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Structures and chemistry of tungsten powder from doped and undoped tungsten blue oxide

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Blue tungsten oxide, both without dopant and doped with aluminium, silicon and potassium was reduced to tungsten by heating at 750 and 900° C in flowing hydrogen. The morphology, chemistry, and crystal structure were determined by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis, X-ray photoelectron spectroscopy and Auger electron spectroscopy. Undoped oxide reduced at a lower rate than did the doped oxide. The potassium, silicon and aluminium appeared to be distributed non-uniformly on the surface of the doped oxide particles. Nucleation of tungsten crystals began earlier in the doped oxides leading to a bimodal distribution of crystal sizes in the doped material. There were pockets of potassium inside the tungsten crystals from the doped blue oxide. This suggests that the tungsten crystals nucleated earlier and at regions of high potassium concentration on the surface of the doped blue oxide. Tungsten was then transported from the surrounding oxide to the nucleus to grow the crystals trapping the potassium inside the crystal. Nucleation of the tungsten crystals occurred more homogeneously on the surface of the oxide that was low in potassium and, of course, on the undoped oxide particles, leading to the smaller size of the tungsten crystals from the undoped oxide.

1. Introduction

The microstructure [1], grain morphology [2], and mechanical properties such as grain boundary sliding and creep or sag [3] of tungsten incandescent lamp filaments are related to the powder from which the wire was made. Processing from doped and reduced tungsten powder to the final wire can affect such properties but cannot produce a wire with the desired characteristics unless the starting powder is properly constituted. The proper microstructure and grain morphology are produced by doping tungsten blue oxide with aluminium, silicon and potassium-containing compounds, which ultimately produce internal bubbles of potassium in the tungsten ingot, [4, 5]. Further processing deforms these bubbles into strings of finer bubbles in the wire [1, 6]. The effects of dopant and reduction conditions of the blue oxide on the resulting tungsten powder characteristics are the subjects of this report.

2. Experimental procedure

The powders used in this study were obtained from the Chemical and Metallurgical Products Department of the General Electric Company, Cleveland, Ohio. These were examined by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron (XPS), and scanning Auger electron spectroscopy (AES). Near-surface chemical analysis was done using energy dispersive X-ray analysis (EDX).

Samples of blue oxide were placed in a tungsten boat to a depth of 3 mm and were reduced in hydrogen flowing at the rate of $0.014\,m^3\,h^{-1}$ ($0.5\,ft^3\,h^{-1}$) at temperatures of 1023 and 1173 K (750 and 900° C, respectively) for various times.

3. Experimental results

3.1. APT

The starting material is ammonium paratungstate (APT) [$5(NH_4)2O12WO_35H_2O$] consisting of monoclinic crystals shown in Fig. 1a at low magnification and in Fig. 1b at higher magnification to reveal the surface characteristics of the particles.

3.2. Blue oxide

The morphology, size, and surface chemistry of the blue oxide are likely to be important in determining the distribution of dopant. The blue oxide is obtained by heating APT in hydrogen at 700 to 900 K (430 to 650° C) and retains the block-like shape of the original APT particles as is seen in Fig. 2a. Higher magnification (Fig. 2b) shows details of the surface which is rougher than the APT (but still relatively smooth) and has many cracks. X-ray diffraction (discussed later) identifies the oxide as a mixture of WO_3 and $WO_{2.9}$.

The doped blue oxide is prepared by wetting the powder with a solution of potassium disilicate, then, while the powder is still wet, adding a solution of aluminium trichloride. The powder is then dried at 100° C. The distribution of dopant was examined by SEM, Fig. 3a. The three spots marked by the arrows in the figure were analysed by EDX; a representative EDX spectrum is shown in Fig. 3b. These three regions showed the presence of potassium and chlorine. Other features on the surface of this particle

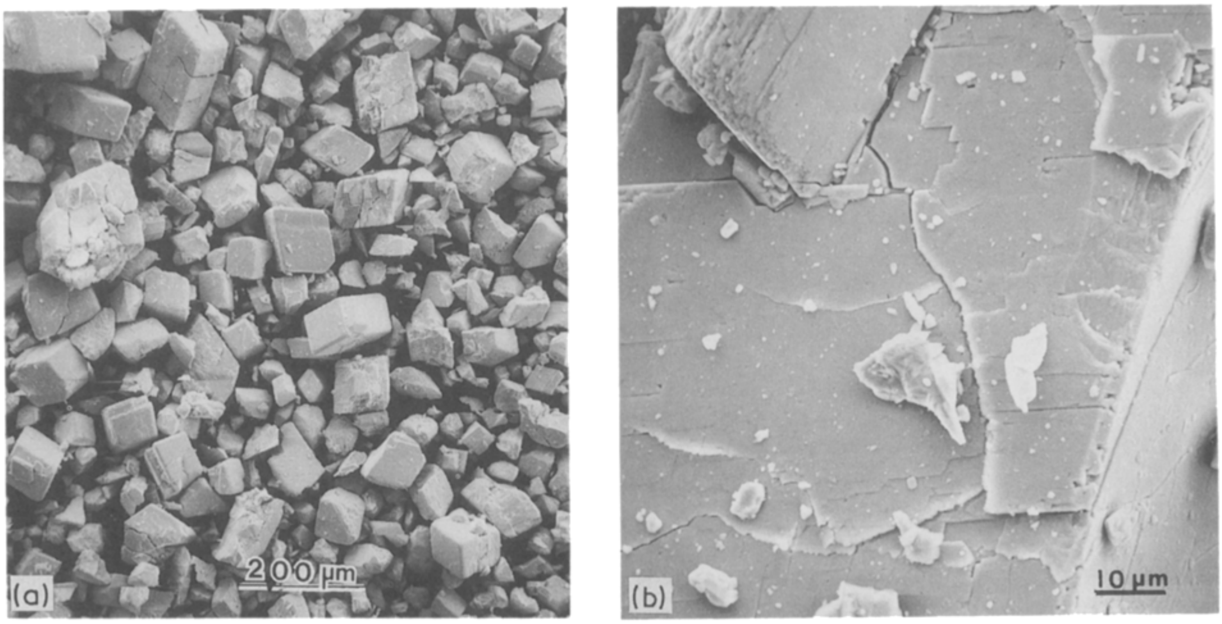

Figure 1 (a) Scanning electron micrograph (SEM) of ammonium paratungstate. (b) SEM of APT at higher magnification.

showed only tungsten. Note that silicon and aluminium are not easily detected because their X-ray lines overlap with tungsten. The analysis depth of EDX is on the order of a micrometre, hence much of the signal comes from inside the particle. A more surface sensitive technique is XPS which sees only the top $< =4$ nm of the sample. The surface composition of the doped blue oxide and powders reduced for various times at 900° C is given in Table I.

The X-ray spot size is about 600 μm, so many particles are included in this analysis. Ion sputtering (to remove the atmospheric contaminants) was not attempted; the carbon and some of the oxygen are undoubtedly present as a result of handling and exposure to the air, but the potassium comes solely from the dopant. The tungsten oxidation state can be determined from XPS, and this is discussed below.

3.3. Reduction at 900° C

The appearance of the doped powder changes noticeably as it is reduced. After 2.5 min at 900° C in flowing hydrogen, the particles retain the morphology of the blue oxide particles but have begun to form the needles typical of $WO_{2.72}$, and worm-like features typical of WO_2 [7]. Examination of Figs 4a and b reveals the presence of a few nearly spherical faceted tungsten crystals located in pockets at the surface of the particles.

