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# The controlled reduction of copper tungstate in $H_2O/H_2$ mixtures

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The controlled reductions of copper tungstate, copper tungstate plus blue tungsten oxide and CuO plus $WO_3$ have been studied at temperatures of 500, 600 and 700° C using $H_2/H_2O$ mixtures in a glass thermobalance. The copper–tungsten oxide composite powder products have been characterized by X-ray diffraction analysis and scanning electron microscopy. The morphologies of the copper–tungsten oxide products have been related to the morphologies of copper–tungsten powders obtained by dry hydrogen reduction. It is shown that widely varying copper–tungsten oxide morphologies may be obtained as precursors for metal powder production by control of the $H_2/H_2O$ ratio in the reducing gas mixture.

## 1. Introduction

Previous studies on the chemical control of particle morphology of tungsten, tungsten alloy and tungsten compounds [1, 2], have recently been extended to the production of Cu–W composite powders by the hydrogen reduction of copper tungstate [3]. The morphologies of the Cu–W powders have been determined and explained in relation to the possible schemes of reduction of tungstates proposed by Guerassimov [4]. The reduction of copper tungstate takes place according to the reaction:

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

followed by the successive reduction of the lower tungsten oxides to produce tungsten metal. However, the tungsten component does not always appear to behave according to predictions based on the reduction of the pure tungsten oxides.

Previous work on the reduction of blue tungsten oxide ($W_{20}O_{58}$ plus $WO_3$) in controlled $H_2/H_2O$ atmospheres [2] has shown that the morphology of tungsten metal powders can be changed dramatically by ensuring that $W_{18}O_{49}$ is produced as a product of partial reduction prior to a final dry hydrogen reduction to give tungsten metal. Consequently, the present study has been carried out on the reduction of copper tungstate in controlled $H_2/H_2O$ atmospheres to determine whether the morphological changes associated with the formation of $W_{18}O_{49}$ in the reduction of pure blue tungsten oxide may be achieved in the reduction of the tungstate. It was also anticipated that the controlled reduction experiments would allow the morphologies of the Cu–W powders produced by dry hydrogen reduction to be explained. The roles played by the lower oxides $W_{20}O_{58}$, $W_{18}O_{49}$ and $WO_2$ in determining changes in particle morphology are difficult to establish during dry hydrogen reduction because of their transient existence and because of the range of degrees of reduction that exist in experimental samples at any point in time.

The aims of the present study were not to reduce completely the copper tungstate but to prepare various copper–tungsten oxide mixtures that could be precursors for the direct production of Cu–W powders of unusual morphologies for the ultimate manufacture of Cu–W electrical contact material.

## 2. Experimental procedure

### 2.1. Materials

Hydrated copper tungstate was prepared in the manner described previously for the study of the dry hydrogen reduction of copper tungstate [3]. This precipitated tungstate was dehydrated at the appropriate reduction temperatures before the controlled $H_2/H_2O$ reductions were commenced.

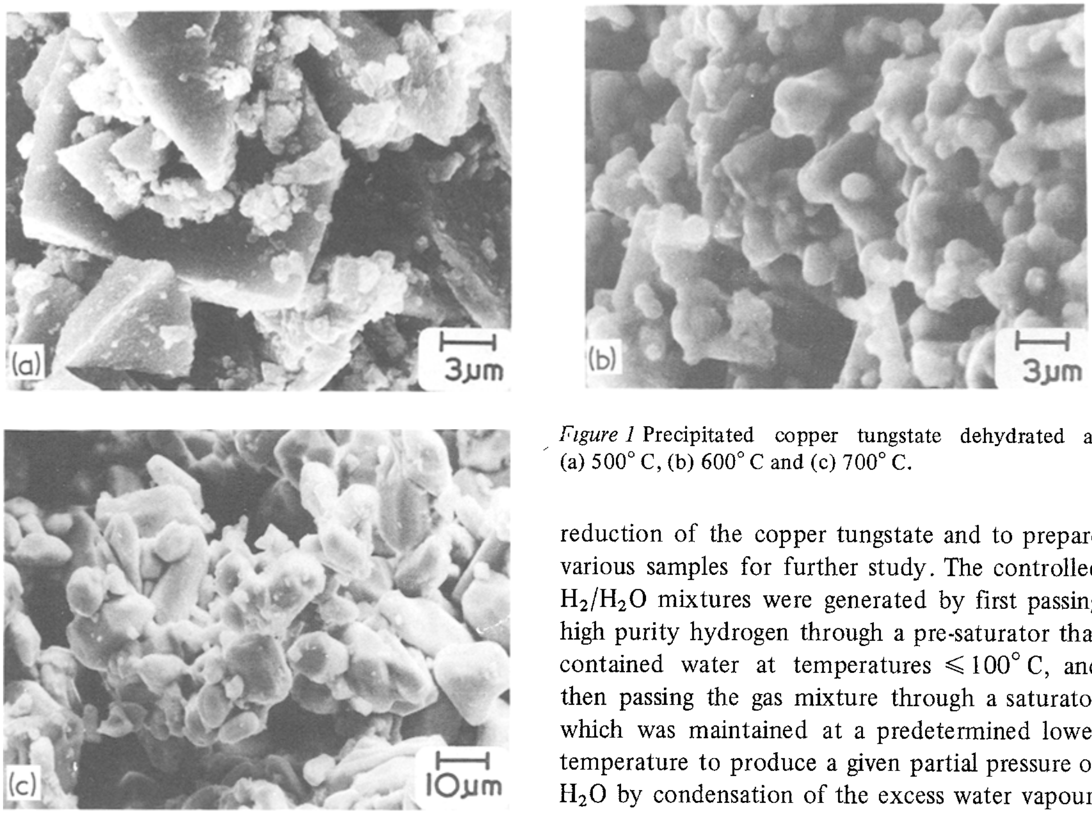

*Figure 1* Precipitated copper tungstate dehydrated at (a) 500° C, (b) 600° C and (c) 700° C.

