Synthesis of Nano-Sized WC-Co Powders by Reduction-Carburization Process

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The feasibility of producing nano-sized WC and WC-Co powders by reduction and carburization of WO_3 and Co_3O_4 under hydrogen and methane atmospheres was evaluated. WC powders of 1 μm in particle size were obtained from WO_3 on reduction and carburization at 950°C. On the other hand, nano-sized WC-Co powders with a particle size of ~100 nm could be produced by a two-step reduction process, using a blend of WO_3 and Co_3O_4. Critical control parameters in this process, such as the gas flow rate, temperature and treatment time, were found.

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1. Introduction

WC-Co has been the most widely used material in the cutting tool industry. There has been a continuing emphasis on the improvement of the cutting efficiency of these materials. Recent reports on the enhanced properties of ultrathin (<500 nm) and nanocrystalline (<100 nm) WC-Co based tool materials have focused considerable attention on a variety of different routes for producing the nano-sized WC powders. Two typical methods that have been used for this purpose are (high-energy) ball-milling and a solution technique.

The solution technique has been developed for producing nano-sized WC-Co and WC particles (agglomerate) in the size range of 60–300 nm. This technique involves reduction and carburization of oxide powders precipitated from aqueous solutions of metal nitrates and is known to provide a uniform WC dispersion in metal matrix powders, resulting in enhanced mechanical properties after sintering. High-energy ball-milling of submicron WC powders has been reported to reduce the size to 6 nm. Another method for producing nano-sized WC is an ion arc method. However, mainly cubic WC₁₋ₓ is synthesized by this method, which material is not suitable for cutting tool applications.

Regardless of the production techniques employed, controlled carbo-reduction is a key step in successful production of nano-sized WC in a Co matrix. The reduction of WO_3 is known to be a complex process. Gao and Kear have shown that the reduction temperature determines not only the crystal structure of W, but also the final form of the tungsten carbide. A study, which has been reported on the reduction of cobalt oxide, was limited to CoO, which undergoes reduction more readily than Co_3O_4. Little work has been reported on the reduction of Co_3O_4.

In order to retain the fine structure obtained from various routes, special efforts are being made to suppress the coarsening of fine carbide particles. A small amount of carbide such as VC, Cr₂C₃, or TaC can be added to nano WC-Co systems as a growth inhibitor for this purpose. Several mechanisms for the inhibition of growth have been proposed as follows. The preferential segregation of V or Cr, the lower surface energy of WC due to the presence of V or Cr, and the effect of secondary solutes on the dissolution of WC in a Co melt.

Hydrogen is typically used for oxide reduction. The use of CO has also been proposed for reducing tungsten oxide at low temperatures. However, because CO transformed into CO₂ during reduction process, difficulties in the control of the partial pressure of oxygen in a CO/CO₂ mixture do not permit the general use of this mixture. For the carburization process, carbon black powder is commonly used as the carburizing agent, which is also effective in the control of the stoichiometry of tungsten carbide. However, a previous study revealed a tendency for carbon segregation on the surface of the WC particles. Moreover, high-temperature processing (~1400°C) is required for the solid-state carburization process. It should be noted that, of all the gas-based carburizing agents, CH₄ is the most effective and stable up to 1000°C. Other hydrocarbons, such as C₂H₂, C₂H₄, and C₂H₆, have been found to generate extra carbon at lower temperatures and are not able to carburize tungsten completely.

The acceptability of these synthesis routes would depend on the reliability and the rate of production. In this work, an efficient technique based on reduction and carburization processes was investigated in terms of the design of production processes for various nano-sized WC-Co powders. In this study, a mixture of WO_3-Co_3O_4 powders was milled, reduced, and carburized using methane (CH₄), in order to determine optimum production conditions, as well as to maintain the fineness of the microstructure. The optimization of the processing parameters such as temperature, type of gas, reaction time and gas flow rate was examined, as those relate to homogeneous nano WC-Co alloys. The present work is an attempt to better understand these factors, as they relate to more effective processing.