TABLE I X-ray photoelectron spectroscopy of doped WO_3 reduced at 900° C in 0.014 m^3 h^{-1} hydrogen

Time (min)	W (at %)	C (at %)	O (at %)	K (at %)	Si (at %)
0	13	21	52	2.0	12
2.5	18.1	21.7	52.8	7.3	
7	19.4	23.8	45.1	11.7	
15	21	24.3	41.9	12.6	
30	15.2	24.5	42.9	17.4	
	26	35	38.6	0.4*	

*Factory reduced and acid washed. Before the powder is pressed into ingot form, the doped and reduced powder is washed with acids to remove the majority of the dope elements. The powder is then rinsed with water to remove the acids.

The particles still retain their original morphology after 5 min at 900° C but the size of the pockets and the number of tungsten crystals have increased, as seen in Figs 5a and b. Fig. 6 shows details of the faceting of the tungsten crystals.

Heating for 7 min at 900° C increases the number of tungsten crystals with the particles still maintaining the original blue oxide morphology as seen in Fig. 7. Now, however, the tungsten crystals have holes at the surface. Fig. 8 shows a cluster of these crystals. Polished cross-sections of the particles, Fig. 9, shows the presence of holes in the interior of the crystals [8]. Examination by EDX indicates the presence of potassium in the interior holes of the crystals.

After 15 min at 900° C, the early morphology is largely destroyed, as seen in Fig. 10a. The sample now consists mainly of clusters of large and small crystals (Fig. 10b). The large crystals have holes on the surface, but the small crystals do not appear to have holes, to the limit of resolution of the SEM.

The reduction of the undoped powder occurs in the same way as the doped powder but more slowly. Some noticeable differences are found in the fully reduced powder (15 min at 900° C). Undoped powder reduced for 15 min retains the early (APT) morphology to a much greater degree than the doped powder, as seen in Fig. 11a. It is also quite evident from Fig. 11b that the crystals are much smaller than in the doped sample. Furthermore, there are no holes on the surface of the crystals formed from the undoped blue oxide or in the interior as revealed by sectioning. The undoped powder also shows much more sharply defined facets compared with the doped powder (compare Fig. 11b with Fig. 10b).

An interesting result was obtained when a sample consisting of 80% doped oxide and 20% undoped oxide was heated for 45 min at 900° C to ensure

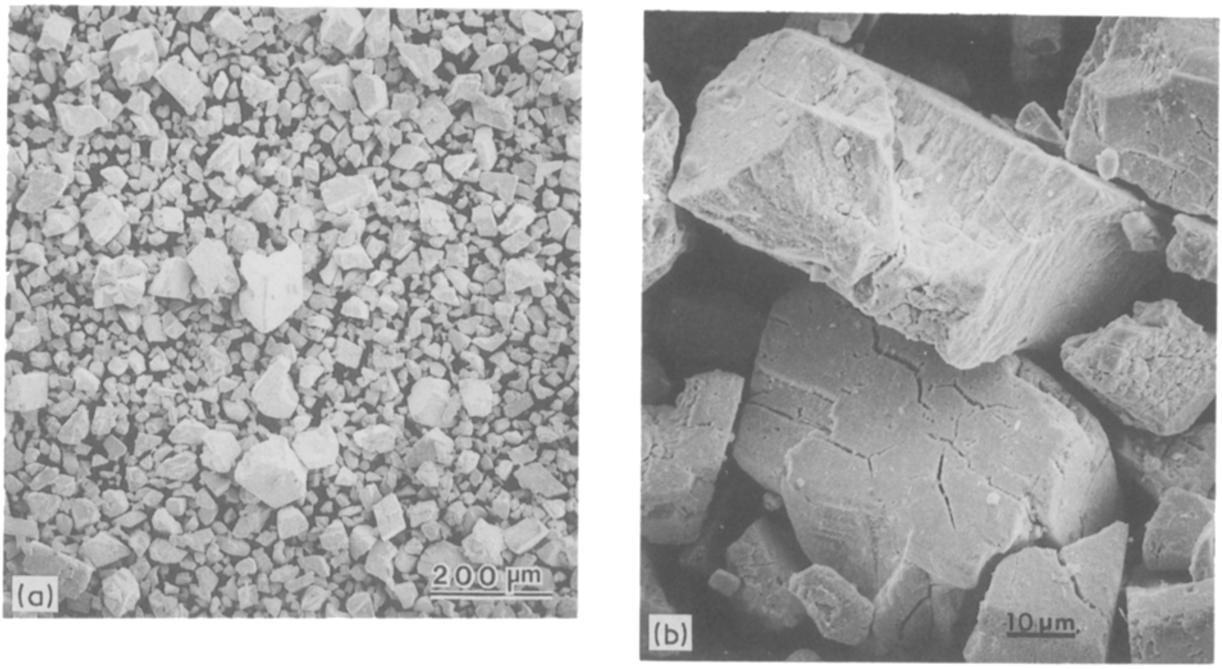

Figure 2 (a) SEM of doped blue oxide. (b) SEM showing the surface characteristics of the doped blue oxide.

complete reduction. As seen in Figs 12a and b, there is a mixture of cubic, faceted crystals (Fig. 12a) which are usually seen in undoped material and some poorly faceted crystals with holes which are usually associated with doped powder (Fig. 12b). Spot surface analysis of individual crystals by AES revealed potassium everywhere on the sample (as well as tungsten and oxygen).

X-ray diffraction provides information about the bulk composition of the powder and complements surface techniques such as SEM and XPS. Diffraction patterns of doped and undoped samples reduced for various times are given in Fig. 13. The doped blue oxide consists of mainly triclinic WO_3, with some $WO_{2.9}$. After 2.5 min at 900° C, the bulk of this powder has been transformed to WO_2, while the sample heated for 7 min is a mixture of WO_2 and tungsten metal. Complete reduction to tungsten metal is achieved in 15 min at 900° C. Comparing these results with those from the undoped powder, it is clear that the undoped powder is reduced more slowly; at 7 min, the undoped sample still has a significant amount of WO_2. By 15 min, both samples are completely reduced but recall that their surface morphology is quite different as seen in SEM. The implications of these results will be discussed below.

X-ray photoelectron analysis of the doped and undoped powders, after various times at temperature, reveals an interesting trend in the surface composition, Table I, and some information on the surface oxidation state of tungsten, Fig. 14. As seen in Table I, the amount of potassium in the top 4 nm increases as