Figs. 1a to c show typical micrographs of the dehydrated tungstate produced at 500, 600 and 700° C.

Equimolar mixtures of CuO and $WO_3$ were also prepared for reduction under controlled conditions so that a comparison of the behaviour of the tungstate and that of a mechnical mixture of oxides containing the same Cu/W ratio could be made. The $WO_3$ samples were produced from either freeze-dried or orthorhombic ammonium paratungstate. These samples of ammonium paratungstate, and their thermal decomposition to give blue oxide and $WO_3$, have been described previously [5, 6].

Mechanical mixtures of the precipitated tungstate with blue tungsten oxide (50 : 50 wt%) were also prepared for controlled reduction to determine any morphological and structural effects that may be caused by alterations of the Cu–W ratio from equimolar in the initial samples and in the final products.

## 2.2. Controlled $H_2/H_2O$ reduction

A glass spring thermobalance was used with controlled $H_2/H_2O$ atmospheres to investigate the reduction of the copper tungstate and to prepare various samples for further study. The controlled $H_2/H_2O$ mixtures were generated by first passing high purity hydrogen through a pre-saturator that contained water at temperatures $\leqslant 100°$ C, and then passing the gas mixture through a saturator which was maintained at a predetermined lower temperature to produce a given partial pressure of $H_2O$ by condensation of the excess water vapour. Reduction experiments were carried out at temperatures of 500, 600 and 700° C with $H_2O$ partial pressures in the range 18 to 241 mm Hg and a total $H_2/H_2O$ pressure of 1 atm. Reduction periods ranging from 0.5 to 9 h were used to prepare samples for further characterization, however, most emphasis was placed on short-term experiments that could possibly approach commercial process times.

## 2.3. Material characterization

The products obtained in the controlled reduction experiments were identified by X-ray diffraction analysis with a "Siemens Kristalloflex" diffractometer and CuK$\alpha$ radiation. The morphologies of the intermediate copper–tungsten oxide composite mixtures were studied using a "Cambridge Stereoscan 180" scanning electron microscope fitted with a "Kevex" energy dispersive detector for microprobe analysis.

## 3. Results and discussion

### 3.1. Reduction processes and identification of products

The conditions used in the various experiments and the product phases identified by X-ray diffraction analysis are presented in Tables I to III. There

TABLE I Products of reduction of precipitated copper tungstate

| Reduction time (h) | Temperature (° C) | $P_{H_2O}$ (mm Hg) | Product |
|---|---|---|---|
| 5 | 500 | 18 | $WO_2$ + Cu |
| 5.5 | 500 | 29 | $WO_2$ + Cu |
| 4 | 500 | 57 | $W_{20}O_{58}$ + $WO_2$ + Cu |
| 2 | 500 | 74 | $W_{20}O_{58}$ + $WO_2$ + Cu |
| 4 | 500 | 96 | $W_{20}O_{58}$ + $WO_2$ + Cu |
| 0.75 | 500 | 122 | $W_{20}O_{58}$ + $WO_2$ + Cu |
| 1.5 | 500 | 154 | $W_{20}O_{58}$ + $WO_2$ + Cu |
| 3 | 500 | 241 | $W_{20}O_{58}$ + Cu |
| 4 | 600 | 105 | $WO_2$ + Cu |
| 4 | 600 | 154 | $W_{20}O_{58}$ + $WO_2$ + Cu |
| 2 | 600 | 169 | $W_{20}O_{58}$ + $WO_2$ + Cu |
| 0.5 | 600 | 241 | $W_{20}O_{58}$ + $W_{18}O_{49}$ + Cu |
| 0.75 | 600 | 241 | $W_{18}O_{49}$ + Cu |
| 5 | 700 | 105 | $WO_2$ + Cu |
| 1 | 700 | 169 | $W_{20}O_{58}$ + $WO_2$ + Cu |
| 4 | 700 | 169 | $W_{20}O_{58}$ + $WO_2$ + Cu |
| 9 | 700 | 169 | $W_{20}O_{58}$ + $WO_2$ + Cu |
| 0.5 | 700 | 241 | $W_{20}O_{58}$ + Cu |

is no doubt that the products obtained in many of the experiments were not the equilibrium phases for those temperatures and pressures. However, the general trends in the phases detected were in accord with thermodynamic predictions.