2. Experimental

WO₃ (Aldrich USA, 20 μm) and Co_3O_4 (Aldrich USA, <1 μm) powders were used as starting materials. Batches of powder (~30 g) were ball-milled in an attritor (KMD-1BV, Koryo, Korea) for 10–30 h at 300 rpm, to achieve homogeneous mixing and particle size refinement. The weight ratio of WC balls to powder was maintained at 40:1 and methanol was
used as the milling medium. The powders (∼5 g) were heated under flowing hydrogen (99.99%) or methane (99.99%) gas. The gas flow rate was maintained at 200 mL/min. The degree of reaction was initially estimated from the weight changes, and the optimum conditions for processing were determined by the morphology of the powders and the phases formed in the system. The analyses were performed using x-ray diffraction (M18XHF-SRA, MAC Science Co., Cu-Kα, 50 kV–100 mA, Japan), scanning electron microscopy (JSM-840A, JEOL, Japan, 40 kV), and transmission electron microscopy (JSM-200CX, JEOL, Japan, 200 kV).

3. Results and Discussion

3.1 Effect of milling

Figure 1 shows SEM micrographs of the milled powders of WO₃, Co₃O₄ and a powder mixture of WO₃ and Co₃O₄ (W : Co = 94 : 6 in weight ratio) in an attritor for 30 h. As is evident from this figure, the particle sizes of the oxides were reduced to ∼100 nm after the 30 h of milling in all cases. Because the initial sizes of WO₃ and Co₃O₄ are 20 and <1 μm, respectively, the milling process was found to be effective in reducing the size of the raw powders to ∼100 nm. The mixture of WO₃ and Co₃O₄ powders showed a tendency to agglomerate but the individual oxides retained their fine sizes. Such nano-sized particles would be expected to enhance the solid-gas reaction in post-treatment steps, i.e., reduction and carburization.

3.2 Reduction of oxides

The reduction temperatures for WO₃ and Co₃O₄ powders were determined from DTA analyses under a nitrogen gas flow. As shown in Fig. 2(a), the onset temperature for WO₃ decomposition is not well defined. However, a previous study⁹ has shown that WO₃ is reduced to α-W at temperatures above 650°C. Further, α-W tends to form the WC phase under a carburizing atmosphere. On the other hand, the Co₃O₄ phase begins to decompose around 790°C and is transformed completely to Co at temperatures above 928°C as shown in Fig. 2(b). Based on these results, reduction temperatures of 600 and 700°C were examined for WO₃ and temperatures of 750, 850 and 950°C for Co₃O₄ in a search for optimum processing conditions under a hydrogen atmosphere. In order to examine the effectiveness of the gas-powder par-

![Fig. 1](image1.png)  
**Fig. 1** Powder morphology of (a) WO₃, (b) Co₃O₄ and (c) WO₃-Co₃O₄ (W : Co = 94 : 6) after attrition-milling for 30 h.

![Fig. 2](image2.png)  
**Fig. 2** DTA analysis for the stability of (a) WO₃ and (b) Co₃O₄ in nitrogen atmosphere.
particle reaction, the unmilled WO$_3$ and Co$_3$O$_4$ powders were tested with a mixture of nitrogen and hydrogen (3:1) during 3 h. The flow rate of the reducing gas was maintained at a constant level of 200 mL/min for all cases. Figures 3 and 5 show the XRD results using unmilled- (Fig. 3) and milled-oxide powders (Fig. 5) after the reduction step. As shown in Fig. 3(a), the unmilled WO$_3$ was partially reduced to W at 700°C within 3 h. The unmilled Co$_3$O$_4$ powder was completely reduced at temperatures above 950°C under identical conditions (Fig. 3(b)).

