Novel Route to Submicrometer Tungsten Carbide

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A mixture of graphite and scheelite ($CaWO_4$) have been mechanically milled together for 40 h. The resultant powder and an unmilled powder were examined by thermal analysis, isothermal annealing, and X-ray diffraction to determine the effect of milling on the reduction of scheelite to tungsten carbide. The milled powder underwent a rapid reduction reaction at 800°C − 300°C lower than the unmilled powder. The reduction sequence to WC was shown to differ for the two powders with W_2C intermediate in the milled powder and W in the unmilled powder. The milled powder showed complete reduction to WC in 1 h at 1,000°C, whereas the unmilled powder was incompletely reduced, even after 1 h at 1,200°C. Separation of the final phases was readily achieved by a simple acid leach, leaving WC grains around 200 nm in size.

Introduction

Tungsten carbide is probably the most common hard material in use today for cutting edges and other high-strength applications. It is conventionally made by reacting elemental tungsten with carbon at high temperature (~2,000°C) in a hydrogen atmosphere, although it has been shown recently that extended milling can also induce reaction between the elements at room temperature (Matteazzi and Le Caer, 1991; Wang et al., 1995, 1997). For use in cermets, the final tungsten carbide powder needs to be extremely fine grained, as it has been shown that the smaller the particles of tungsten carbide, the harder the final composite (Mehl, 1972). Consequently, the WC formed by the conventional route has to be ground to size. Elemental tungsten is produced from either wolframite ($FeWO_4$) or scheelite ($CaWO_4$). Wolframite is converted to scheelite by a dissolution/precipitation step, after which the scheelite undergoes a further conversion to ammonium tungstate, which is calcined to form WO_3. Finally, the WO_3 is thermally reduced using hydrogen to form metallic tungsten (Stephen, 1979). Any alternative route that reduces the number of steps and chemical input is potentially of commercial importance.

The direct reduction of scheelite to WC occurs at $>1200°C$ (Terry and Azubike, 1990; Terry et al., 1994; Johnston and Nguyen, 1996), although the reduction was not complete, even after 20 h at 1200°C (Terry and Azubike, 1990). The rate-determining step for the formation of WC was found to be carbon diffusion. In these investigations a stoichiometric excess of carbon was used and the critical separation of carbon and CaO from the WC was either poor (Terry and Azubike, 1990) or not reported (Johnston and Nguyen, 1996):

$$CaWO_4 + 4C \Rightarrow CaO + WC + 3CO. \tag{1}$$

Previous studies showed that major enhancements in solid-state reaction rate can be achieved by ball milling powders together prior to thermal processing (Welham, 1996, 1997b; Welham and Willis, 1998). It was also found that carbon usage was more efficient with only a slight stoichiometric excess of carbon necessary for complete reduction. In addition, this technique has been shown to produce micronized particles directly after milling (Welham, 1998), and thermal reduction of these composite particles would be expected to lead to a similarly sized product.

This article examines the effect of extended ball milling on the carbothermic reduction of scheelite with the view of forming micronized tungsten carbide powder.

Experimental Studies

The feed materials consisted of $>99.9\%$ graphite (<10-μm particle size) and a natural scheelite that was found to contain ~4 wt. % quartz; no other major ($>0.1\%$) elemental impurities were detected. The scheelite was milled for 1 h to reduce the particle size to <10 μm. Both powders were dried in air at 110°C for 24 h and then used.

Two mixtures were prepared in accordance with the stoichiometry of Reaction 1. These mixtures were loaded into laboratory-scale tumbling-ball mills (Calka and Radlinski, 1991), and five 25.4-mm-dia. 420C stainless-steel balls were loaded into one of the mills, giving a ball:powder mass ratio of 50:1. The mills were then evacuated to $\approx 10^{-2}$ Pa and rotated at 165 rpm for $\approx$ 40 h, after which no change in pressure within the mills was detected, indicating that gas hadn't evolved nor had it leaked into the mill. The sample of powder derived from the mill that contained the balls was subsequently called "milled," while the sample run without balls was termed "mixed."

Samples of both powders were annealed under flowing argon for 1 h at temperatures from 500°C to 1,300°C. A sample of milled powder that had been heated at 1,000°C for 1 h was subjected to an agitated leach for 1 h at 1% slurry density in ~ 0.1 M HCl to remove any soluble products.

The products were analyzed by X-ray diffraction (XRD) using monochromatic Co k_α radiation ($\lambda = 1.78896$ Å) using a count time of 1 s per 0.02° step.