At 500° C the precipitated tungstate yielded $WO_2$ + Cu at low partial pressures of water vapour, whilst at higher partial pressures increasing amounts of $W_{20}O_{58}$ were detected in the product. At the highest partial pressure of water vapour studied ($P_{H_2O}$ = 241 mm Hg) metallic copper and $W_{20}O_{58}$ alone were the product phases. As in the case of the interrupted reduction experiments using dry hydrogen at 500° C, $W_{18}O_{49}$ was not detected at this temperature. This observation is in accord with the W–O phase diagram [7, 8] and shows that the reduction of the tungsten oxide component of copper tungstate occurs in the manner that may be predicted from observations of pure tungsten oxides. It is interesting to note that $WO_2$ + Cu was detected with $P_{H_2O}$ values of 18 and 29 mm Hg even after 5.5 h. If the data given in the JANAF tables [9] is used to calculate the equilibrium $P_{H_2O}$ in a 1 atmosphere mixture of $H_2/H_2O$ at 500° C, a value of 43 mm Hg results for the reduction reaction

$$2H_2(g) + WO_2(s) \rightarrow W(s) + 2H_2O(g).$$

On this basis it may be predicted that an extended holding of the products obtained at 500° C and

TABLE II Products of reduction of precipitated copper tungstate and blue oxide mixture

| Reduction time (h) | Temperature (° C) | $P_{H_2O}$ (mm Hg) | Product |
|---|---|---|---|
| 1 | 700 | 203 | $W_{20}O_{58}$ + $W_{18}O_{49}$ + Cu |
| 1.5 | 700 | 203 | $W_{20}O_{58}$ + $W_{18}O_{49}$ + $WO_2$ + Cu |
| 5 | 700 | 203 | $W_{18}O_{49}$ + $WO_2$ + Cu |
| 1 | 700 | 241 | $W_{20}O_{58}$ + $W_{18}O_{49}$ + Cu |

TABLE III Products of reduction of CuO + $WO_3$ mixture

| Reduction time (h) | Temperature (° C) | $P_{H_2O}$ (mm Hg) | Product |
|---|---|---|---|
| 3 | 700 | 203 | $W_{18}O_{49}$ + $WO_2$ + Cu |
| 2 | 600 | 154 | $W_{18}O_{49}$ + $W_{20}O_{58}$ + Cu |
| 2 | 600 | 241 | $W_{18}O_{49}$ + Cu |
| 3.5 | 500 | 203 | $W_{20}O_{58}$ + Cu |
| 6 | 500 | 203 | $W_{20}O_{58}$ + Cu |
| 4 | 500 | 29 | $W_{20}O_{58}$ + $WO_2$ + Cu |

the low partial pressures of water vapour would eventually result in a mixture of copper and tungsten.

At 600° C the sequence of tungsten oxides detected along with the metallic copper changed from $WO_2$ to $WO_2 + W_{20}O_{58}$ mixtures, to $W_{20}O_{58} + W_{18}O_{49}$ mixtures, to eventually $W_{18}O_{49}$ alone as the partial pressure of water vapour was increased. It is apparent that $WO_2$ was the lowest oxide produced and pure $WO_2 + Cu$ mixtures were obtained with a $P_{H_2O}$ of 105 mm Hg. This is in complete agreement with thermodynamic predictions which indicate that water vapour partial pressures less than 391 mm Hg but greater than 87 mm Hg in a 1 atm. $H_2/H_2O$ mixture will produce $WO_2$ as the stable oxide. At the next two higher partial pressures of water studied (154 and 169 mm Hg) $W_{20}O_{58}$ was detected along with $WO_2$ and copper. $W_{18}O_{49}$ was not detected in these products which were obviously non-equilibrium products. At the highest partial pressure used $W_{18}O_{49}$ was detected, initially along with $W_{20}O_{58}$ at short reaction periods and eventually as the only oxide after extended reduction times. The thermodynamically stable oxide for the range of $P_{H_2O}$ used is $WO_2$, and it is apparent that in the mid-range of $P_{H_2O}$ used any $W_{20}O_{58}$ that had time to be reduced must have produced $W_{18}O_{49}$, which was immediately reduced further to yield $WO_2$. Hence the rate-controlling step in the reduction sequence was the production of $W_{18}O_{49}$ from $W_{20}O_{58}$. However, at the highest $P_{H_2O}$ used (241 mm Hg) $W_{18}O_{49}$ was stabilized sufficiently to be detected in the products even though this value of $P_{H_2O}$ is below the range that may be predicted for the formation of $W_{18}O_{49}$ (758 mm Hg $> P_{H_2O} >$ 391 mm Hg). These predictions are based on JANAF data [9] and are only approximate. This is apparent because the use of this data predicts higher values of $P_{H_2O}$ for the stabilization of $W_{18}O_{49}$ than for the stabilization of $W_{20}O_{58}$ [1]. Nevertheless, it is evident that the production of $W_{18}O_{49}$ is caused by kinetic limitations because $WO_2$ is the equilibrium phase under the experimental conditions used.

