydrated at the respective reduction temperature prior to the admission of hydrogen to the glass spring thermobalance. It is evident that the reduction rates at 600 and 700° C are almost the same; however, reduction at 500° C occurs much more slowly. This reduction at 500° C was interrupted at various stages and samples were taken for investigation by X-ray diffraction analysis. The phases identified in the partially-reduced products are indicated on Fig. 5. It can be seen that metallic copper is produced in the very early stages of reduction along with $W_{20}O_{58}$ and a small amount of WO_2, which confirms the prediction of Guerassimov [3] and shows that the reduction of copper tungstate occurs according to the general scheme given by Equation 2, namely:

$$MWO_4(s) + (4-x)H_2(g) \rightarrow M + WO_x + (4-x)H_2O \quad (2)$$

after which the tungsten oxides are reduced in dry hydrogen to yield tungsten metal:

$$WO_x(s) + xH_2(g) \rightarrow W(s) + xH_2O(g). \quad (3)$$

The production of tungsten metal is achieved by the successive reduction of progressively lower tungsten oxides.

The form of the reduction curve at 500° C shows a marked decrease in rate when WO_2 remains as the only tungsten oxide to be reduced, and is similar to the kinetic curves obtained by the present authors for the reduction of blue tungsten oxide at 600° C [1]. However, in the reduction of blue oxide at 500° C [1], WO_2 was never detected and it was postulated that the reduction of $W_{20}O_{58}$ to WO_2 was the slowest step in the overall process. This situation is obviously changed in the case of the copper tungstate. It appears, therefore, that whilst the reduction of the copper tungstate may be represented generally by Equations 2 and 3, the rates of the series of reactions represented by Equation 3 are changed relative to the situation that exists when the pure individual tungsten oxides are reduced. In effect the $W_{20}O_{58}$

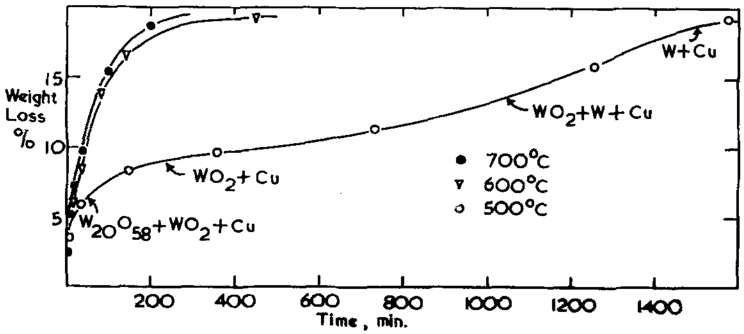

Figure 5 Relationships between weight loss and time for the reduction of dehydrated precipitated copper tungstate at 500, 600 and 700° C.

