Formation of WC powders using carbon coated precursors

G. A. SWIFT*, R. KOC‡
*Department of Mechanical Engineering and Energy Processes, Southern Illinois University,
Carbondale, IL 62901-6603, USA*
E-mail: rkoc@mse.ufl.edu

This paper deals with the formation of tungsten carbide from carbon coated tungstic oxide precursors. This study makes use of differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and transmission electron microscopy (TEM). DSC and TGA data for both coated and mixed 17.2 wt% carbon containing tungstic oxide demonstrate the superiority of the coated precursor in the formation of tungsten carbide, as conversion is initiated at lower temperature. XRD patterns of products from each 100°C isotherm from 900–1400°C, inclusive, illustrate the formation as it proceeds through lower oxides into tungsten then carburizes into tungsten carbide for both the mixed and coated samples. © *2000 Kluwer Academic Publishers*

1. Introduction

Carbides typically have the advantages of high values for melting temperature, strength, wear resistance, and low thermal expansion coefficient. While many ceramic materials also benefit from a low mass density, extremely high values for these properties often outweigh any detriment, such as high weight. Among these is tungsten carbide (WC) [1].

WC combines many desirable properties. WC has high hardness, high melting temperature, high fracture toughness, high thermal conductivity, and low thermal expansion coefficient. WC is therefore used for many applications. As a cemented carbide (a combination of a carbide with a metallic binder; in the case of WC, cobalt is the typical binder), WC is used in cutting tools, saw blade tips, cement drills, and many other high wear applications [1–3]. WC is also used in the manufacture of high temperature furnace crucibles and other components. Newer applications include use in catalysis industries and aerospace coatings [4–6].

Most ceramic parts are produced by sintering powders. Sintering is a process by which the powders are raised to a temperature sufficient to cause mass transfer and densification. WC is typically sintered with Co, to produce the cemented carbide.

WC production generally proceeds as a two-step process. First, the oxide is reduced to high purity tungsten in a hydrogen atmosphere. The tungsten metal is then mixed with carbon and reacted at temperatures of 1400–1600°C to produce the carbide [2]. This process requires both high temperature and a long time to complete, so WC produced through this method generally has large particles and agglomeration, thus requiring milling. Additionally, the use of carbon black introduces impurities into the product [7].

Kodambaka performed the initial research into use of carbon coated precursors for enhanced production of tungsten carbide. Kodambaka succeeded in synthesizing high quality, submicron WC powders at temperatures as low as 1100°C [7]. As neither DSC nor TGA experiments had been performed to illustrate the differences between the two methods, this research was undertaken. The TGA and DSC experiments in this work made use of very small sample sizes and fast heating and cooling rates, while Kodambaka used large sample sizes and very slow heating and cooling rates.

The benefit of using coated precursors results from the intimate contact achieved between reactants, while conventionally mixed powders possess intermittent contact at best, regardless of the mixing time used. Thermodynamic data does not account for contact between reactants, while poor contact can prevent reactions from occurring at their ideal thermodynamic temperatures. The intimate contact achieved using coated precursors allows the best possibility for a reaction to proceed as per thermodynamic considerations. Additionally, as the carbon source for the coating is a hydrocarbon gas, there is no risk of impurities as with conventional mixing of carbon black. These factors contribute to the superiority of the precursor method, as better quality powders are produced at lower temperatures and shorter times than conventional methods [8–11].

The methods employed in this research were thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). DSC data for the reactions of both coated and mixed samples

* *Present Address*: California Institute of Technology, Department of Materials Science, Pasadena, CA 91125, USA.
‡ *Present Address*: University of Florida, Department of Materials Science and Engineering, Gainesville, FL 32611, USA.

illustrated the reaction onset temperatures. The products resulting from the TGA experiments were further characterized using XRD.

2. Experimental procedure
2.1. Precursor preparation

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, while carbon black (Monarch 880, Cabot, Waltham, MA) was used for the mixture.

The coated precursor was prepared by cracking C_3H_6 gas at 550°C, with pyrolytic carbon coating the WO_3.