In the experiments conducted at 700° C with precipitated tungstate, $WO_2 + Cu$, $WO_2 + W_{20}O_{58} + Cu$ or $W_{20}O_{58} + Cu$ were detected as the product phases. $W_{18}O_{49}$ was not detected in any of the reduction products even with the highest $P_{H_2O}$ used (241 mm Hg) which had previously been shown to yield $W_{18}O_{49}$ in the reduction of blue oxide [2]. The range of $P_{H_2O}$ values that may be predicted for the formation of $W_{18}O_{49}$ at 700° C is 758 mm Hg $> P_{H_2O} >$ 429 mm Hg, whilst the range for $WO_2$ at the same temperature is 429 mm Hg $> P_{H_2O} >$ 142 mm Hg. It is thus apparent that the equilibrium phase ($WO_2$) is produced at the low and medium values of $P_{H_2O}$. The absence of $W_{18}O_{49}$ indicates that, as in the case of reduction of 600° C, the rate-controlling step in the reduction sequence would appear to be the reduction of $W_{20}O_{58}$ to $W_{18}O_{49}$; that is, any $W_{18}O_{49}$ is reduced immediately to $WO_2$.

Thermodynamic predictions and experimental evidence of the temperature dependence of the copper tungstate reduction reaction indicate that the partial pressure of water vapour required to stabilize any given lower tungsten oxide increases as the temperature is increased. Consequently, the production of $W_{20}O_{58}$ and Cu after short reduction periods at 700° C using a $P_{H_2O}$ of 241 mm Hg is not in general agreement with the production of Cu, $W_{18}O_{49}$ and $W_{20}O_{58}$ at 600° C with the same $P_{H_2O}$ over similar reduction times. It was expected that both $W_{18}O_{49}$ and $W_{20}O_{58}$ would be produced at 700° C. However, this variability in what are non-equilibrium products at short reduction times may be associated with the difficulty involved in the rapid retrieval of samples from the thermobalance, which required to be flushed with an inert gas and cooled prior to specimen recovery.

Tables II and III give the identification of the products of reduction of the mixtures of precipitated copper tungstate and blue oxide and CuO and $WO_3$ respectively. Table II shows that $W_{18}O_{49}$ was always obtained as some part of the product at 700° C using partial pressures of water vapour of 203 mm Hg and 241 mm Hg. Only these two values of $P_{H_2O}$ were used because the major interest in this part of the study was to determine whether $W_{18}O_{49}$ could be produced from the tungstate plus blue oxide using conditions under which $W_{18}O_{49}$ had been prepared previously from blue oxide alone [2]. It is evident from Table II that either the increase in the overall tungsten level in the mixture of tungstate and blue oxide or the presence of the blue oxide as an additional pure oxide has allowed significant proportions of $W_{18}O_{49}$ to be produced in accordance with the predictions based on the previous experimental work on pure tungsten oxides. Consequently, it

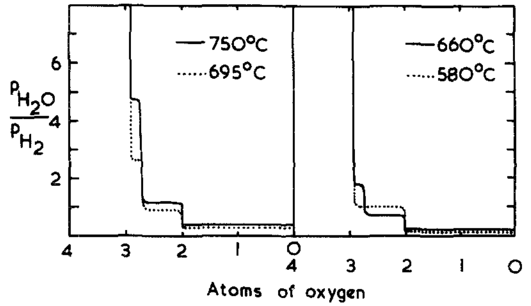

*Figure 2* Relationship between $P_{H_2O}/P_{H_2}$ and number of atoms of oxygen in the reduced solid product (after Guerassimov [4]).

appears that the relative rates of reduction of the lower oxides are dependent upon the source of the oxides.

The data obtained for a restricted range of reduction conditions using the equimolar mixture of CuO and $WO_3$ are presented in Table III. At 500° C, as before, there is no evidence of $W_{18}O_{49}$ which is in accordance with the W–O phase diagram. The mixtures of phases obtained are in agreement with the data obtained for the precipitated tungstate. At 600 and 700° C copper–tungsten oxide mixtures containing $W_{18}O_{49}$ were produced, which again shows that it is easier to obtain $W_{18}O_{49}$ from samples containing separate additions of $WO_3$ or blue oxide than it is from the pure tungstate. However, this cannot be explained on a thermodynamic basis.

The thermodynamics of the equilibria of copper tungstate with hydrogen, water vapour and the various tungsten oxides may conveniently be represented in the manner used by Guerassimov [4]. This representation is given in Fig. 2 where the equilibrium constant ($K_p = P_{H_2O}/P_{H_2}$) is plotted as a function of the atoms of oxygen in the reduced solid product for a series of temperatures. Calculated data for reduction at 580° C, when $W_{18}O_{49}$ is not stable, is included in Fig. 2 along with the data of Guerassimov [4]. The range of $H_2O/H_2$ ratios required to stabilize the various tungsten oxides are clearly seen. These ratios are far higher than those used in the present work which yield atmospheres that are too reducing for the stabilization of the higher oxides $W_{20}O_{58}$ and $W_{18}O_{49}$ as equilibrium products. However, as indicated earlier, the aim of the present work was to interrupt controlled reduction sequences after short periods that could approximate to commercial process times when the different oxides were present. From Fig. 2 it may be predicted that at 700° C $H_2O/H_2$ ratios less than 2.8 but equal to or larger than 1 will stabilize Cu + $W_{18}O_{49}$, whilst ratios less than 1 but equal to or larger than 0.2 will stabilize Cu + $WO_2$. Similarly a ratio less than 8 (the maximum shown on Fig. 2) but greater than or equal to 2.8 will produce Cu + $W_{20}O_{58}$. The data plotted for the reduction of copper tungstate at 580° C, that is just below the minimum temperature required for $W_{18}O_{49}$ formation, is based on available data for the reduction of pure $WO_3$ [4, 9], and explains the sequence of phases observed in both the dry hydrogen reduction [3] and the present controlled $H_2/H_2O$ reduction of the tungstate. The data for the reduction of $WO_3$ may be used because of the immiscibility of the copper and tungsten oxides, and copper and tungsten metal. In situations where alloying of the tungsten and the other metal is possible (Fe, Co and Ni, which will be treated in a future communication) the free energies of formation of the various intermetallic compounds require to be considered in the overall reduction equation.

