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Tungsten powder from carbon coated WO_3 precursors

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This paper deals with the formation of tungsten powder from carbon coated tungstic oxide precursors. This study makes use of differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and X-ray diffraction (XRD). TGA data allowed for calculation of the activation energy as 626 ± 18.2 kJ/mol. XRD characterized the products resulting from the reaction of the carbon coated WO_3 for each isotherm. These diffraction patterns support the hypothesis that reduction to W proceeds through the formation of lower oxidation states. This is the first isolation of a metal powder using the carbon coated precursor process. © *2001 Kluwer Academic Publishers*

1. Background

Tungsten (W) has a wide variety of applications due to its impressive properties: high melting temperature, high electrical conductivity, and high temperature strength. W has therefore found applications as filaments, electrical contacts, refractory applications, and cutting tools [1–4]. Investigation into use of tungsten heavy alloys (WHAs) for armor penetration applications [5].

The most commonly applied method for producing quality W powder is reduction of the oxide in hydrogen. Carbothermal reduction of tungstic oxide (WO_3) has long been recognized as the inferior of hydrogen reduction for tungsten powder production, due to its higher temperature requirement and the resulting impure powders. The higher temperature generally produces large particles, while impurities from carbothermal reduction generally result, due to an impure carbon source [1–4]. For tungsten powder production, the formation of carbides is also possible. Carbothermal reduction does have the advantages of faster time to complete the reaction and lower risk due to the absence of H_2 gas.

For several years, the carbon coated oxide precursor method developed by Koc *et al.* for silicon carbide production has been adapted for making powders of nitrides, borides, and other carbides [6–11]. In all cases, use of the coated precursor for production of the given ceramic powder has resulted in a product superior in all ways to its mixed analog. The powders meet all the requirements for sintering ceramic powders: fine size, non-agglomerated, spherical, pure and single phase, and of narrow size distribution. In addition, carbothermal reduction is generally the least expensive method, when applicable, for producing powders, due to the low cost of precursors. The precursor method reduces cost and time by allowing reactions to complete in shorter times at lower temperatures, with no need for milling the as-produced powders.

The precursor method has the advantage of using a pure carbon source for carbothermal reduction. A hydrocarbon gas is pyrolyzed in a reaction vessel into which has been loaded the oxide powder to be coated. The cracking of the gas frees carbon, which is attracted to the surface of the powder, coating the particles in a uniform manner. This coating provides intimate contact between the reactants, unattainable by any standard mixture. This intimate contact allows reduction to proceed near the theoretical reaction temperature. In conventional mixtures, which possess intermittent contact at best, reaction near the theoretical temperatures is very unlikely. Using a hydrocarbon gas for the carbon source ensures no impurities as would result with conventional mixing of carbon black [6–11].

Kodambaka *et al.* performed the initial research into use of carbon coated WO_3 precursors while investigating enhanced production of tungsten carbide [10]. It was noted that tungsten was formed during the process, in agreement with previous well-established work [2–4]. It was decided to investigate this formation, as no previous work has been performed on the isolation of a metal by the precursor method.

The methods employed in this research were Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and X-ray Diffraction (XRD). The activation energy of the W formation reaction was calculated from the TGA data for the coated precursor.

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DSC data for the formation of W from the coated precursor, and WC from both coated and mixed samples illustrated the reaction onset temperatures. The products resulting from the TGA experiments were characterized using XRD.

2. Experimental procedure

The WO_3 used for this research was yellow tungsten trioxide powder (Starck, Germany), shown in Fig. 1, with specific surface area 5 m^2/g. Propylene gas, C_3H_6, was the source of carbon for the coated precursor.

The coated precursor was prepared by cracking C_3H_6 gas at 550°C, with pyrolytic carbon coating the WO_3. As this process has been proven to be surface area activated, each oxide particle was coated by a like amount of porous amorphous carbon (Fig. 2). Cracking was continued until the WO_3 had been coated to 13.2 wt% C.