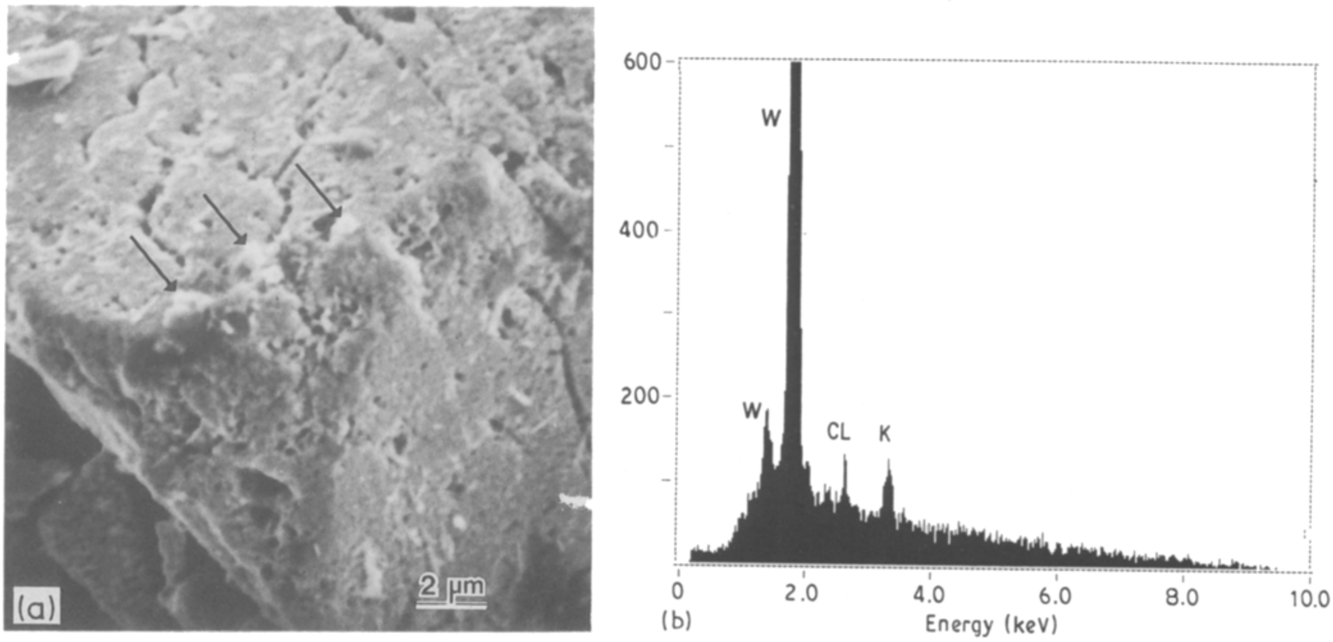

Figure 3 (a) Doped blue oxide with clumps high in potassium marked by arrows. (b) EDX spectrum of spot marked by middle arrow in Fig. 3a.

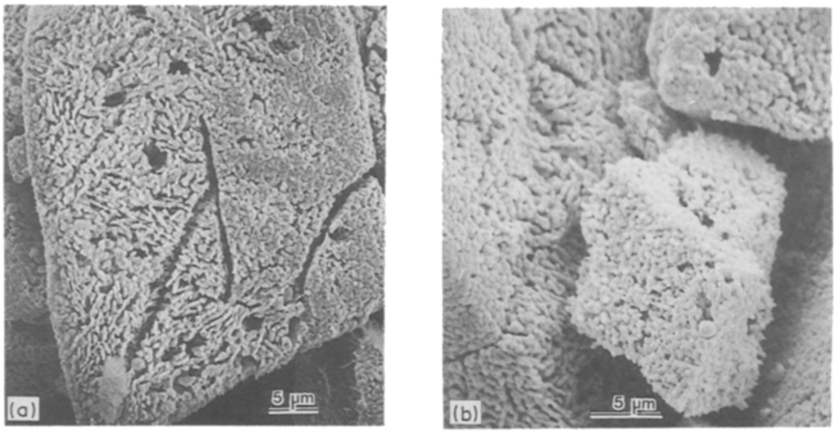

Figure 4 Doped blue oxide heated 2.5 min at 900° C in $0.014\,\mathrm{m}^3\,\mathrm{h}^{-1}$ hydrogen showing tungsten crystals in pockets in the oxide.

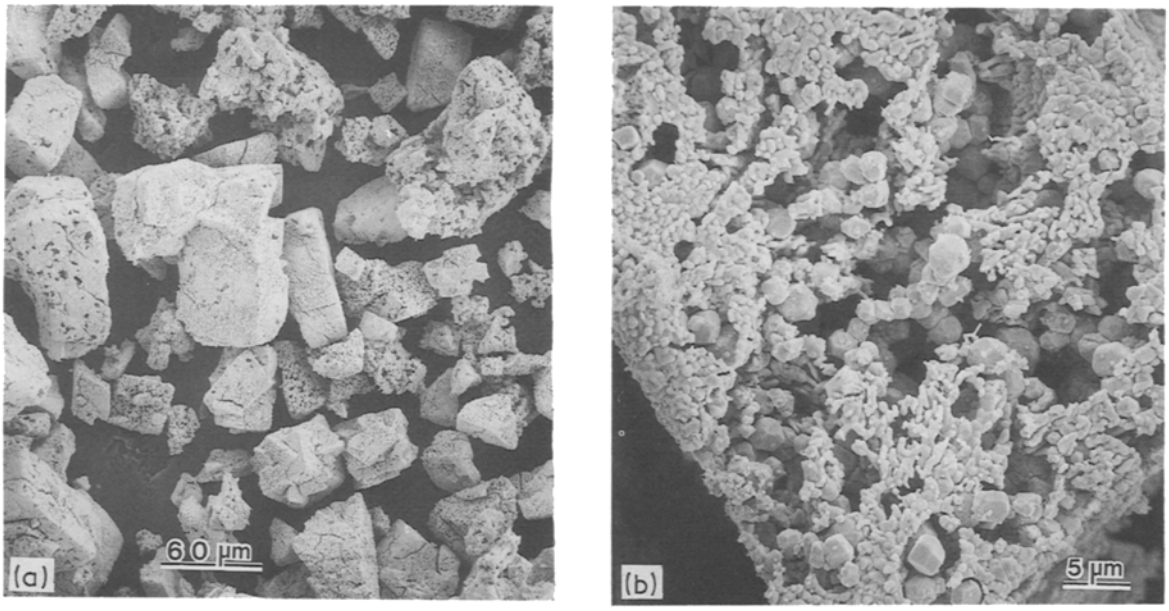

Figure 5 (a) Doped blue oxide heated for 5 min in hydrogen. (b) Tungsten crystals in doped oxide heated for 5 min at 900° C.

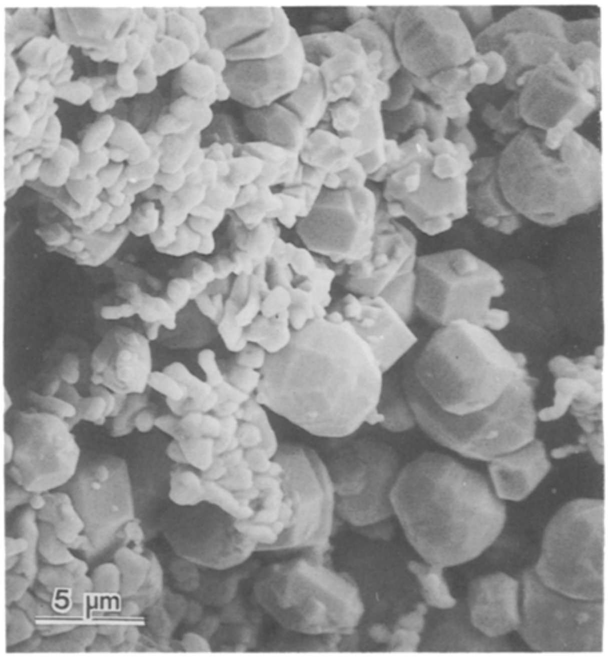

Figure 6 Faceted tungsten crystals and oxide forms in powder heated for 5 min.