### 3.2. Morphologies of $H_2O/H_2$ reduction products

Figs. 3a to d show typical micrographs of the products of controlled reduction of the precipitated tungstate at 500, 600 and 700° C. The product at 500° C, which was shown by X-ray diffraction to consist of metallic copper and $WO_2$, can be seen to consist of two distinct types of material. Large rounded, or sometimes slightly faceted, crystals are evident on the surfaces of what had originally been the cake-like agglomerates of the precipitated tungstate. The major part of the product consists of an almost stringer-like agglomeration of very small rounded particles some 0.2 $\mu$m approximately in diameter. The larger particles on the surface of the fine particle agglomerates are some 1 to 2 $\mu$m in diameter. The whole overall structure is very similar to that of the tungsten–copper composite material obtained by the dry hydrogen reduction of the precipitated tungstate [3]. Electron-probe microanalysis has shown the large particles to be pure copper whilst the background material is a mixture of copper and $WO_2$. Copper–$W_{20}O_{58}$ mixtures, which were also obtained at this temperature in the controlled reduction experiments, had the same overall appearance as that shown in Fig. 3a, but generally contained fewer large copper particles. It is apparent that in all the low temper-

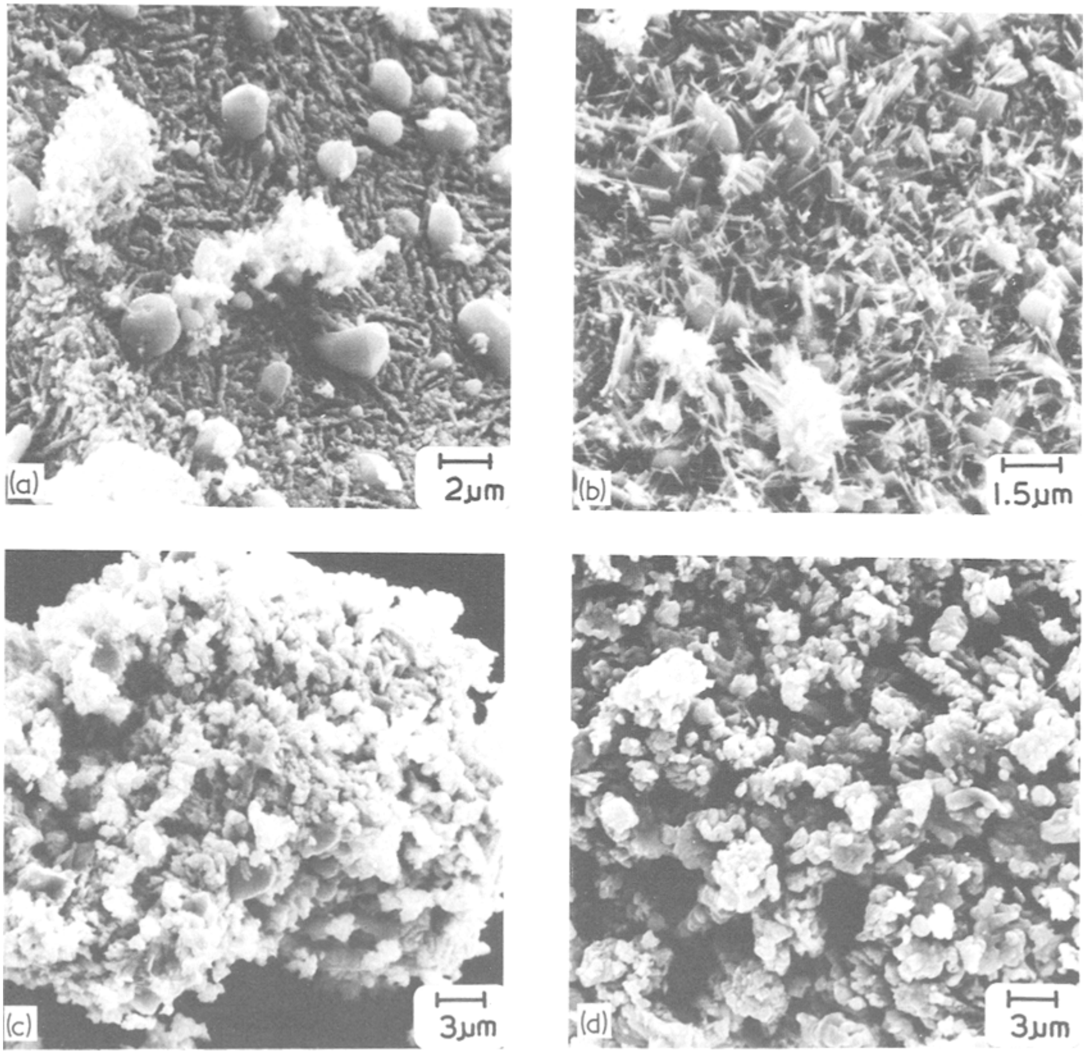

*Figure 3* Morphologies of copper–tungsten oxide composites obtained from precipitated tungstate: (a) Cu + $WO_2$ at 500° C; (b) Cu + $W_{18}O_{49}$ at 600° C; (c) Cu + $WO_2$ at 600° C; (d) Cu + $WO_2$ at 700° C.

