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Note

THE EFFECT OF THE AMMONIUM PARATUNGSTATE SOURCE ON THE TUNGSTEN CRYSTALLITE SIZE

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Previous work by the authors [1] has shown that ammonium paratungstate (APT) can be directly reduced to tungsten with particle sizes large enough to allow use in cobalt-bonded tungsten carbide. APT decomposes to form $WO_{2.95}$ by 500°C. From 500°C to approximately 1230°C the following reduction sequence is followed

$$WO_{2.95} \rightarrow WO_{2.72} \rightarrow WO_2 \rightarrow W$$

The tungsten crystallite size was seen to increase with faster heating rates, larger sample sizes (i.e. bed thickness) and slower hydrogen flows over the sample. This appeared to be the result of retarding the nucleation of tungsten nuclei by controlling the rate at which reaction products are removed from the reaction site. This was shown when the tungsten crystallite size increased with an increase in the temperature range of the reduction reaction. Consequently, a smaller number of nuclei grew to a larger size. In that study a single source of APT was used. This work investigated two other sources of APT and compared the results with those originally found.

The three APT sources were chosen because they represented a range of densities, sodium levels and crystal morphologies. In each case these powders were processed at the optimized conditions developed in the previous study [1]. These APT sources are shown in Table 1. The bulk density differences can be explained by examining the particle size analysis of the powders. Sample No. 1 had the broadest distribution conforming most closely to the Andreasen limits for optimum packing. As a result, this sample had the highest bulk density. The other samples had increasingly narrow distributions. X-ray diffraction indicated that the principal phase present in all samples was ammonium paratungstate pentahydrate $5\,(NH_4)_2 \cdot 0.12\,WO_3 \cdot 5\,H_2O$, with a secondary phase of ammonium tungstate hydrate $(NH_4)_2WO_4 \cdot n\,H_2O$. Scanning electron microscopy showed differences between the powders. Samples 1 and 2, produced by the same manufacturer, appeared rounded and cracked. Sample 3 had well formed crystal faces and very few cracks.

A heating rate of 10°C min^{-1} was used for the heat treatment of the three powders. Three thousand mg samples were heated in covered 16 mm alumina crucibles [1]. These conditions enabled the tungstates to be heated to the highest temperatures before reaction completion.

TABLE 1

APT powder characterization data

Supplier	Density ($g\ cm^{-3}$)	Sodium content * (ppm)	Silicon content ** (ppm)
APT powder No. 1 G.T E. Sylvania, Towanda, Pa.	2.83	7	30
APT powder No. 2 G.T.E. Sylvania, Towanda, Pa.	2.48	25	10
APT powder No. 3 Union Carbide	2.03	2.4	10

* Atomic absorption

** Spectrographic analysis.

Table 2 lists the average particle size for each sample. Sample No. 3 is seen to have the largest crystallite size, with sample No. 1 just slightly smaller.

A low sample density (i.e. No. 3) could serve to assist the flow of reaction products away from the reaction site through the more open structure. This would result in a lower final reaction completion temperature and a smaller particle size. Conversely, the denser sample (i.e. No. 1) would tend to restrict flow, raise the completion temperature of the final reduction reaction, and as a result increase the particle size.

Thermal analysis of each of the three powders showed no significant differences in the temperature range of the final reduction reaction (Table 2). The total weight loss for each of the three samples was essentially the same; therefore, the bulk density differences were ruled out as a cause for the particle size differences. In addition, the size variations are not consistent with the density variations.

The previous work [1] had shown that the low temperature decomposition of the APT destroys the original morphology of the powder; therefore, the differences in original powder morphology cannot be a factor in the size differences.

The remaining difference in the powders is in their chemical composition.

TABLE 2

APT reduction data

	Total wt. loss in hydrogen * (%)	Final reaction completion temp. (°C)	Tungsten crystallite size (μm)
APT powder No. 1	29.01	1230	2.0
APT powder No. 2	28.83	1230	1.9
APT powder No. 3	28.81	1230	2.2

* TG data for samples heated at 10°C min^{-1} in 10 l h^{-1} hydrogen in alumina crucibles with covers. Sample size = 3000 mg.

Sample No. 1 has a high silicon content and sample No. 2 has a high sodium content. Lardner [2] and Peters [3] have suggested that the sodium level must be monitored because of its substantial effect on reducing the tungsten size. These results support this hypothesis, with sample No. 2 having the highest sodium level and the smallest particle size. Sample No. 3 had the lowest sodium level and yielded the largest particles. It appears that sodium serves as a nucleating agent; therefore, the greater the sodium content the greater the number of tungsten nuclei and the smaller the average particle size.

REFERENCES

1 J.G. Lake and W.R. Ott, Thermochim. Acta, 32 (1979) 225.
2 E. Lardner, Powder Metall , 13 (1970) 26.
3 R. Peters, personal communication, 1976.