The overall carbothermal reduction reaction to be studied for formation of tungsten was:

$$WO_3 + 3C \rightarrow W + 3CO(g) \qquad (1)$$

Thermodynamically, this reaction occurs between 600°C and 700°C, while actual processing sees completion above 1050°C. Reaction (1) is known to proceed via the successive formation of lower oxides of tungsten. These oxides include WO_2, W_5O_{14}, $W_{18}O_{49}$, $W_{20}O_{58}$, and $W_{24}O_{68}$. The formation of the carbides WC, W_2C, and W_3C, is also possible, depending upon the carbon content used [2–3].

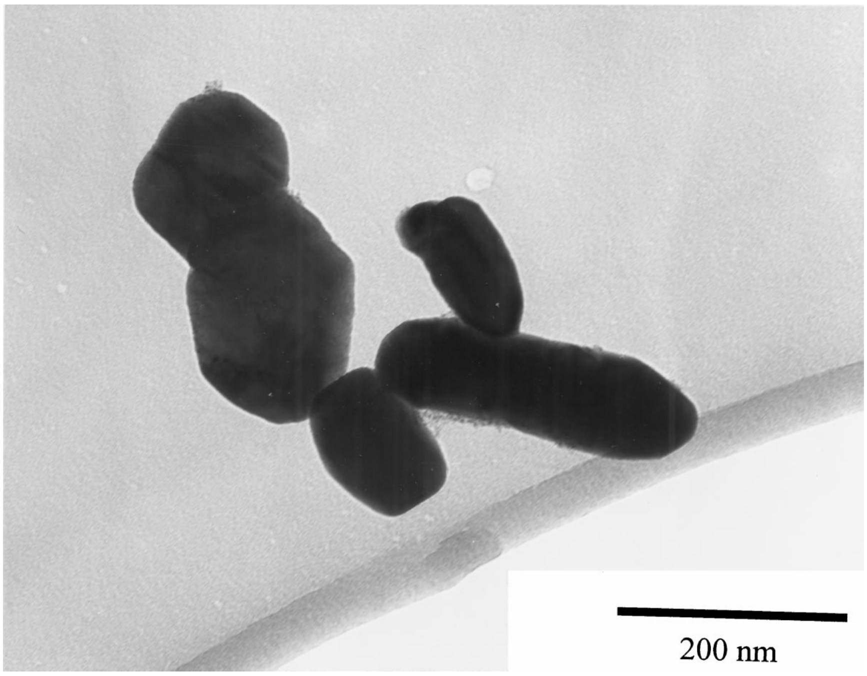

Figure 1 TEM of Starck WO_3 powder.

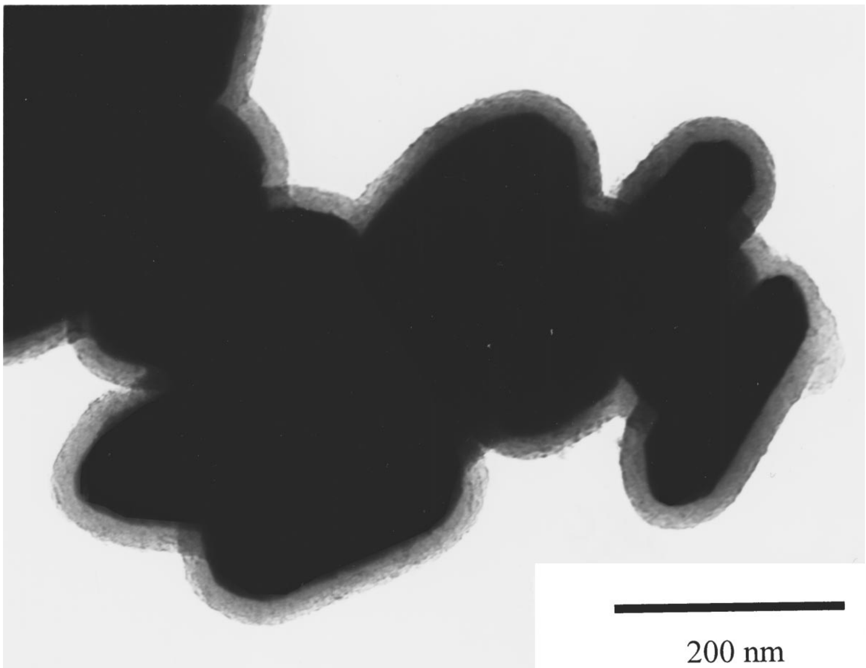

Figure 2 TEM of carbon coated WO_3 precursor.