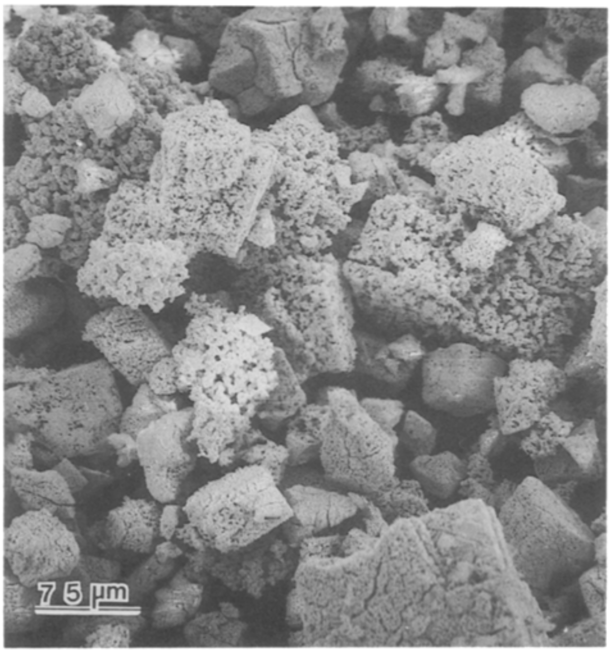

Figure 7 Doped blue oxide heated for 7 min at 900° C.

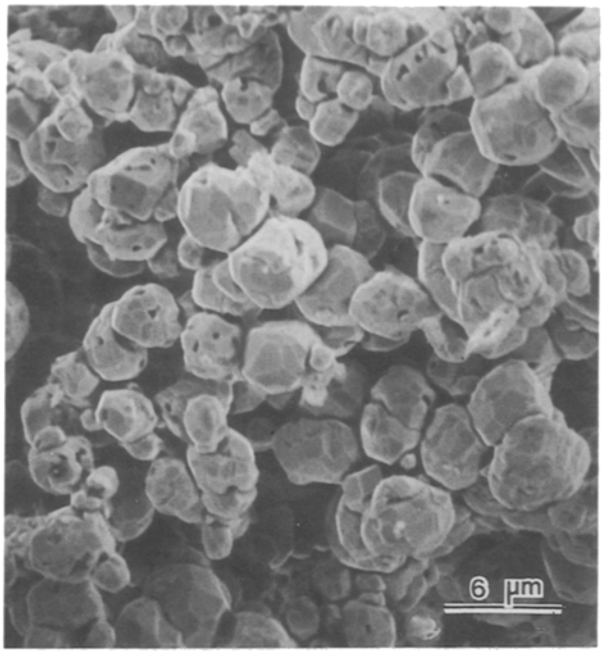

Figure 8 Holes on the surface of tungsten crystals in the doped oxide heated for 7 min at 900° C.

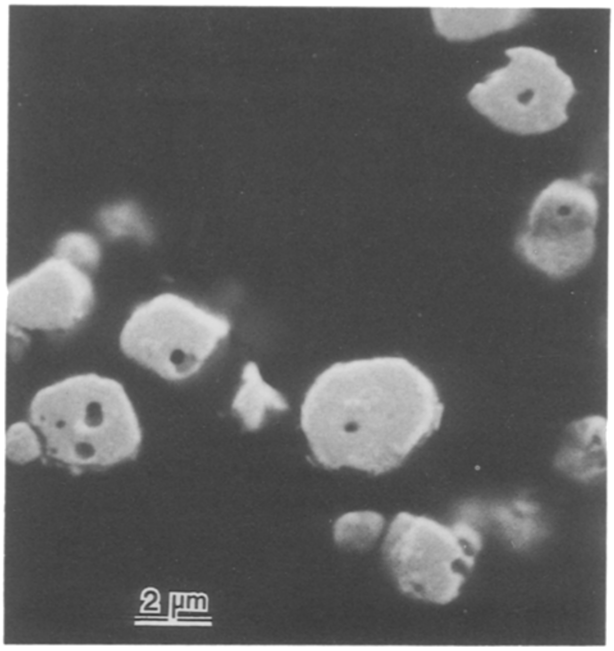

Figure 9 SEM of sections of tungsten crystals heated for 7 min at 900° C.

the powder is reduced. Either potassium is migrating to the surface, or species covering the potassium are being removed. This trend has interesting implications concerning the role of dopants during reduction, as discussed below. The surface concentration of oxygen tends to decrease as the sample is reduced. This trend is mirrored in the oxidation state of tungsten (Fig. 14). The surface spectrum of the doped blue oxide has two peaks in the tungsten region with binding energies of 35.76 and 37.89 eV. As reduction at 900° C proceeds, the tungsten peaks shift to 31.39 and 33.54 eV although the oxide peaks are still present. Spectra at 2.5 and 7 min at 900° C show an intermediate oxide, likely WO_2 as well as tungsten metal. This trend follows that found by X-ray diffraction. Since these samples are not analyzed immediately after reduction, there is certainly some atmospheric oxidation occurring at the surface, hence the presence of WO_3. It is, however, interesting to note that the undoped blue oxide reduced for 15 min has less oxide than does the corresponding doped sample.

3.4. Reduction at 750° C

The reduction of both doped and undoped oxide proceeds more slowly at 750° C as may be seen in the XRD patterns in Fig. 15. At 22 min, there is a mixture of WO_2 and tungsten, and, even at 45 min, some WO_2 remains. Optical examination of the doped powder reduced for 45 min shows the presence of large particles retaining the original blue oxide morphology with relatively large crystals of tungsten in pockets of the particle (Fig. 16a). Some of the crystals are

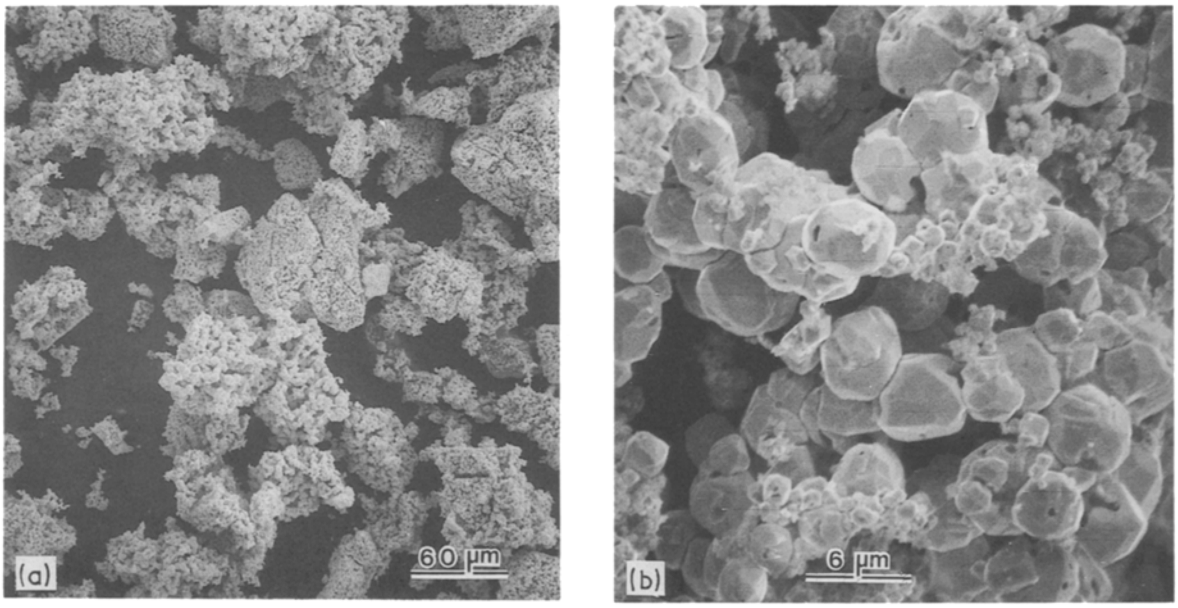

Figure 10 (a) SEM of doped blue oxide heated for 15 min at 900° C. (b) SEM of doped oxide heated for 15 min showing different sizes of tungsten crystals.