ture reductions a significant proportion of the metallic copper has sintered together to produce the larger globules, whilst the tungsten oxide component is left in a finely disseminated form along with the remaining copper. It is also apparent that the oxide/metal composite shown in Fig. 3a is the precursor of the copper–tungsten composite powder produced from the same tungstate by dry hydrogen reduction at 500° C [3], and it is evident that the gross separation and sintering of the copper phase takes place whilst the tungsten is still the oxide.

Two typical micrographs are shown in Figs. 3b and c of the copper–tungsten oxide composites produced at 600° C. Fig. 3b shows the copper–$W_{18}O_{49}$ mixture produced with the high partial pressures of water vapour, whilst Fig. 3c is representative of the copper–$WO_2$ mixtures produced with the lower partial pressures of water vapour. The typical whisker-like morphology of $W_{18}O_{49}$ (Fig. 4) is evident in Fig. 3b along with some rounded particles of widely varying sizes which have been analysed to be pure copper. As in the product at 500° C, some part of the copper composite has sintered together leaving the tungsten oxide in its widely disseminated characteristic morphology. There appears to be less sintering of the copper to form large particles in this material compared to the Cu–$WO_2$ composite shown in Fig. 3a and this is presumably because of

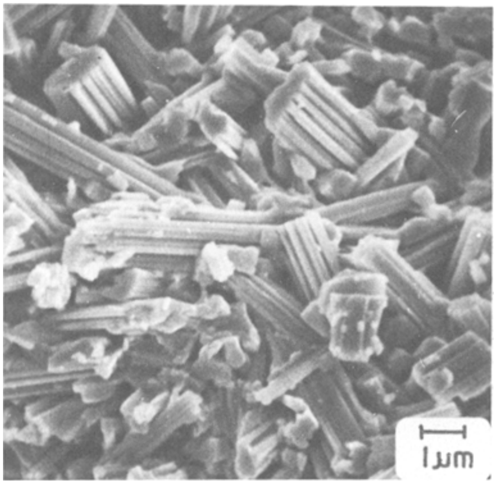

*Figure 4* Morphology of $W_{18}O_{49}$ produced from pure blue tungsten oxide.

the differing reduction times used. It is thus apparent that to produce a fine dispersion of the two phases as short a reduction period as possible is required. The Cu–$WO_2$ composite produced at 600° C (Fig. 3c) is quite different in morphology from the Cu–$WO_2$ material produced at 500° C. The higher temperature product can be seen to contain a few rounded copper particles; however, the majority of the composite powder consists of a fairly fine mixture of Cu and $WO_2$ of just submicron size.

The various products of reduction of the precipitated tungstate at 700° C all possessed the particle morphology shown in Fig. 3d. Both $WO_2$–Cu and $W_{20}O_{58}$–Cu mixtures consisted of mixtures of the metallic and oxide phases which were hardly distinguishable by morphology alone. The copper particles tended to be more spherical than the oxide particles. The oxide particle size has increased above that obtained at 600° C, which in turn was larger than that at 500° C; however, there was an almost complete absence of the large rounded copper particles in the higher temperature product even after fairly extended periods at temperature. It would, therefore, appear that the sintering of the copper takes place more readily as the slow low temperature reduction processes occur rather than on holding at temperature once a fairly stable copper–lower oxide dispersed mixture has been produced.

Figs. 5a and b show representative micrographs of the product of reduction at 700° C of the 50:50 wt% mixture of the precipitated tungstate (after dehydration) and blue oxide produced from freeze-dried ammonium paratungstate. In contrast to the tungstate alone at this temperature, there is evidence of masses of needles of $W_{18}O_{49}$ that have been produced under the conditions of temperature, time and water vapour partial pressure which were similar to those that yielded either $WO_2$ + Cu or $W_{20}O_{58}$ + $WO_2$ + Cu for the precipitated tungstate. These observations confirm the X-ray diffraction analysis discussed in the previous section and show that $W_{18}O_{49}$ can be produced from the blue oxide component of the mixture under these