Each oxide particle was coated by a like amount of porous amorphous carbon, as this process is surface area activated. Coating was continued until the WO_3 had been coated to 13.2 wt% C. The coated precursor is shown in Fig. 2. Mixing was performed using appropriate amounts of WO_3-C or WO_3 and carbon black for 60 minutes in a Spex Mixer/Mill (Model 8000, Spex, Metuchen, NJ). Following Kodambaka's recommendation, the precursor was prepared with less than the stoichiometric 17.165 wt% C, with carbon black being added to bring the total carbon content to 17.2 wt% C. The mixture was prepared with a like amount of carbon. The slight excess was intended to help alleviate the difficulties caused by poor reactant contact. The overall carbothermal reduction reaction to be studied was:
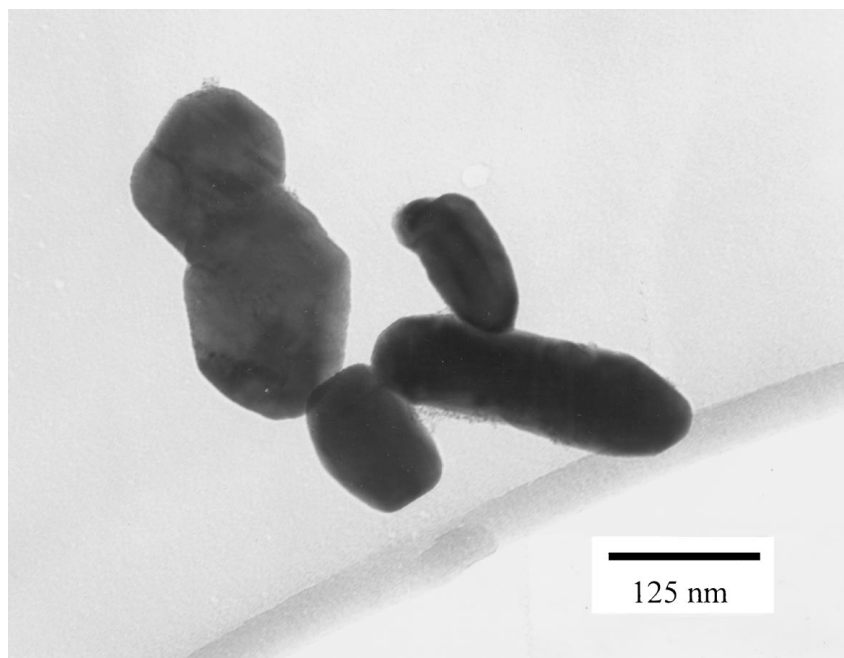

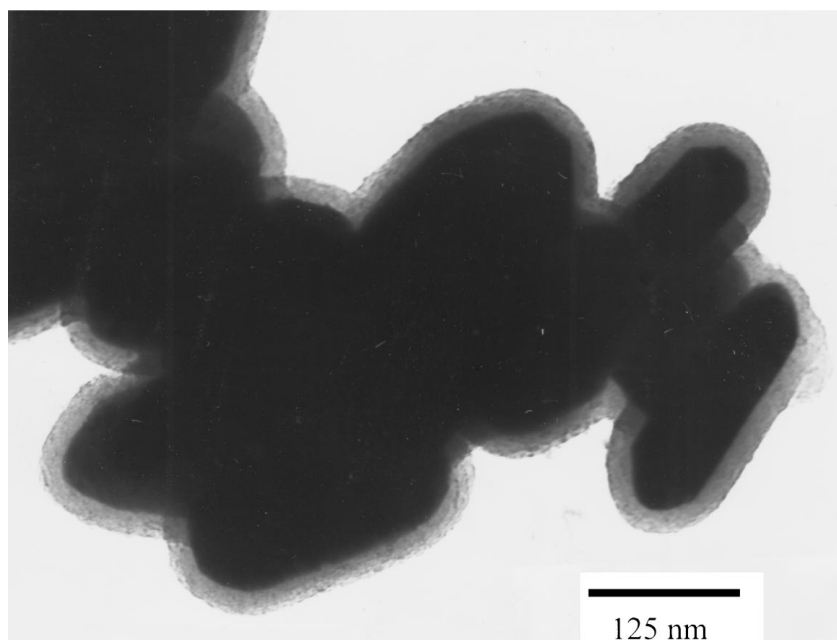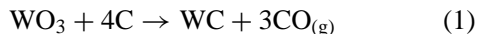
Figure 1 TEM of Starck yellow WO_3.