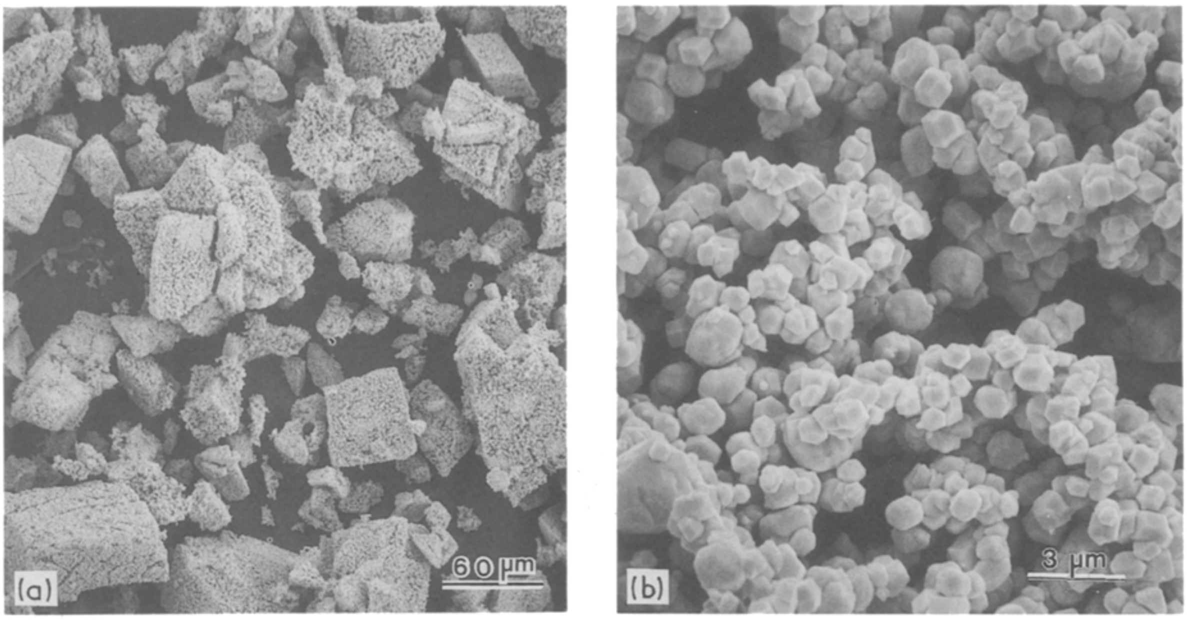

Figure 11 (a) Undoped blue oxide heated for 15 min at 900° C. (b) Undoped oxide heated for 15 min showing sharply faceted crystals without surface holes.

shown at higher magnification in Fig. 16b. Other areas of this sample consist of clusters of tungsten crystals with holes that appear to have grown more uniformly. (Fig. 16c). In contrast, the undoped blue oxide heated for 45 min at 750° C does not show any large tungsten crystals in the large particles; an example of this sample is given in Fig. 17a. In general, the reduced undoped sample consists of much smaller tungsten crystals than are found in the doped sample (compare Fig. 17b with Fig. 16c).

4. Discussion

It is evident from the results above that the presence of the dopant has an affect on the characteristics of the reduced tungsten powder. Most obvious is the presence of potassium inside and on the surface of the tungsten powder deriving from doped blue oxide. Other differences include the presence of pits on the surface of doped tungsten metal, the smaller size and more cubic form of crystals from undoped powder, and the wider size distribution of doped tungsten crystals. Related to these properties is the fact that (at 900° C) doped powder reduces more rapidly than does undoped powder. That is, tungsten crystals are observed to nucleate earlier in the doped oxide than in the undoped oxide, leading to a larger range of sizes of the tungsten crystals in the doped oxide than in the undoped oxide.

Our analysis indicates that the potassium is present in discrete clumps of dopant on the surface of the doped blue oxides. These clumps affect the reduction and formation of the tungsten crystals by providing nucleation sites for tungsten crystal growth. Once a crystal is nucleated, tungsten is transported to the growing crystal by means of vapour as described by

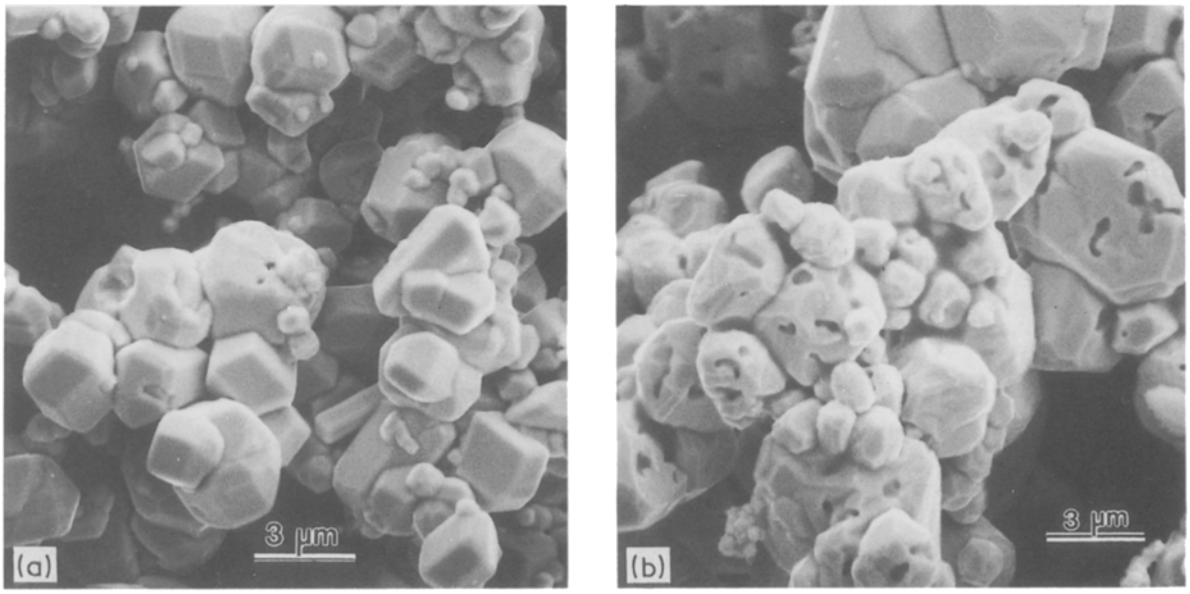

Figure 12 SEM of mixture of 80% doped and 20% undoped blue oxide heated for 45 min at 900° C; (a) showing mostly undoped crystals, and (b) mostly doped crystals.