Results and Discussion

It is clear from Figure 1 that there was no evidence of reaction in either powder at 500°C, with no mass loss recorded. At 600°C the milled powder started to lose mass, indicating that reaction was occurring. By 800°C the majority of mass loss had occurred, with a further increase in mass loss evident up to 1,200°C. The onset for the unmilled powder was at 900°C, and the complete reaction was apparent at 1,200°C. It is interesting to note that above 1,200°C both samples lost mass beyond that expected from Reaction 1.

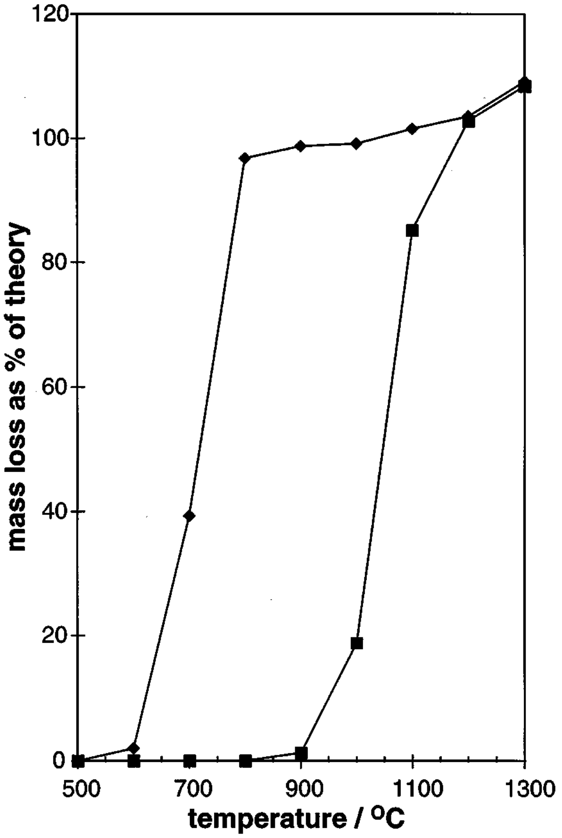

Figure 1. Mass loss, as a fraction of that expected for reduction of scheelite by reaction 1, after 1 h of isothermal annealing: ♦—milled; ■—unmilled powders.

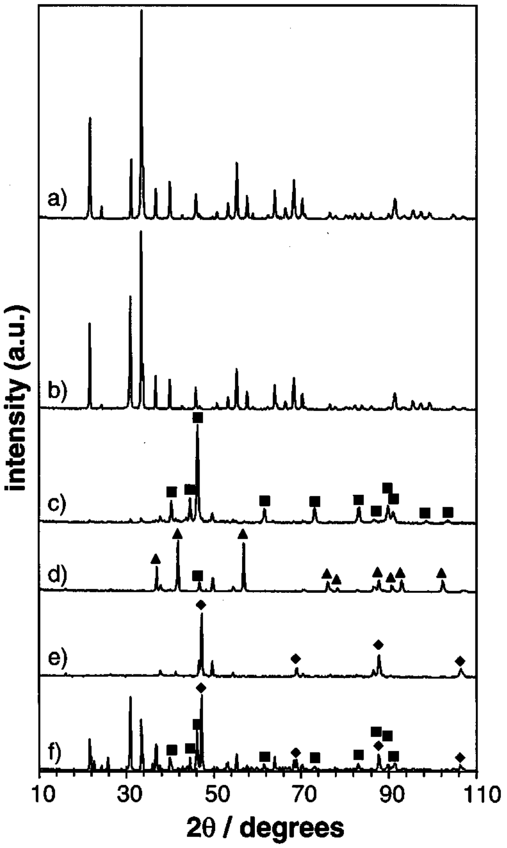

Figure 2. XRD traces of (a) as-received scheelite, milled powder heated at (b) 500°C, (c) 800°C, (d) 1,300°C, and (e) 1,500°C for 1 h; (f) unmilled powder heated at 1,000°C for 1 h: ■—W_2C; ▲—WC; ♦—W.

XRD traces for selected powders are shown in Figure 2, with a trace for the natural scheelite shown as Figure 2a. There was no conclusive evidence that CaO was present, although the main peak was present at 43.7° in most annealed powders; confirmatory peaks were absent due to low intensity. Heating to 500°C showed no evidence of reaction, with scheelite the dominant phase in Figure 2b. The apparent increase in the intensity of the peak at ~ 31° is due to the presence of graphite, which was absent from the raw scheelite powder in the trace (shown in Figure 2a). After heating to 800°C, the trace shown in Figure 2c was obtained and clearly shows that there was little scheelite remaining, the major phase present being W_2C. Increasing the annealing temperature led to an increasing fraction of WC until it was the only confirmed phase present at 1,200°C. Clearly, the addition of carbon to W_2C is a slow process which is probably controlled by carbon diffusion, as noted previously (Terry and Azubike, 1990; Terry et al., 1994; Johnston and Nguyen, 1996).