The reduction of WO$_3$ could be improved as a result of increasing the hydrogen content of the gas mixture and a reduction in the size of the oxide particle. Thus it was possible to use a short reaction time under those conditions. The comparison of XRD data between unmilled- and milled-tungsten oxide powders after the reduction step of 700°C, using pure hydrogen as the reducing agent for 1.5 h, was performed as shown in Fig. 4(a). Compared with these results in Fig. 4(a), it was noted that an initial smaller particle size resulted in almost complete reduction of WO$_3$. The effect of increasing the hydrogen content of the gas mixture is shown in Fig. 4(b). It was evident that tungsten oxide powders were more easily reduced with an increase in the hydrogen content as we saw in Fig. 4(b). Eventually, proper combinations among the variables such as temperature, initial particle size and reducing gas, is discussed in the following section, resulted in almost complete reduction of WO$_3$. Through these results, the optimized conditions for the reduction step were determined and used in the experiments of Fig. 5. The ball-milled WO$_3$ powders were reduced at 700 and 800°C under pure hydrogen gas for 1.5 h. Under this condition, though some of the WO$_3$ remained, WO$_3$ powders were substantially reduced into W above 800°C as shown in Fig. 5(a). In the meantime, the blend of WO$_3$-Co$_3$O$_4$ powders (W : Co = 94 : 6) was subjected to a temperature in the range of 700–950°C under pure hydrogen gas for 1.5 h. In the case of the ball milled WO$_3$-Co$_3$O$_4$ blend, although a small amount of WO$_3$ remained, complete reduction was essentially achieved at temperatures above 900°C as shown in Fig. 5(b).

The morphology of the powder or powder blend was examined after the completion of the high-temperature reduction. The WO$_3$ and Co$_3$O$_4$ powders, which were reduced at 800 and 850°C for 1.5 h, respectively, retained a discrete spherical shape and their sizes were <100 nm. More interestingly, the size of the WO$_3$-Co$_3$O$_4$ powder blend, which was reduced at 950°C for 1.5 h, is about 100 nm in diameter. This shows that the initial size of the ball-milled powder of 100 nm can be maintained during the high-temperature reduction process.

**Fig. 3** XRD data after high temperature reduction of unmilled powders under a nitrogen and hydrogen gas mixture (N$_2$/H$_2$ = 3/1) for 3 h: (a) WO$_3$ and (b) Co$_3$O$_4$.

**Fig. 4** Comparison of XRD data after high temperature reduction: (a) between unmilled and milled (for 30 h) WO$_3$ powders under 100% hydrogen gas flow at 700°C for 1.5 h. (b) between using 25% H$_2$ (N$_2$/H$_2$ = 3/1) and using 100% H$_2$ gas (N$_2$/H$_2$ = 0/1) with unmilled WO$_3$ powders at 700°C for 1.5 h.
3.3 Carbo-reduction of oxides

For the effective synthesis of WC from WO₃, a continuous process was employed. As in other reduction schedules, the process consists of a high-temperature reduction at a fixed temperature (700, 800 or 950°C) under a hydrogen flow for 1 h, followed by carburization using a methane flow for 20 min. Subsequent cooling was done in argon to prevent the powders from being re-oxidized. Figure 6(a) shows the XRD profiles of reduced and carburized WO₃. These findings indicate that the complete transformation of WO₃ into WC can be achieved only at temperatures above 950°C. At a lower temperature (800°C), W₂C, a carbon-deficient tungsten carbide, was simultaneously formed, along with WC. The SEM investigation reveals that the WC powders coarsen to about 500 nm (Fig. 6(b)) when the process is completed at 950°C. On the other hand, the powders obtained at lower temperatures (700°C and 800°C) were found to have a much finer size range (∼100 nm). This suggests that it would be difficult to synthesize nano-size WC at temperatures above 900°C, due to rapid diffusion and growth.

For the WO₃-Co₃O₄ blend, the reduction and carburization procedures were carried out in either a one-step or two-step process as shown in Fig. 7. The terms one-step (Fig. 7(a))
or two-step (Figs. 7(b) and (c)) indicate that the processing is done at one or two different temperature(s), by varying the conditions for the gas flow. The processes of Figs. 7(a) and (b) were used for the WO$_2$-Co$_2$O$_4$ blend (W : Co = 70 : 30) and the process of Fig. 7(c) was used for the WO$_2$-Co$_3$O$_4$ blend (W : Co = 90 : 10). From the XRD analysis (Fig. 8(a)), it is evident that the powder mixture prepared by the one-step process from WO$_2$-Co$_2$O$_4$ blend (W : Co = 70 : 30) at 950°C retains WC, Co and $\eta$ (Co$_3$W$_2$C or Co$_3$W$_3$C), with particle size in the range of 300–500 nm (Fig. 8(b)). The $\eta$ phase is a well-known phase, which is known to be detrimental to the performance of WC-Co cutting tools. A two-step process was investigated, in order to retard the growth of WC in the first step by separately reducing Co$_3$O$_4$ in the second step. It was thought that the production of the $\eta$ phase could be prevented under such conditions.