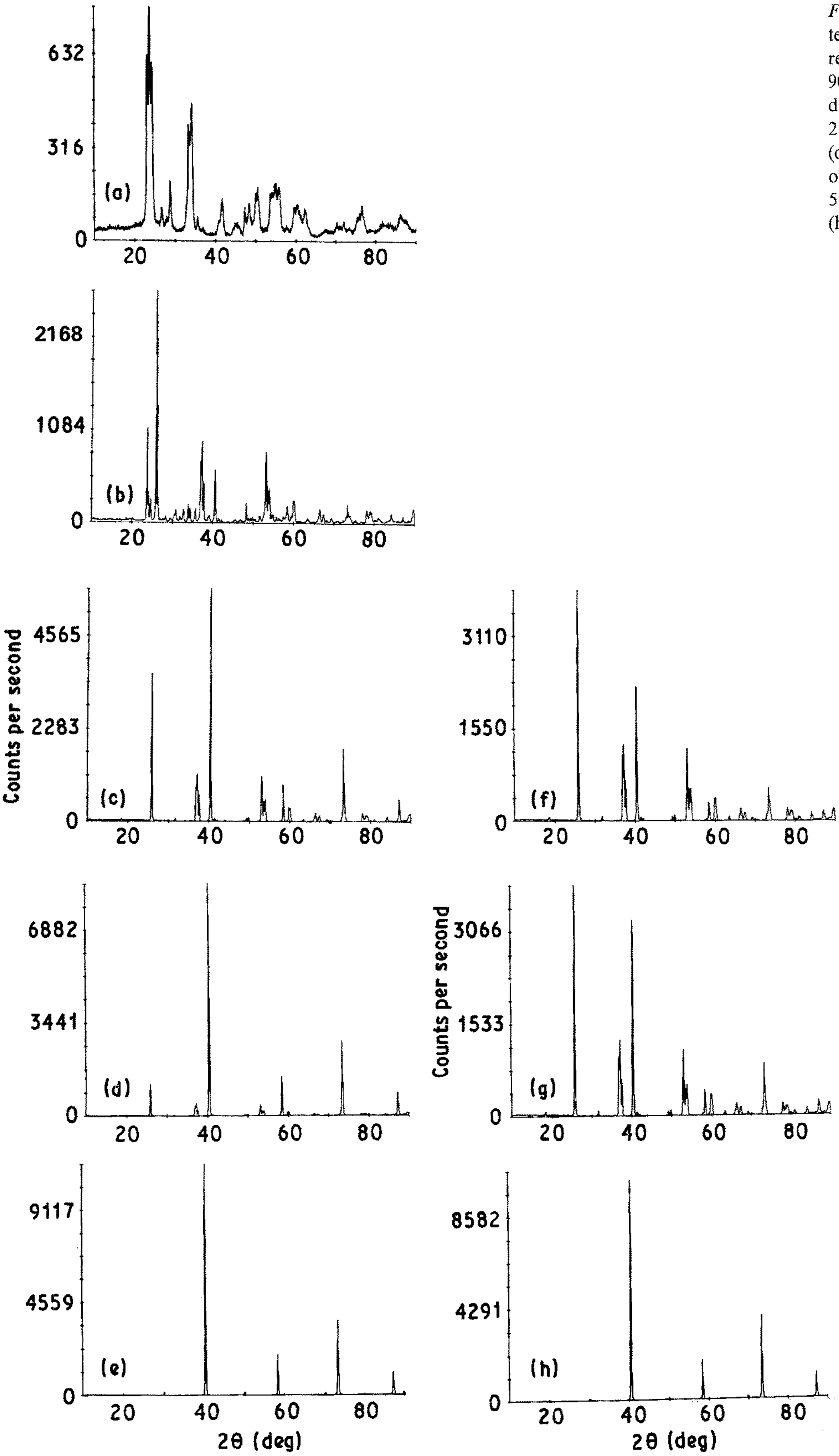

Figure 13 X-ray diffraction patterns from doped blue oxide reduced for various times at 900° C in flowing hydrogen. (a) doped oxide, (b) doped oxide, 2.5 min, (c) doped oxide, 5 min, (d) doped oxide, 7 min, (e) doped oxide, 15 min, (f) undoped oxide, 5 min, (g) undoped oxide, 7 min, (h) undoped oxide, 15 min.

Haubner, *et al.* [7]. Transport occurs via $WO_2(OH)_2$, the most volatile compound in the tungsten–oxygen–hydrogen system [7, 9]. Since the arriving tungsten grows around the freshly nucleated tungsten, the potassium is trapped inside the growing crystal. If there is more than one clump of potassium present, the growing crystal will encompass more than one pocket of potassium, as has been observed in the sectioned crystals. The oxide nearest the growing crystal supplies the tungsten first, accounting for the presence of the crystals in pockets in the oxide (WO_2). The early formation of tungsten crystals is not seen for the undoped oxide at least to 45 min at 750° C, for example. Without nucleating sites, that is, the clumps of dopant, nucleation occurs later and in a more uniform manner in the undoped oxide. The tungsten crystals are, therefore, smaller and more uniform in size in the undoped powder compared with the doped powder. Similar effects have been seen by Haubner *et al.* when phosphorus is added to the blue oxide [10].

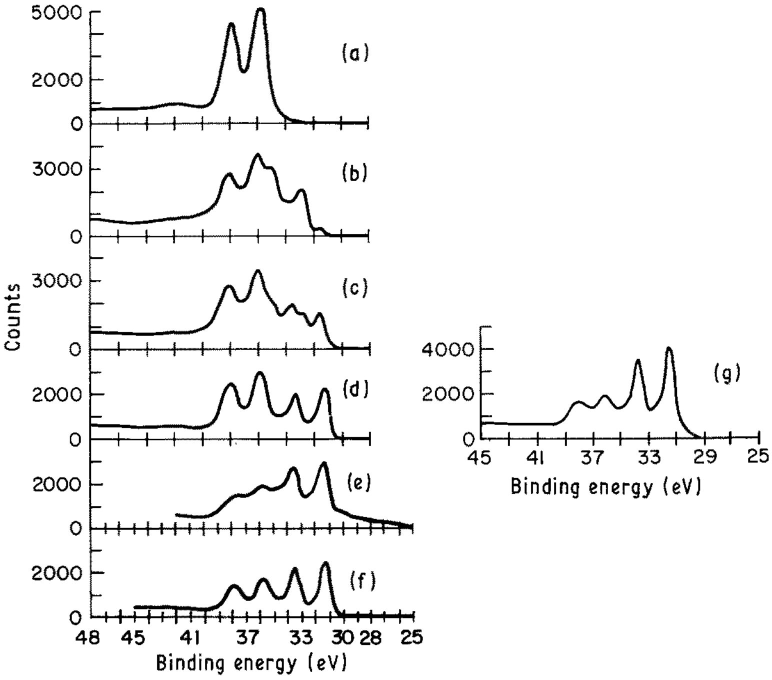

Figure 14 XPS spectra for doped and undoped samples heated at 900° C. (a) doped blue oxide, (b) doped 2.5 min, (c) doped 7 min, (d) doped 15 min, (e) doped 30 min, (f) production powder acid washed, (g) undoped blue oxide 15 min.