The trace at 1,000°C is shown in Figure 2f for the unmilled powder. There is still a significant fraction of scheelite present, and although the most intense peak is for elemental tungsten, the presence of W_2C is indicated by several peaks. Clearly, the reaction route is somewhat different from that of the milled powder, in which elemental tungsten was not detected below 1,400°C. Increasing the annealing temperature to 1,200°C led to the absence of scheelite and the formation of WC in addition to W_2C.

Both milled and unmilled powders lost mass at 1,300°C. The trace for the milled sample heated at 1,300°C is shown in Figure 2d. Although the predominant phase is WC, the main peak for W_2C is now evident. At 1,400°C the W_2C peaks increased as those of WC decreased and peaks for elemental tungsten emerged. The sample heated at 1,500°C for 1 h was found (trace shown in Figure 2e), to be composed primarily of elemental tungsten. There was no evidence of either W_2C or WC being present. Thus, it would seem that the mass loss at $>1{,}200°C$ was due to carbon loss from WC to form W_2C and then W. Carbon loss reportedly occurs at all temperatures, but is considered unimportant below 2,000°C (Storms, 1967). Clearly, this is not the case here, with all carbide converting to W at 1,500°C.

A sample of milled powder annealed at 1,000°C for 1 h was leached for 1 h in 3% HCl to remove the expected CaO. The mass loss was 24.3%, which is slightly greater than the 22.3% predicted from the products of Reaction 1. XRD of the leached powder showed that WC and W_2C were both present. Although the WC peaks were somewhat more intense than those for W_2C, the main peak of $WO_3 \cdot H_2O$ was also evident. This minor phase was thought to be due to a dissolution/hydrolysis reaction involving the small amount of residual scheelite. Indeed, similar leaching of scheelite resulted in the formation of canary-yellow $WO_3 \cdot H_2O$ powder. The slightly greater mass loss than expected from Reaction 1 may be due to the partial dissolution of one or both of the carbides.

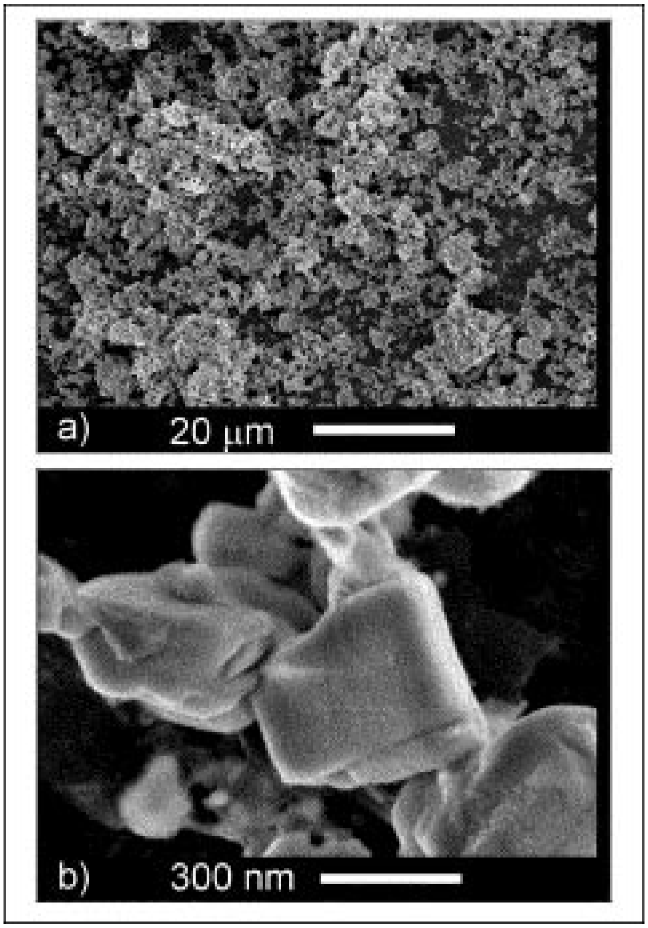

Figure 3. Scanning electron micrographs of the powder obtained by leaching a sample of milled powder for 1 h in 3% HCl.