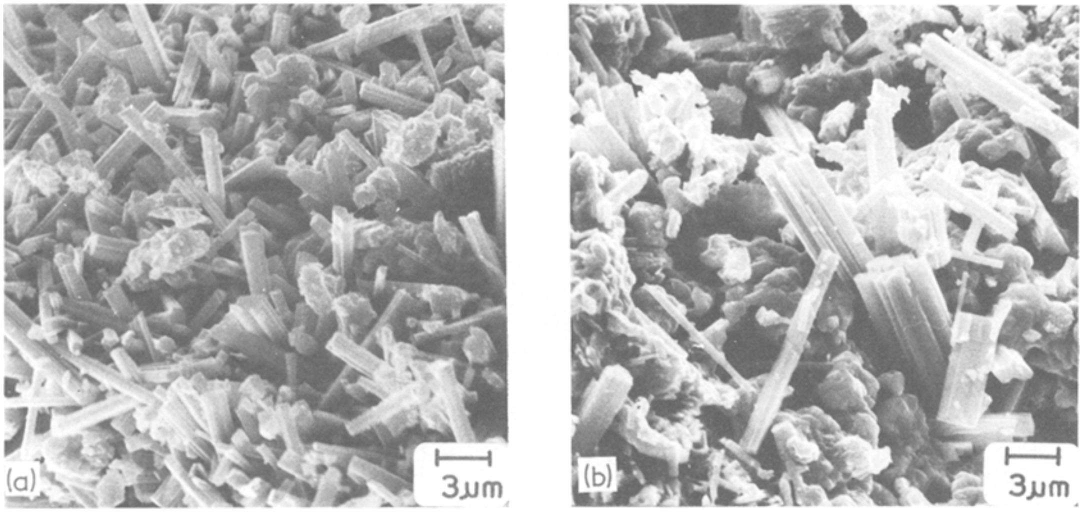

*Figure 5* Morphologies of copper + $W_{18}O_{49}$ composites obtained at 700° C from precipitated tungstate and blue oxide mixtures: (a) $P_{H_2O}$ = 203 mm Hg; (b) $P_{H_2O}$ = 241 mm Hg.

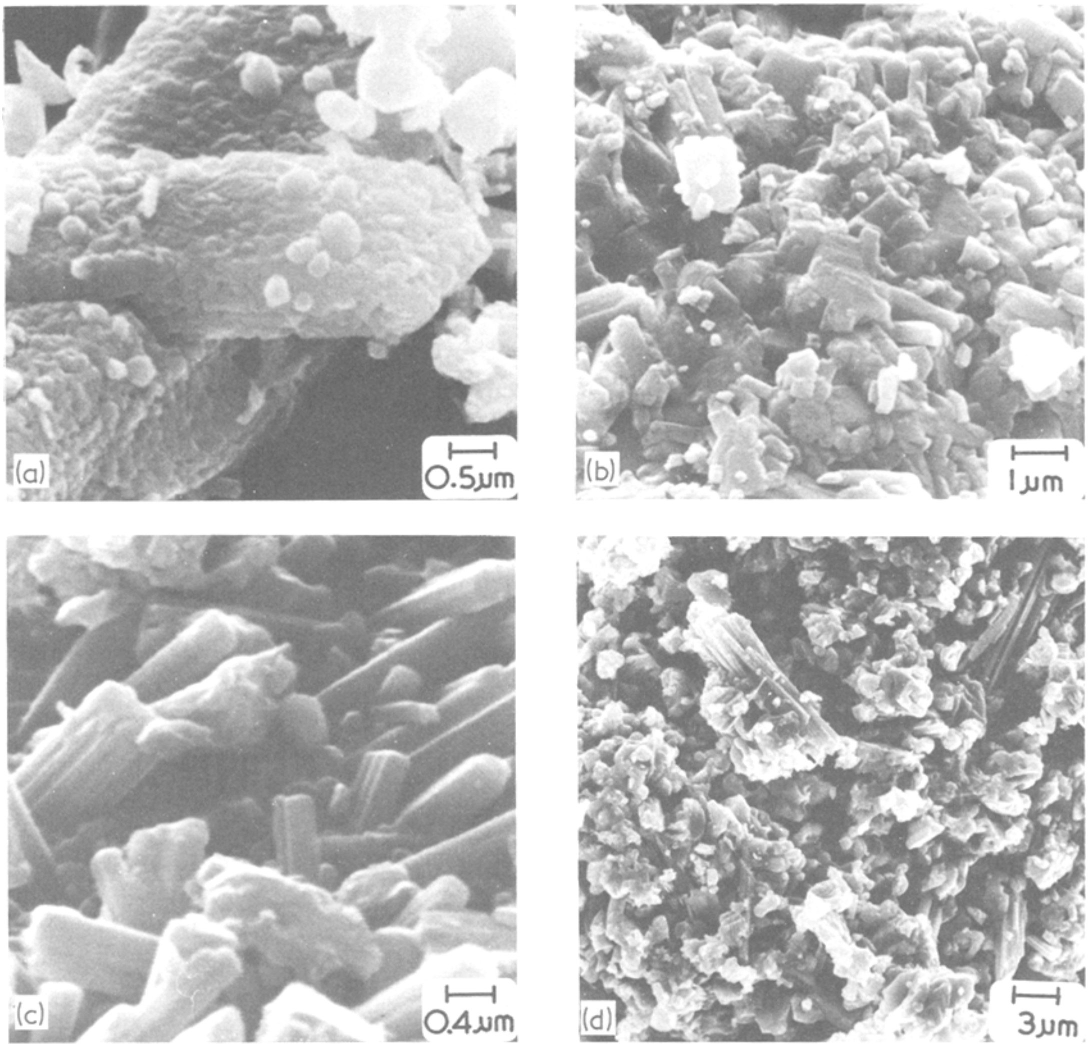

*Figure 6* Morphologies of copper–tungsten oxide composites obtained from mechanical mixtures of CuO and $WO_3$. (a) Cu + $W_{20}O_{58}$ at 500° C from CuO + lath-like $WO_3$. (b) Cu + $W_{20}O_{58}$ (+ traces $W_{18}O_{49}$) at 600° C. (c) Cu + $W_{18}O_{49}$ at 600° C. (d) Cu + $W_{18}O_{49}$ + $WO_2$ at 700° C.