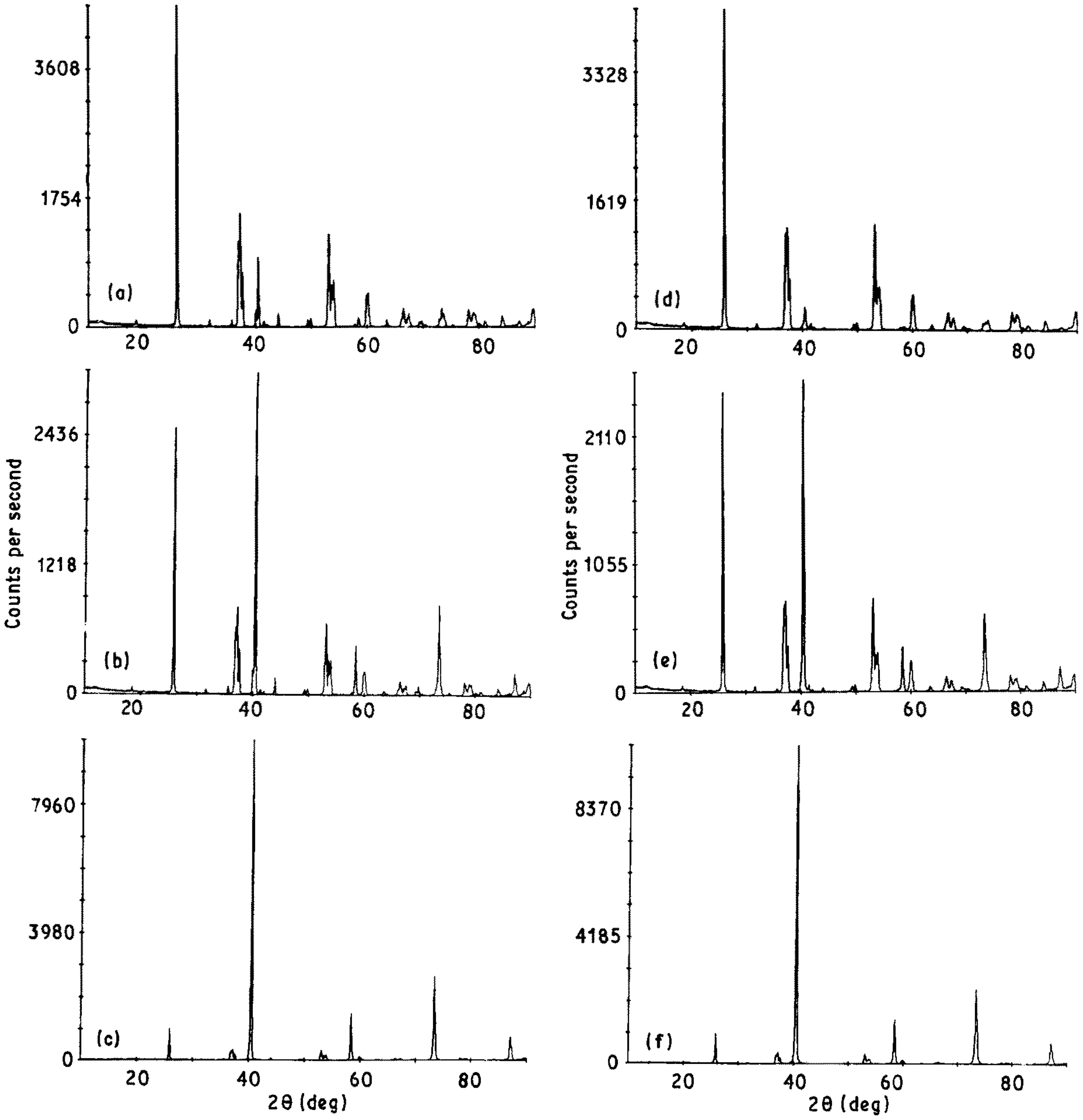

Figure 15 XRD patterns for doped and undoped samples heated at 750° C. (a) doped, 15 min, (b) doped, 22 min, (c) doped, 45 min, (d) undoped, 15 min, (e) undoped, 22 min, (f) undoped, 45 min.

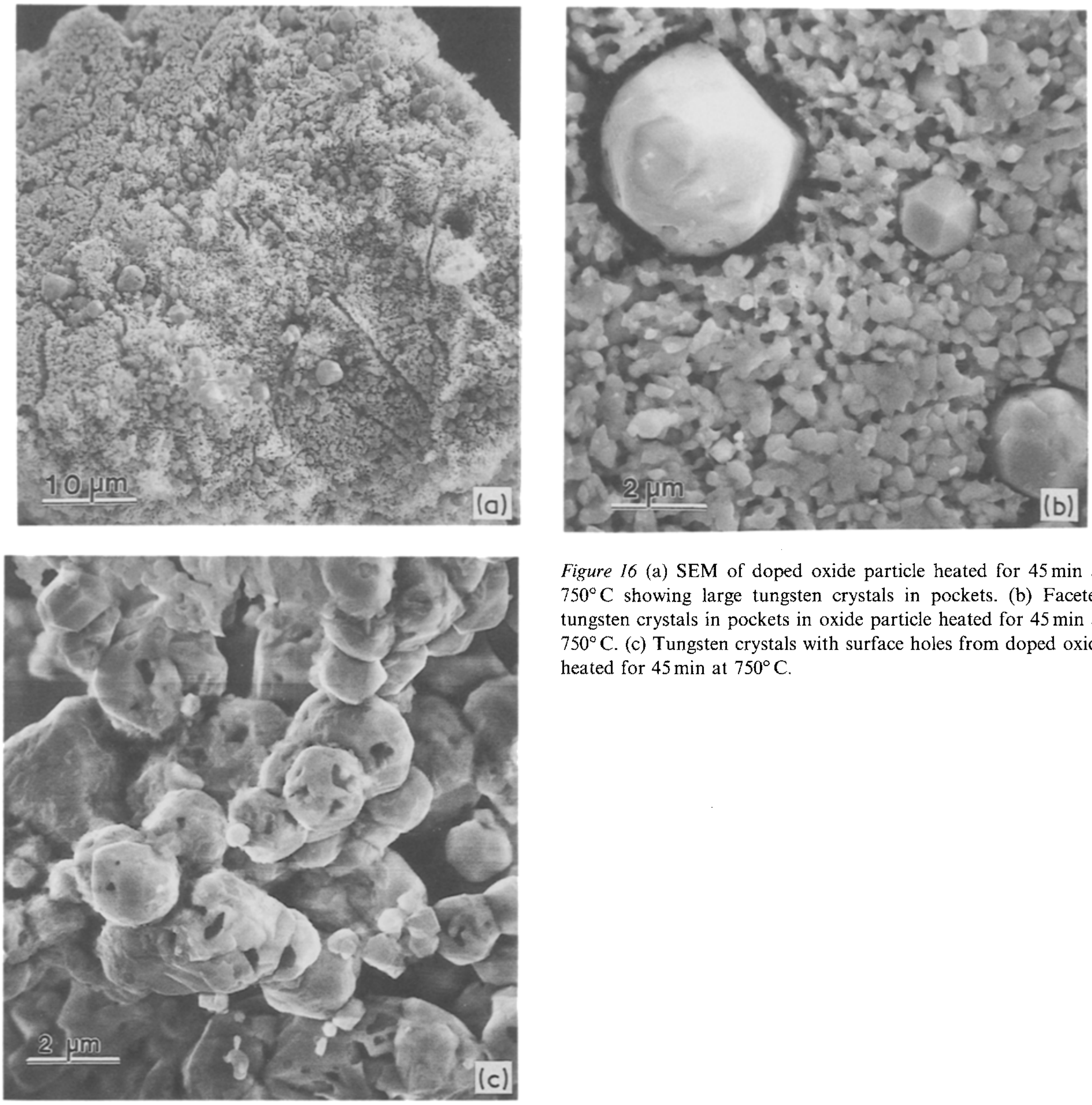

Figure 16 (a) SEM of doped oxide particle heated for 45 min at 750° C showing large tungsten crystals in pockets. (b) Faceted tungsten crystals in pockets in oxide particle heated for 45 min at 750° C. (c) Tungsten crystals with surface holes from doped oxide heated for 45 min at 750° C.