Figure 2 TEM of carbon coated WO_3.

$$WO_3 + 4C \rightarrow WC + 3CO_{(g)} \qquad (1)$$

Thermodynamically, reaction (1) occurs below 700°C, while actual processing sees the reaction completing above 1400°C. WC formation is known to proceed via the successive formation of lower oxides of W, eventually reducing into W, followed by carburization into WC. The oxides formed include WO_2, W_5O_{14}, $W_{18}O_{49}$, $W_{20}O_{58}$, $W_{24}O_{68}$ with possible formation of other carbides: W_2C and W_3C. The theoretical weight loss for this reaction is 30.02 wt%.

2.2. Experimentation

DSC reactions used samples of ~35 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 900–1400°C, inclusive. Each isotherm was performed at least twice to ensure consistent results. (Note: fraction converted = wt% loss/theoretical wt% loss.) Additionally, since large scale synthesis requires a slow heating rate, experiments were performed using a 4°C/min heating rate to observe the differences in weight loss between the precursor and the mixture. These slow rate tests used 35.0 mg of each sample; these tests were also repeated to ensure consistency.

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°C/min to determine major species present after reaction at the given temperature.

3. Results and discussion

3.1. DSC

Fig. 3 shows the DSC patterns for reaction of both the WO_3-C mixture and the coated/mixed WO_3 precursor. The patterns are markedly different. Similar to the contrasting patterns noted with DSC of TiC formation [11], the mixture experiences a second reaction which is absent in the coated/mixed precursor. The precursor pattern does complete its reactions first, but not at a significantly lower temperature; neither had reactions above 1100°C.

3.2. TGA

When TGA was performed, it was noted (Fig. 4) that conversion completes nearly instantaneously; there is negligible conversion at 800°C, nearly total conversion at 900°C, with 1000°C showing complete conversion for the coated/mixed precursor. For the mixture, shown in Fig. 5, there is significantly less conversion at 900°C than with the coated/mixed precursor, with the 1000°C conversion being comparable. This data show that the precursor is superior to the mixture in that a greater amount of conversion occurs at lower temperature.

The TGA curves from the slow heating rate experiments are given in Fig. 6. The reactions for each begin at nearly the same temperature, with the precursor completing very shortly before the mixture. The mixture
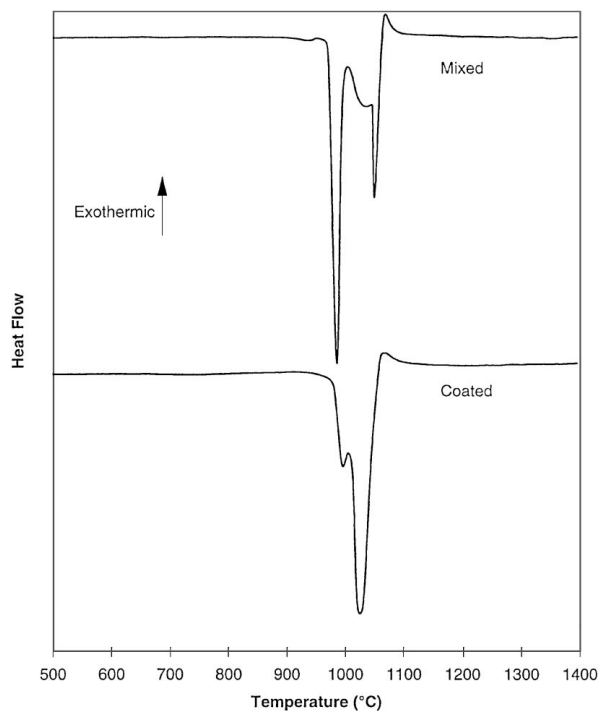