Micrographs of the leached powder are shown in Figure 3. It is clear from the upper image that the particles are of reasonably uniform size with very few particles $>5\ \mu m$. Most of the larger particles show signs of porosity, suggesting that they were probably a composite of carbide and CaO, from which the CaO was removed by the acid. The composite would have been ~57 vol % CaO. It is possible that sonication of these particles would cause them to break up into smaller fragments. The lower image shows a more detailed view of the submicron particles. The particle in the center of the image seems to be cubic in nature, implying it is WC (W_2C is hexagonal). These particles show no evidence of porosity, indicating that the thermal reduction product is around 300 nm, which is excellent for subsequent use in cermets (Schwartzkopf and Kieffer, 1960).

It is clear that milling has a significant effect on the kinetics and reaction pathway for the carbothermic reduction of scheelite. Without milling, elemental tungsten is formed as an intermediate phase prior to carburization, whereas milled powders showed no evidence of elemental tungsten with the direct formation of W_2C.

Although the particle size of the milled powder ($\sim 1\ \mu m$) was comparable to that used in a previous investigation (Terry and Azubike, 1990), complete conversion to WC occurred within an hour at 1,100°C, compared with incomplete reaction after 20 h at 1,200°C (Terry and Azubike, 1990). It was previously demonstrated that ultrafine scale mixing of phases occurs during extended milling, with identification of distinct component phases beyond the resolution of elemental mapping ($\sim 1\ \mu m$) after milling for only 5 h (Welham, 1998). There is also indirect evidence that milling for 100 h mixes the phases on a <20-nm scale (Welham and Williams, 1999), suggesting that the longer the milling time the more intimate the mixing is. Extremely fine mixing leads to shorter diffusional paths, potentially changing the rate-determining step from solid-state diffusion to, ultimately, chemical-reaction control. For the milled powder, the reaction route formed W_2C directly, while the mixed powder formed W. Clearly the first reduction stage was different in the milled powder. However, in both powders the reaction of W_2C and carbon to form WC was slow and was probably controlled by the diffusion of carbon into the particle (Schwartzkopf and Kieffer, 1960; Storms, 1967).

It is reported (Schwartzkopf and Kieffer, 1953; Samsonov, 1964) that W_2C is 20–25% harder than WC, and that the difficulty in producing pure W_2C by conventional routes has prevented its commercial application as a hard material. The milled sample that was annealed at 800°C was composed primarily of W_2C, and it is probable that further optimization, for example, by reducing the carbon content, could lead to a reliable process for the production of bulk amounts of W_2C.

The overall process for production consists of three stages: milling, reduction, and leaching significantly less than the conventional process outlined earlier. Of these three stages, the most critical is milling, with longer milling times lowering the temperature and increasing the reaction rate (Welham, 1996, 1997a,b). Unfortunately, milling is extremely expensive and the economics of this process are dependent upon the costs associated with grinding.

The mill used in these investigations is extremely inefficient at transferring energy. Other mills are considerably more intensive than tumbling mills (Tkacova, 1989), and their application to this system would be expected to reduce the milling time considerably. If it is assumed that the five balls and the mill interact with each other once per revolution, then over 40 h a total of 2 million interactions occur per gram of feed powder. A vibratory mill typically operates at 10 Hz, using (conservatively) 20 pieces of media. Assuming that each piece of media interacts with four others per vibration cycle, there are a total of 4000 interactions per second. Thus, for 1 g of powder, the time necessary for two million interactions is 500 s, almost 300 times less than for the mill used here. This rough calculation does not account for differences in the mass of the media, or the much greater velocity of the media in a vibratory mill. A more exacting mathematical model (Maurice and Courtney, 1996) has suggested that although a ball mill may achieve the same result as a vibratory mill, it would take 700 times longer; however, this is yet to be experimentally proven for any system.

Conclusions

Extended ball milling of a mixture of natural $CaWO_4$ and graphite has been shown to decrease the formation temperature of WC by 300°C when compared with a physical mixture. In the milled powder, W_2C was the major intermediate phase, unlike the unmilled mixture, in which elemental tungsten was predominant. Both systems showed a slow carburization process in forming WC and showed an essentially identical product profile at 1,200°C. Higher temperatures led to the loss of carbon from WC, forming W_2C and then elemental tungsten. The unwanted calcium oxide was readily dissolved away from the carbide by a simple acid-leaching step, leaving WC powder with a grain size of around 200 nm. This much simplified manufacturing route has enormous potential for the low-cost manufacture of tungsten carbide and possibly the harder W_2C phase.

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