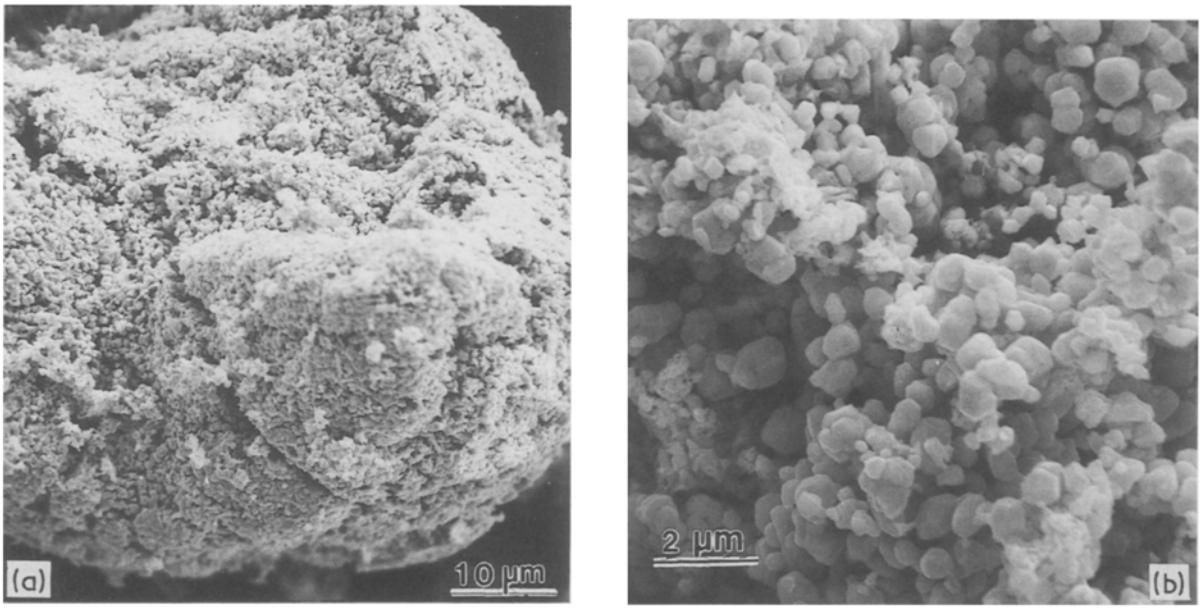

Figure 17 (a) Undoped oxide heated for 45 min at 750° C. (b) Small tungsten crystals in undoped sample heated for 45 min at 750° C.

One of the most consistent and identifiable differences between doped and undoped powder is the difference in faceting characteristics. Faceting may be related to the ratio H_2O/H_2, which changes during the reduction of the oxide. Tungsten crystals formed earlier in the reduction (those associated with patches of dopant) will see a higher H_2O/H_2 ratio than will the crystals nucleated and growing later in the process, i.e., those crystals that nucleate without the assistance of the dopant. The atmosphere would certainly be expected to affect the facet morphology.

An additional role of the dopant, potassium, may be to assist in the vapour transport of the tungsten, as suggested by the following experiment. A cylindrical crucible of CVD tungsten, formed from tungsten hexachloride, sealed on one end, was heated for 60 h at 1800° C in hydrogen to remove all traces of oxide. A piece of potassium, weighing 4 mg, was then placed in the crucible, and a piece of tungsten screen was wedged in the crucible to hold the potassium in place. The crucible was then sealed by electron beam-welding a cap on the open end. The pressure of air in the crucible was about 1×10^{-5} torr. After sealing, the crucible was again heated for 60 h at 1800° C in hydrogen. Upon removing the screen from the crucible, it was discovered that tungsten had been transported from the interior of the crucible to the screen and had nucleated and grown tungsten crystals on the surface of the wire, as is seen in Fig. 18. Notice the faceted appearance of these crystals and the absence of holes on the surface. The formation of surface holes in reduced doped powder could be explained by K-assisted vapour phase transport of tungsten; potassium inside the tungsten crystals could work its way to the surface by the same mechanism that caused the growth of tungsten crystals on the screen in the crucible.

The presence of potassium vapour during reduction is also indicated by the XPS measurements, which show an increasing concentration of potassium on the surface of the powder with increasing reduction time; these results are consistent with a flux of potassium, in some form, through the sample during reduction. However, this potassium-containing vapour appears to have no effect upon the morphology of the tungsten crystals, since we find crystals with well developed facets and no holes (in powders from doped oxides) that have the appearance of never having been doped. In fact, if doped and undoped powders are mixed and reduced at 900° C for 45 min, the two powders may be readily identified in SEM in terms of the presence or absence of surface holes and the facet morphology. Thus, potassium deposited on the surface of the tungsten crystals is not sufficient to produce the pockets in the interior of the crystals required for control of grain morphology in the wire.

A more detailed model of how doping occurs on WO_3 has been proposed by L. V. McCarty* which may shed more light on the XPS potassium results. He suggested that the combination of silicate and aluminium chloride forms a gel which binds the potassium in place on the surface of the blue oxide. On heating in hydrogen, the gel breaks down (while tungsten crystals are nucleating at dopant patches) allowing the potassium not already entrapped in the tungsten crystals to be transported throughout the powder and to settle on the surfaces of the suboxide or tungsten metal particles. This may account for the increase in XPS potassium signal as reduction proceeds.

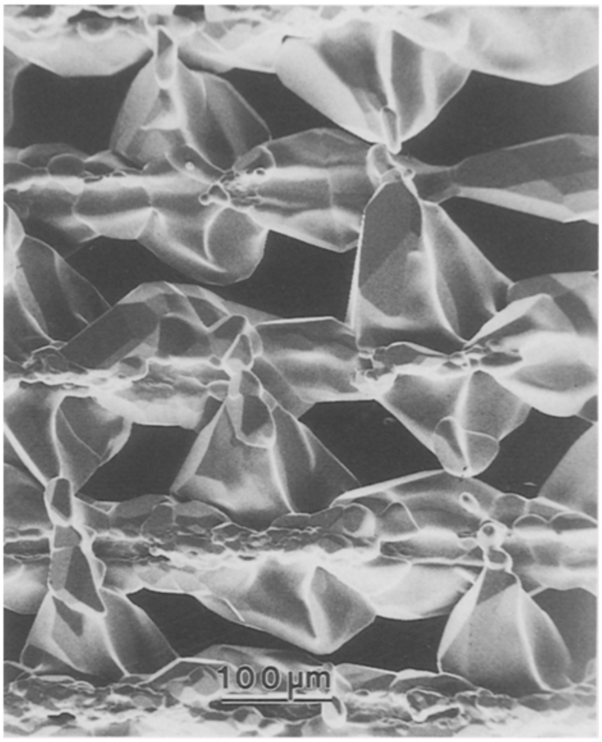

Figure 18 SEM of screen from crucible with 4 mg potassium heated for 60 h at 1800° C.

5. Summary and conclusions

Blue tungsten oxide (WO_3) both undoped and doped with aluminium, silicon, and potassium were heated in flowing hydrogen at 900 and 750° C for various times. The powders were examined by scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, Auger electron spectroscopy, and energy dispersive X-ray analysis. It was determined that the doped oxide was reduced to tungsten at a faster rate than was the undoped oxide. The doped tungsten crystals also contained pockets of potassium. Holes developed on the surface of the doped crystals some time after their formation. Neither holes nor pockets of potassium were found in the undoped tungsten crystals, even when exposed to potassium vapour along with the doped powder during the reduction process.

The dopant-containing potassium was present in discrete clumps on the surface of the doped blue oxide, and early nucleation of tungsten crystals took place at these clumps. Growth of the tungsten crystals then occurred by vapour transport from the oxide. In this way, the potassium was trapped in pockets in the interior of the crystals. Other results indicate that

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*Conversations with L. V. McCarty, formerly of the Chemical and Metallurgical Products Department of the General Electric Co., Cleveland, Ohio.

potassium may assist in the transport of tungsten which could explain the later formation of holes at the surface of the tungsten crystals.

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