Reaction (1) requires 13.451 wt% C for stoichiometric W formation, while a lower content is recommended to inhibit carbide formation, thus the lower content used for this investigation. The theoretical weight loss for complete reduction to W is 31.37%.

DSC reactions used samples of ∼35–40 mg powder. The samples were heated in a Pt crucible at 20°C/min to 1500°C in flowing argon in a Setaram Labsys TG-DTA/DSC (Setaram Corp., Caluire, France).

TGA was performed in the Labsys using a Pt crucible heating at 20°C/min in flowing argon to isotherms of 700–1400°C, inclusive. Each isotherm was performed at least twice to ensure consistent results. The weight loss data obtained from the TGA experiments was used to find the fraction converted (fraction converted = % wt lost/theoretical % wt loss). The fraction converted data was used to calculate the activation energy according to the Arrhenius relation.

XRD was performed on the products of each TGA isotherm (Model DMAX-B, Rigaku, Tokyo, Japan) using Cu K_α($\lambda = 0.1542$ nm) radiation and a scan rate of 2°/min. The following oxides were searched for in the XRD patterns: WO_3 (Card #20-1323), WO_2 (32-1393), W_5O_{14} (41-0745), $W_{24}O_{68}$ (36-0103), $W_{20}O_{58}$ (05-0386), and $W_{18}O_{49}$ (36-0101, 05-0392). Also checked were: W (04-0806), WC (25-1047), W_2C (20-1315), and W_3C (42-0853), as well as a few non-stoichiometric compounds (20-1316, 20-1314). Several peaks are of unknown composition, which may indicate the presence of some Magneli phases [12].

3. Results and discussion

3.1. DSC and TGA

The DSC pattern for W formation is given in Fig. 3. The pattern demonstrates that reaction occurred between 950°C and 1100°C. This result was supported by the fraction converted data of Fig. 4, which shows nearly complete conversion at 1000°C. As discussed later, however, the completion of the reaction does not occur until higher temperature.

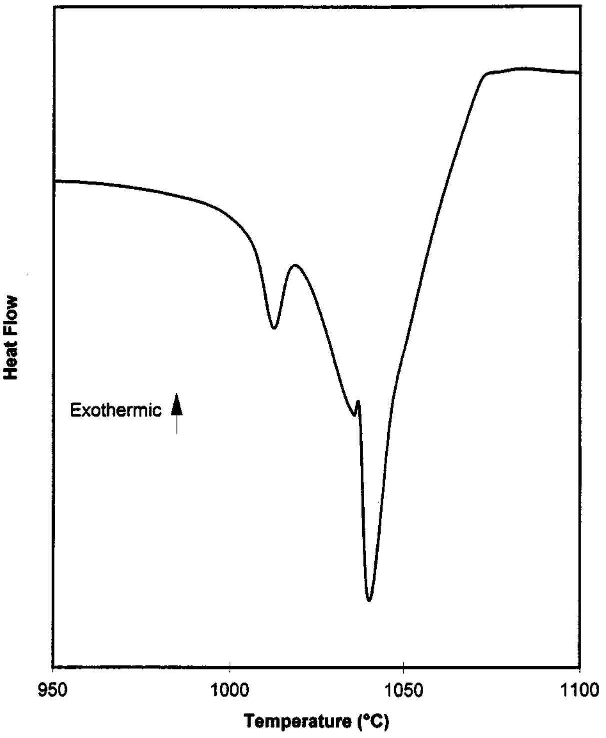

Figure 3 DSC pattern for W formation.