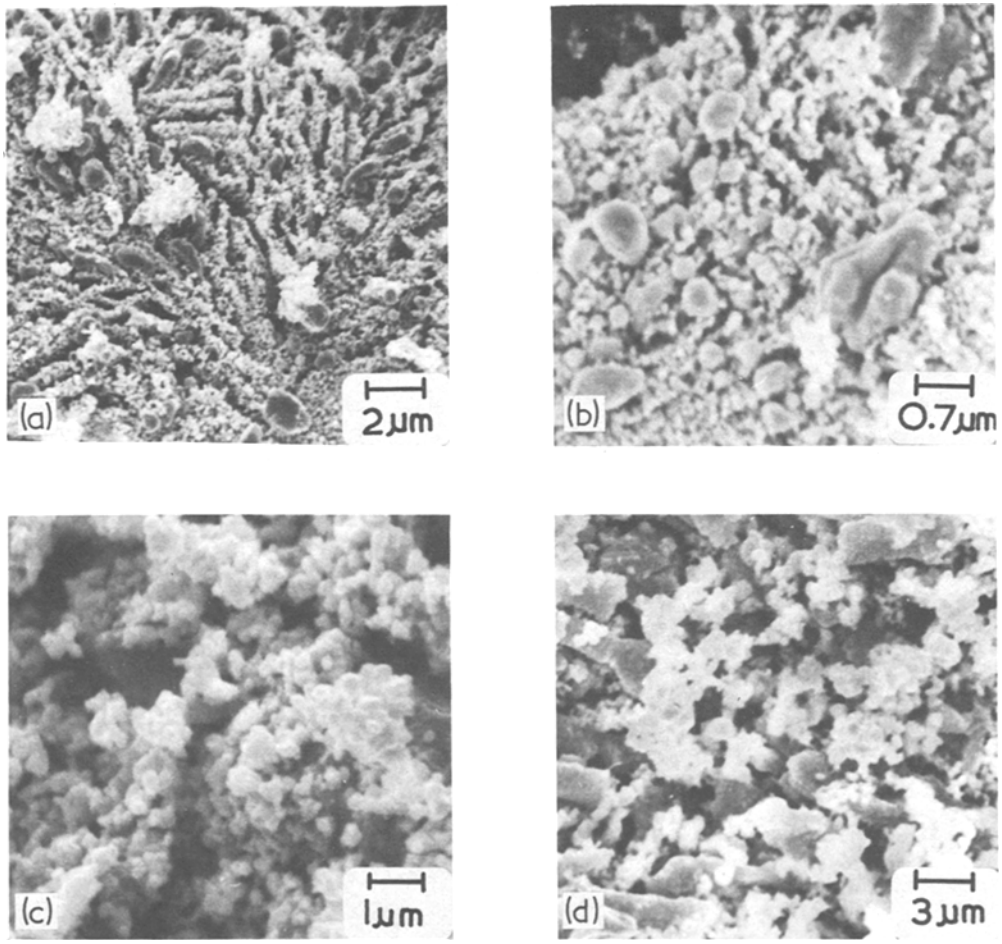

Figure 6 Products of reduction of precipitated copper tungstate at (a) 500° C, (b) 600° C, (c) 700° C.

produced along with copper in the first stage of reduction of the tungstate is reduced more rapidly to WO_2 than $W_{20}O_{58}$ produced from pure WO_3. The consequence is that the phases identified in the products of initial reduction of copper tungstate are Cu, $W_{20}O_{58}$ and WO_2; $W_{18}O_{49}$ was not detected in the products of partial reduction at 500° C.

This observation is in accordance with the W–O phase diagram [7] which shows that there is no region of stability of $W_{18}O_{49}$ at temperatures below 585° C such that the reduction sequence of the tungsten oxides is:

$$WO_3 \rightarrow W_{20}O_{58} \rightarrow WO_2 \rightarrow W.$$

At temperatures greater than 585° C the reduction sequence is:

$$WO_3 \rightarrow W_{20}O_{58} \rightarrow W_{18}O_{49} \rightarrow WO_2 \rightarrow W$$

Diffraction analysis of the end product of reduction at 500° C proved it to be a mixture of copper and the metastable β-W. The production of β-W supports the observations of Mannella and Hougen [8], Morcom *et al.* [9] and the present authors [1] made on the reduction of pure WO_3 or blue oxide mixtures. At the higher temperatures of 600 and 700° C the products were shown to be copper and α-W by X-ray diffraction analysis. It is apparent that the immiscibility of the two metallic phases allows the reduction mechanism of copper tungstate to be considered as equivalent to the reduction of the tungsten oxides once the metallic copper has been produced in the initial stages of reduction.

The observations made on the reduction of the dehydrated precipitated copper tungstate sample were repeated for the tungstate produced from the individual oxides. The same products of reduction were obtained and the same sequence of phases was observed at 500° C. The kinetics of reduction were also very similar to those presented in Fig. 5.

The data presented in Fig. 5 were obtained using a zirconia crucible. Preliminary experiments were carried out using nickel foil as the crucible material. The end products of reduction were analysed by atomic absorption spectro-photometry and shown to contain between 6.3 and 7.4 wt % copper instead of the predicted value of 25.7 wt %. It became apparent that the metallic copper produced from the tungstate in the early stages of reduction dissolved in the nickel crucible which eventually became golden in colour. The overall measured kinetics of reduction using the nickel pans were, however, very similar to those shown in Fig. 5. This indicates that the production of copper and its subsequent solution in the nickel were quite separate processes. Once the specimen crucibles were changed to zirconia the theoretical copper levels were obtained in the products of reduction.