In the two-step process, the temperature for the first step was set at 600–750°C based on the DTA results (Fig. 2). The reason for this temperature range is that WO$_3$ is reduced to the $\alpha$-W phase above 650°C(9) and Co$_3$O$_4$ begins to decompose above 790°C. It was thought that the $\eta$ phase would not be produced by preventing the reduction of Co$_3$O$_4$ during the carburization of WO$_3$ in the temperature range of 600–750°C. The temperature for the second step was fixed at 950°C in order to reduce Co$_3$O$_4$, because the Co$_3$O$_4$ phase was completely reduced at 950°C as shown in Fig. 3(b). Figure 9 shows that WC and Co powders can be produced from WO$_2$-Co$_3$O$_4$ (W : Co = 70 : 30) using the two-step schedule (Fig. 7(b)). However, a small fraction of the $\eta$ phase still exists in the system. This might be due to the partial reduction of Co$_3$O$_4$ at the first step of 600–750°C and the high content of Co (30 mass%). At first, the amount of Co was set at 30 mass% to facilitate XRD analysis. However, the increase in Co content seems to facilitate the $\eta$ formation and particle coarsening. Figure 10 shows, using WO$_2$-Co$_3$O$_4$ blend (W : Co = 90 : 10) as starting material, the formation of the $\eta$ phase at the different temperatures in the first step (Fig. 7(c)) and the microstructure of the produced powder. It was noted that a reduction in the Co content to 10 mass% resulted in a microstructure that was free of the $\eta$ phase (Fig. 10(a)) and showed a decrease in the tendency for coarsening (Fig. 10(b)). The particle size of powder produced at 750–950°C two-step was about 100 nm, as estimated from the SEM analysis (Fig. 10(b)).

Figure 11 shows the corresponding TEM micrograph of Fig. 10(b). This clearly shows that the shape and size of all the particles are uniform throughout the sample. The structure is transparent to the electron beam when the thickness of the particles is less than 100 nm. Thus, the particles produced from the two-step processing are within 100 nm in size. The individual particles in the figure seem to consist of WC particles dispersed in a Co matrix. However, It is clear that each particle is not WC or Co as shown in Fig. 12. Because the distribution of W (Fig. 12(b)) and Co (Fig. 12(c)) throughout the particles is homogeneous, it can be thought that each particle of WC is uniformly covered by Co. The reason for this
is that the WC particle is previously formed in the first step and that Co may diffuse to the surface of the WC particles.

Based on this study it was found that the two-step process represents a potentially useful method for producing WC-Co powders for the purpose of alloy design and production. The unreduced WO₂ is normally reduced during the subsequent carburization with CH₄. Further, the appearance of the W₂C phase can be eliminated by sufficient delivery of carbon to the W. This may be routinely accomplished by extending the time for carburization or by increasing the flow rate of CH₄. Suppressing the early reduction of Co₃O₄ will minimize powder coarsening. The decrease in the amount of Co during carburization will reduce the diffusion process for particle growth.

4. Summary

The WO₃ and Co₃O₄ powders were milled, reduced and carburized to produce nano-sized WC-Co powders. One-step and two-step processes were examined, in order to produce the powders without forming the η (Co₃W₂C or Co₃W₃C) phase. The following is a summary of this study.

1. Attrition-milling was effective in reducing the size of raw WO₃ powders to <100 nm from 20 μm within 30 h.
2. Reduction of WO₃ in a hydrogen atmosphere was not completed in 1.5 h at 700–800°C. However, a subsequent car-
burization process resulted in complete carbo-reduction.

(3) The coarsening of WC and the formation of the \( \eta \) (Co/W, C or Co/W, C) phase were effectively suppressed by employing two different temperatures for the reduction of \( \text{WO}_3 \) and \( \text{Co}_2\text{O}_4 \) powders. The homogeneous distribution of WC and Co was attained.

(4) The two-step process is a feasible method for the production of nano-sized WC-Co powders for the purposes of alloy design and production.

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REFERENCES