experimental conditions. The agglomerated particles were analysed to be mainly copper which contained some trapped tungsten oxide, whilst the masses of whiskers are clearly $W_{18}O_{49}$. An interesting observation is that it appears that the majority of the tungsten component is present as $W_{18}O_{49}$ whiskers. Hence it is apparent that all of the tungsten added as blue oxide to the original mixture is converted to $W_{18}O_{49}$. However, some of the oxide produced from the tungstate must also be converted to $W_{18}O_{49}$; a situation which did not exist for the tungstate alone.

The range of particle morphologies produced from the various equimolar mixtures of CuO and $WO_3$ is shown in Figs. 6a to d. The product obtained at 500° C from a mixture of lath-like $WO_3$ (shown in Fig. 7) which was produced from orthorhombic ammonium paratungstate, and CuO can be seen to consist of typical lathes of the lower oxides $WO_2$ and $W_{20}O_{58}$ onto which either small spherical particles or larger faceted particles of copper have adhered. In the mechanical mixtures reduced at the higher temperatures of 600 and 700° C, where the $WO_3$ component of the initial sample was produced from freeze-dried ammonium paratungstate, more evenly sized mixtures of copper and tungsten oxide were obtained. At 700° C there is clear evidence of a small amount of

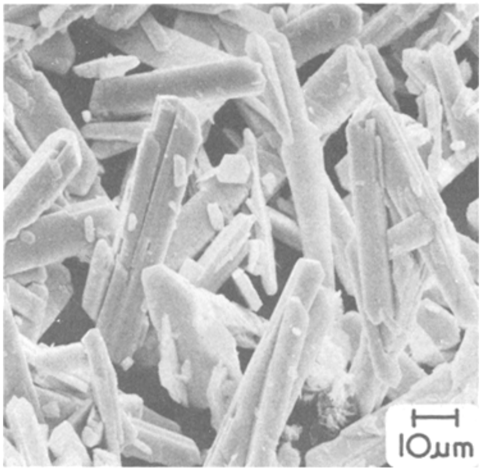

*Figure 7* Morphology of lath-like $WO_3$.

$W_{18}O_{49}$ along with a fairly equiaxed mixture of copper and $WO_2$. At 600° C, using a $P_{H_2O}$ of 154 mm Hg for 2 h, there appears to be the early stages of growth of $W_{18}O_{49}$ as can be seen in Fig. 6b. X-ray diffraction analysis showed the oxide mixture in this sample to be composed of $W_{18}O_{49}$ and $W_{20}O_{58}$. At the same temperature, but with a $P_{H_2O}$ of 241 mm Hg, the resultant particle morphology after a 2 h reduction period was as shown in Fig. 6c. It is evident that the major tungsten oxide is $W_{18}O_{49}$ in its typical corrugated whisker form, whilst the copper is present as irregular agglomerates, some 1 $\mu$m in size, which contain some trapped tungsten oxide, or in some instances as very small (approximately 0.2 $\mu$m in size) regular-shaped particles. As in the case of the tungstate–blue oxide mixtures, $W_{18}O_{49}$ is readily formed when pure tungsten oxides are present in the initial mixtures.

## 4. Conclusions

(1) The products of controlled reduction at 500° C using a $P_{H_2O}$ of the order of 18 to 29 mm Hg are mixtures of $WO_2$ and Cu, which are the precursors of the Cu–W mixtures produced by dry hydrogen reduction at this temperature and determine the ultimate metal powder morphologies.

(2) At 600° C composites of Cu + $W_{18}O_{49}$ and Cu + $WO_2$ can be produced from copper tungstate by control of the $H_2/H_2O$ ratio. These composites have entirely different particle morphologies and may possibly be used to produce Cu–W powders of widely differing particle morphologies.

(3) In general the reduction products obtained in reaction periods ranging from 0.5 to 6 h are not the true thermodynamic equilibrium phases. The reducing gases used are far too reducing in comparison to the experimentally obtained mixtures.

(4) The production of $W_{18}O_{49}$ from copper tungstate alone appears to be quite difficult. However, the addition of blue oxide to copper tungstate allows predictions based on the reduction of the blue oxide to be achieved in practice.

(5) Equimolar mechanical mixtures of CuO and $WO_3$ in general behave similarly to the copper tungstate, but allow the formation of $W_{18}O_{49}$ more readily. It is thus postulated that the rate-controlling step in the reduction of the tungstate is frequently the production of $W_{18}O_{49}$ from $W_{20}O_{58}$, i.e. once $W_{18}O_{49}$ is produced, in general, it is reduced immediately to $WO_2$. This behaviour does not occur for $W_{18}O_{49}$ produced from pure blue tungsten oxide and hence allows the easy production of $W_{18}O_{49}$ from mixtures of tungstate and blue oxide and CuO and $WO_3$.

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