3.2.2. *Morphologies of reduction products*

Typical morphologies of the products of reduction of the precipitated tungstate at 500, 600 and 700° C are shown in Figs. 6a to d. The product at 500° C can be seen to be a porous mass or loose agglomerate of small particles. This morphology is similar to that seen for the precipitated tungstate which was dehydrated at 500° C; however, the reduced sample has a higher degree of porosity. At higher magnifications (Fig. 6b) it is clearly evident that two major types of particle exist within the agglomerate. There are agglomerates of fine particles on which larger spherical, or sometimes slightly faceted, crystals exist. Microprobe analysis proved that the larger particles are exclusively pure copper, whilst the fine agglomerates are mainly tungsten with some copper still retained as fine particles. It is apparent that the copper, which is the first metallic product to be obtained, is produced as fine particles which sinter together during the subsequent reduction of the tungsten oxides over the extended periods required at 500° C. These microstructural observations confirm the mechanism predicted for the reduction of the tungstate and explain the observations made with the use of nickel sample pans. In the case of the nickel pans it can be envisaged that the sintering of the copper, which produced the large copper particles on the outside of the agglomerates of fine particles, means that there is a marked diffusion of metallic copper from the interior of the agglomerates to the nickel supporting foil.

At 600° C, when the reduction times are much shorter than those required at 500° C, a fine particle product results with very little evidence for the gross sintering of the copper component (Fig. 6c). Microprobe analysis of this product shows a uniform distribution of the immiscible copper and tungsten components throughout the product. Similarly, at 700° C, separate particles of reasonably uniform size and shape are obtained as the product of reduction within the frameworks of the original tungstate particles. In general the slightly rounded particles tended to be pure copper whilst the faceted block-like particles were tungsten. However, there was not the clear evidence of separation of the two components as in the product at 500° C. As in the case of the product of reduction at 500° C, the morphologies of both higher temperature reduction products appear to be related to the morphologies of the tungstate particles obtained on dehydration of the precipitated material, and hence indicate the importance of the dehydration process in the determination of the overall morphology of the reduced product.

Figs. 7a to c show representative micrographs of the reduction products at 500, 600 and 700° C of the tungstate produced from the individual oxides. The low temperature product has the form of porous pseudomorphs of the original tungstate particles with only a small amount of separation and sintering of the copper. This morphology is very different from that obtained from the fine particles of the precipitated tungstate at this temperature, and may be advantageous because of the lower degree of gross sintering of the copper. Studies are presently in hand on the sintering of compacts of these powders and on the microstructure of the resultant compacts. At the higher temperatures of 600 and 700° C there is a progressive breaking down of the original tungstate particles which at 700° C produces a collection of particles of irregular shapes and a wide size range (Fig. 7c). There is very little visual evidence to help in the differentiation of the copper and tungsten components.

From Figs. 6 and 7 it is apparent that the two types of tungstate give different powder morphologies after reduction. The fine agglomerates of the precipitated samples give very fine particles some 0.2 μm and less in size at 600° C, with a mixture of equally fine material at 500° C along with the larger sintered copper particles which were in the