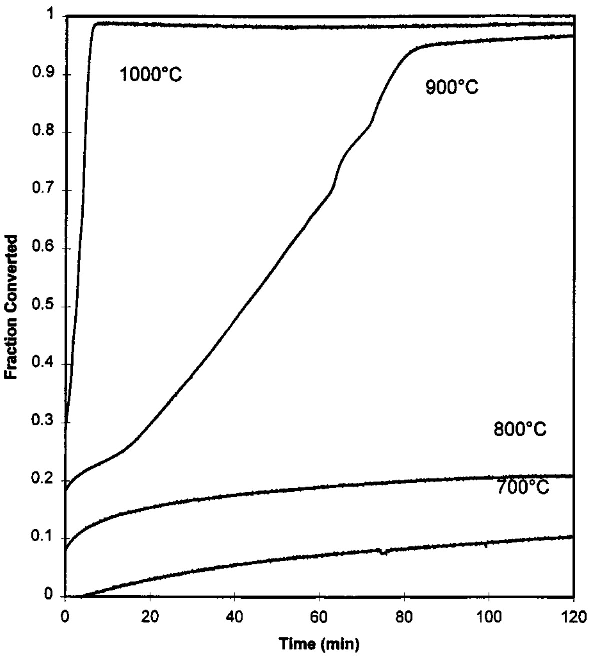

Figure 4 Fraction converted vs. time for W formation.

3.2. XRD

The diffraction patterns for W formation are shown in Figs 5 and 6. The 700°C and 800°C XRD patterns both have an extremely high number of peaks, all corresponding to various oxides of tungsten, with the barest beginnings of W peaks formation being noted.

There is a notable difference between the 800°C and 900°C patterns. The tungsten peaks have increased in intensity, while the number of and relative intensity of

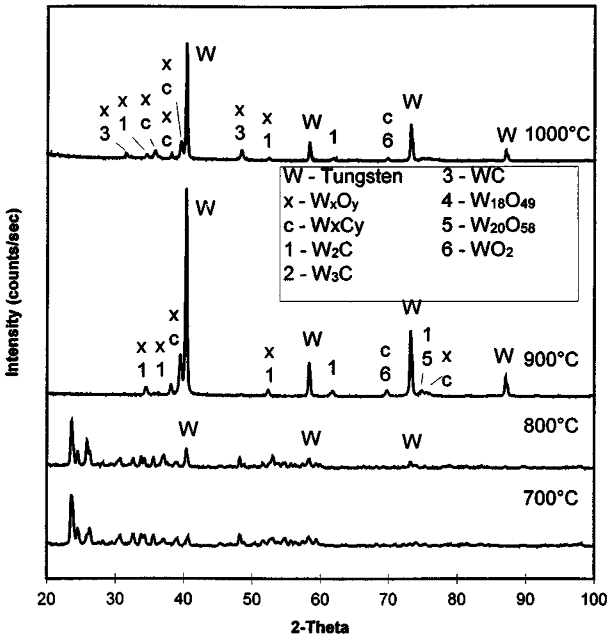

Figure 5 XRD patterns of TGA isotherm products, 700–1000°C.