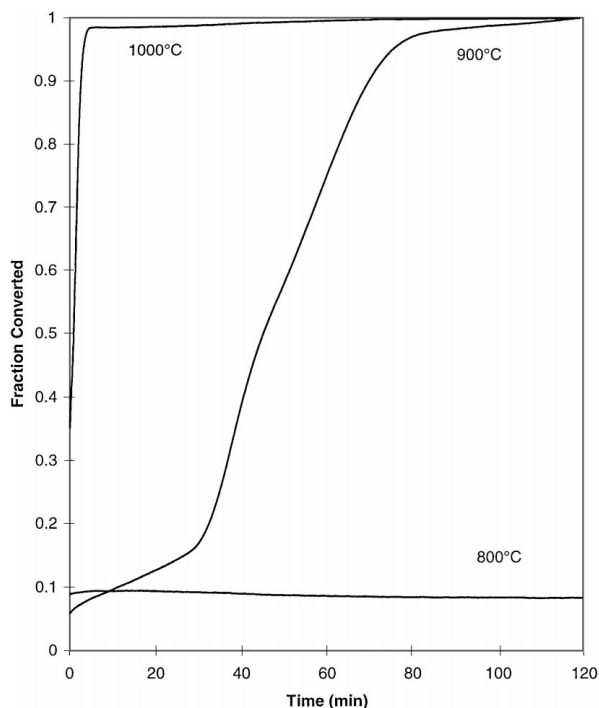*Figure 3* DSC Pattern for WC Formation.

Figure 4 Fraction converted as a function of time for coated WC formation.

does, however, experience a greater total weight loss, in addition to a greater weight loss earlier in the experiment, prior to the onset of the reaction. These greater losses are due to impurities within the carbon black. At a slow rate, there seems little difference between the two samples.

3.3. XRD

3.3.1. Coated/mixed precursor

Products resulting from isotherms from 900°C to 1400°C, inclusive, were analyzed, and are shown in Fig. 7. Even at 900°C, significant reduction of the oxide
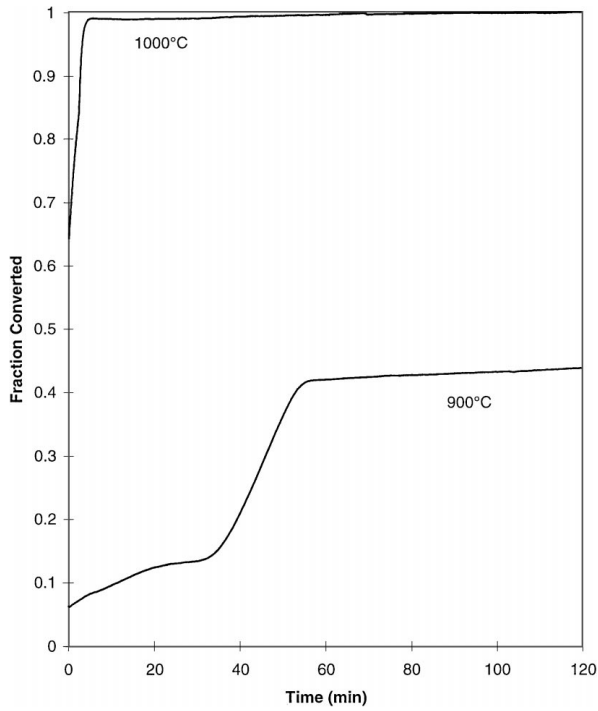
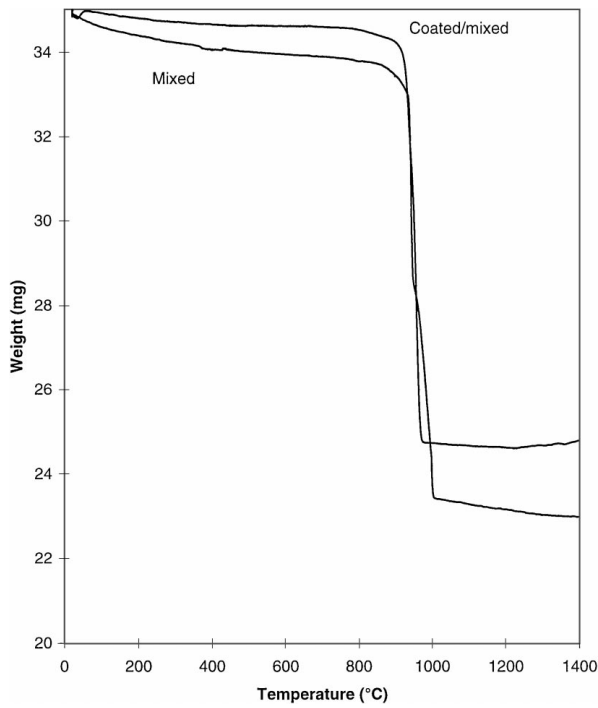*Figure 5* Fraction converted as a function of time for mixed WC formation.