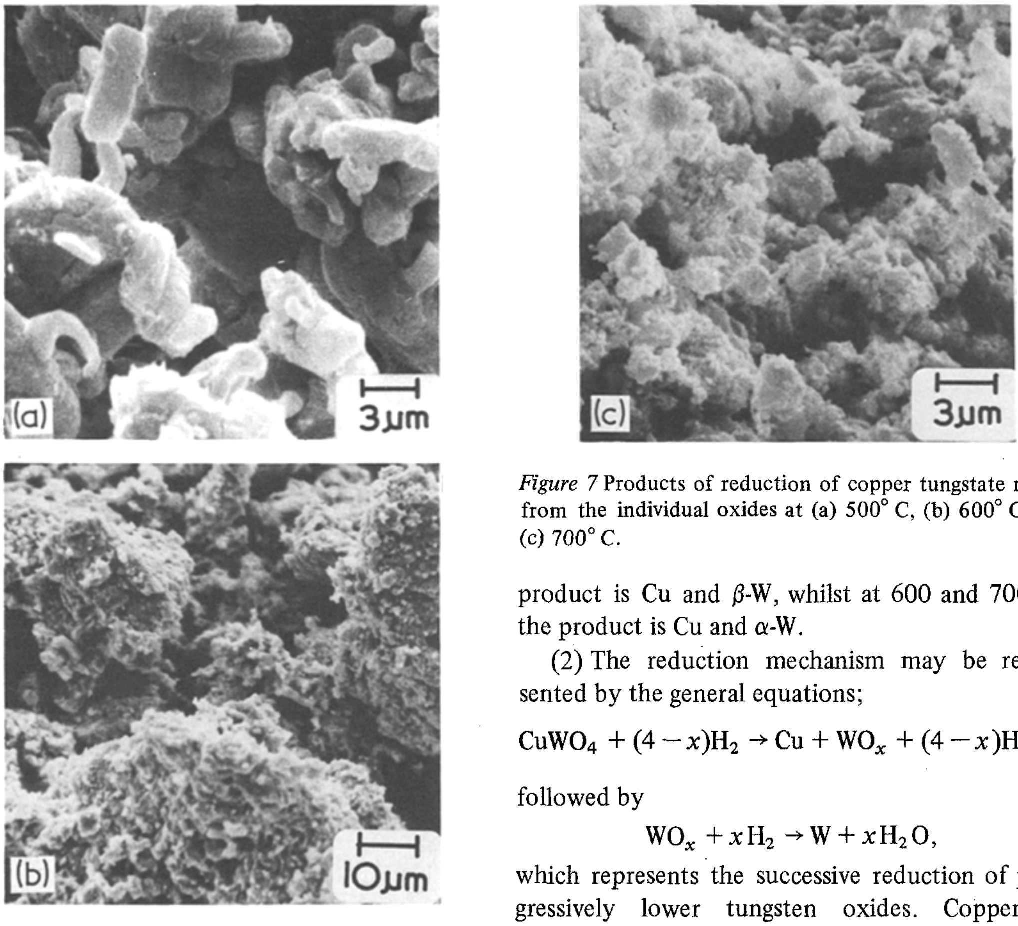

Figure 7 Products of reduction of copper tungstate made from the individual oxides at (a) 500° C, (b) 600° C and (c) 700° C.

size range 0.5 to 1 µm. At 700° C the precipitated tungstate gives slightly larger particles which are retained in the framework of the original tungstate particles. The morphologies of the powders produced at all temperatures were related to the dehydrated products shown in Fig. 4. The tungstate produced from the individual oxides seemed to give the opposite temperature dependence of morphology to the precipitated sample. At 500° C large (3 to 10 µm) porous pseudomorphs of the original particles were produced. At the higher temperatures these pseudomorphs were progressively broken down to yield a fairly fine powder containing sintered agglomerates some 1 to 3 µm in size which appeared to contain many smaller particles. The product at 700° C was very similar in both particle morphology and size to the product obtained from the precipitated sample.

4. Conclusions

(1) Copper tungstate may be reduced in dry hydrogen to yield mixtures of Cu and W of varying particle morphologies. At 500° C the reduction product is Cu and β-W, whilst at 600 and 700° C the product is Cu and α-W.

(2) The reduction mechanism may be represented by the general equations;

$$CuWO_4 + (4-x)H_2 \rightarrow Cu + WO_x + (4-x)H_2O$$

followed by

$$WO_x + xH_2 \rightarrow W + xH_2O,$$

which represents the successive reduction of progressively lower tungsten oxides. Copper is produced as the first metallic phase and tends to sinter together during long low temperature reduction periods.

(3) Precipitated copper tungstate ($CuWO_4 \cdot 2H_2O$) and copper tungstate produced by the reaction of CuO and WO_3 have different morphologies and produce Cu–W powders of quite different morphologies. The morphologies of the products from the precipitated copper tungstate are related to the morphologies obtained for samples dehydrated at the respective reduction temperatures. In general increasing temperatures gave increasing particle sizes for the precipitated tungstate but gave decreasing particle sizes for the tungstate produced from the individual oxides. However, the powders produced at 700° C from both tungstate samples were quite similar in appearance and size.

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