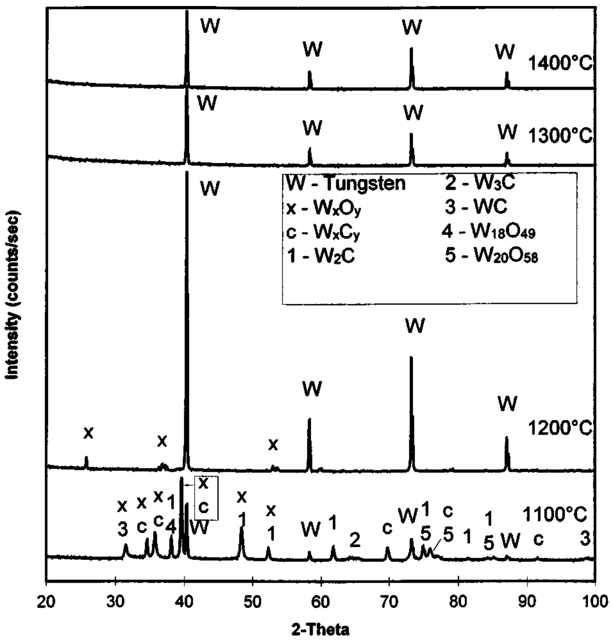

Figure 6 XRD patterns of TGA isotherm products, 1100–1400°C.

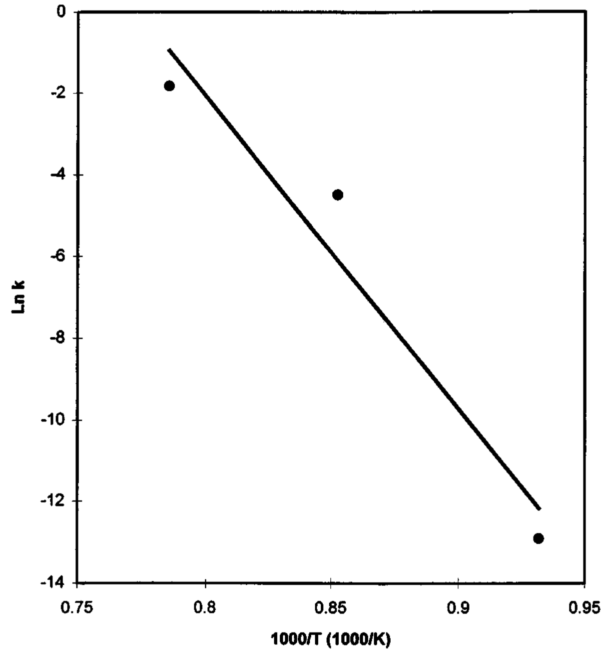

Figure 7 Ln *k* vs. 1000/T for W formation.

the various oxide peaks have decreased. Also, several peaks matching carbides are present.

The 1000°C pattern shows a few reemerging oxide/carbide peaks, with W still the most prevalent compound. The new peaks in the 1000°C pattern are sharper in the 1100°C pattern. W is just one compound among many, with no clear dominance. Carbide formation was occurring at the expense of further reduction of the oxides. As W formation was not complete by 1100°C, as had been expected, further experiments were performed up to 1400°C.

The 1200°C pattern shows the dominance of W in the resulting powder. Only vestiges of tungsten oxides remain. This pattern had the greatest peak intensity of all the products so analyzed. The 1300°C and 1400°C patterns both show only W presence. All other compounds have been eliminated. It is noted that the intensity of the peaks has diminished from that of the 1200°C pattern, indicative of grain growth due to the higher temperature (similar to that noted during TGA investigation of TiC formation [13]).

3.3. Activation energy

The fraction converted data was used to calculate the activation energy. The slopes of the fraction converted plots were used to find the value for ln k, which was then plotted versus 1000/T, shown in Fig. 7. Using $R = 8.314$ J/mol K, the value for E was calculated as 626 ± 18.2 kJ/mol. The 700°C data point was omitted from the linear fit to obtain this value. The linear fit had $R^2 = 0.9419$, indicating a relatively good approximation of the data.

4. Conclusion

Combining the use of TGA, DSC, and XRD, the formation of W by carbothermal reduction of carbon coated WO_3 clearly proceeds through the formation of lower oxides of tungsten. From XRD, the W reaction is essentially completed at 1200°C, with higher temperatures providing the final purification. The activation energy for the formation of W using the carbon coated precursor was calculated as 626 ± 18.2 kJ/mol. Further work is needed to reproduce these results on a large scale. This will allow determination of the properties of the produced powder, such as particle size and shape, and chemical content.

Acknowledgments

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