Figure 6 Weight loss of samples using slow heating rate in flowing Ar.

Figure 7 XRD patterns for coated/mixed WC precursor reacted at various temperatures in flowing Ar for 2 hours.

that no presence was noted of other carbide phases, e.g. W_2C, unlike previous research by Kodambaka.

3.3.2. Mixture

Fig. 8 shows the diffraction patterns resulting from the mixed samples. At 900°C, no significant reduction has occurred, with nearly all the peaks being oxides and unlabelled. The 1000°C pattern, though, shows a marked difference from the 900°C pattern. It seems that all the

Figure 8 XRD patterns for mixed WO_3-C reacted at various temperatures in flowing Ar for 2 hours.

presence has occurred, with WC and W presence being the most notable constituents. The patterns for 1000–1200°C are all very similar, with W and WC being dominant. It is not until 1300°C that WC assumes the dominant role, as the W intensity has decreased relative to the WC intensity. Also at 1300°C, the higher degree 2-theta peaks for WC have sharpened and been labeled as such. At 1400°C, the W presence has been further reduced with WC the only other constituent. It was therefore deduced that slightly higher temperature would see a greater degree of completion of the carburization of the remaining W phase. It is important to note
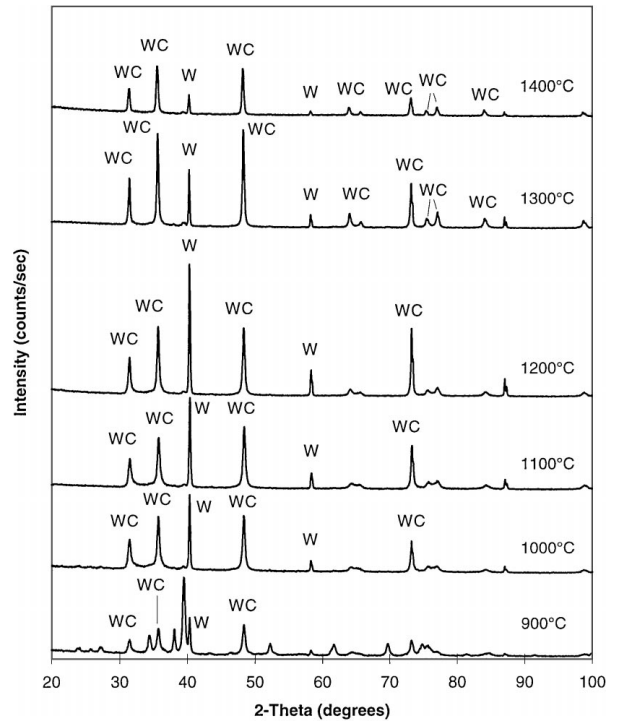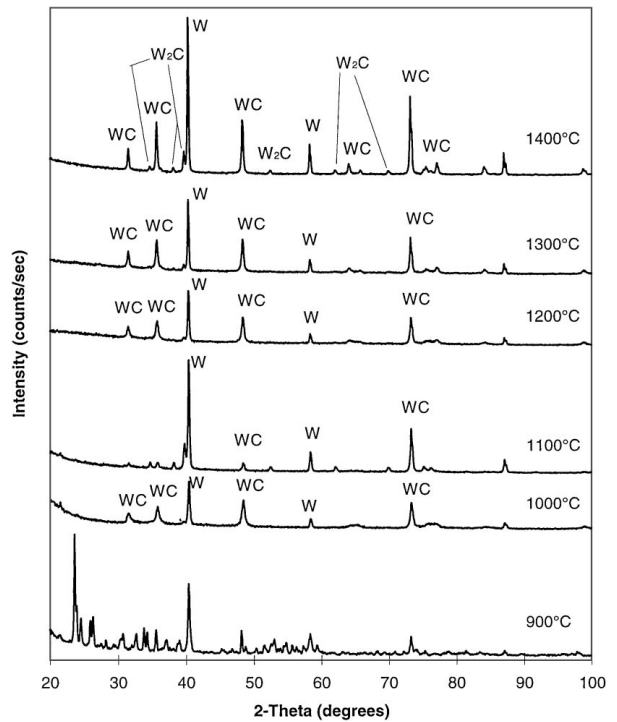
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oxide has already been reduced, with significant WC and W presence. At 1100°C, there was a marked decrease in the peak intensities of the WC relative to the W phase. At 1200°C and 1300°C, the W peak intensity has decreased so that the WC presence is once again clear. However, at 1400°C, there is still a greater presence of W than with the coated precursor, with the presence of W_2C being noted, unlike the coated precursor. These results indicate that a significantly higher temperature would be required to complete the carburization of W into WC. Also, the presence of another carbide phase differentiates this mixture from the coated precursor.

4. Conclusion

Combining the use of TGA, DSC, and XRD, the formation of WC by carbothermal reduction of carbon coated WO_3 clearly proceeds through reduction to W via the formation of lower oxides of tungsten, followed by carburization into WC. From XRD, the WC reaction completes above 1400°C, with higher temperatures providing the final purification into WC. DSC patterns of fully mixed WO_3-C and coated/mixed WO_3-C illustrated the faster reaction initiation and completion of the partially coated precursor. The fraction converted data also support this conclusion, even though the activation energy was not calculated. It is important to note that the work of Kodambaka, upon which this is based, produced high purity WC of submicron size. The differences noted here are the result of the different reaction conditions (heating/cooling rates, atmosphere, sample size), and the reaction system. Previous work has noted differences between the products resulting from large scale synthesis and that from this manner of work [11].

References

1. T. Y. KOSOLAPOVA, "Carbides: Properties, Production, and Applications" (Plenum Press, New York, 1971).
2. P. SCHWARTZKOPF and R. KIEFFER, "Refractory Hard Metals-Borides, Carbides, Nitrides, and Silicides" (The MacMillan Company, New York, 1953).
3. G. D. RIECK, "Tungsten and its Compounds" (Pergamon Press, Oxford, 1967).
4. L. LECLERCQ, M. PROVOST, H. PASTOR, G. GRIMBLOT, A. M. HARDY, L. GENGEMBRE and G. LECLERCQ, *Journal of Catalysis* **117** (1989) 371.
5. M. J. LEDOUX, C. H. PHAM, J. GUILLE and H. DUNLOP, *Journal of Catalysts* **134** (1992) 383.
6. D. GARG and P. N. DYER, in Materials Research Fall Meeting, 1989.
7. S. K. KODAMBAKA, Carbothermal synthesis of tungsten carbide powder using tungsten oxide containing precursors, M.S. thesis, SIUC, 1996.
8. R. KOC and G. GLATZMAIER, US Patent No. 5. 417. 952 (1995).
9. G. GLATZMAIER and R. KOC, US Patent No. 5. 342. 494 (1994).
10. R. KOC and J. S. FOLMER, *Journal of the American Ceramic Society* **80**(4) (1997) 952.
11. G. A. SWIFT and R. KOC, *Journal of Materials Science* **34** (1999) 3083.