Synthesis of Ultra Fine Titanium-Tungsten Carbide Powder from Titanium Dioxide and Ammonium Metatungstate

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In the present study, the focus is on the synthesis of ultra fine titanium-tungsten carbide powder by the carbothermal reduction process. The starting powder was prepared by the combination of drying and calcination methods using titanium dioxide powder and an aqueous solution of ammonium metatungstate to obtain a target composition of 60 mass% TiC-40 mass% WC, i.e., (Ti₁₋ₓWₓ)C. The synthesized oxide powder was mixed with carbon black, and this mixture was then heat-treated under a flowing argon atmosphere. The changes in the phase structure, thermal gravity and particle size of the mixture during heat treatment were analyzed using XRD, TG-DTA and SEM. The synthesized oxide powder has a mixed phase structure of anatase-TiO₂ and WO₃ phases. This composite oxide powder was carbothermally reduced to titanium-tungsten carbide by solid carbon through three steps with increasing temperature; the reduction of WO₃, the reduction of TiO₂ and formation of tungsten carbides, and the formation of titanium-tungsten carbide. The synthesized (Ti₁₋ₓ,Wₓ)C powder at 1673 K for 10.8 ks has an average particle size of about 200 nm. [doi:10.2320/matertrans.MER2008271]

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1. Introduction

Hard metal based on WC/Co has been widely used for wear-resistant machine parts or tool materials because it has superior mechanical properties, such as wear resistance and high temperature strength, etc.¹ In order to increase the mechanical properties and resistance to “cratering” at elevated temperatures, TiC is added to WC/Co hard metal. WC/TiC/Co system hard metals were devised for machining steels and other ferrous alloys, the purpose of the TiC content being to resist the high-temperature diffusive attack that causes chemical breakdown and “cratering”. WC/TiC/Co system hard metals have two distinct carbide phases, angular crystals of almost pure WC and rounded TiC/WC “mixed crystals”.²⁻⁴ Because of differential diffusion effects, the latter often show a “cored” structure. The third phase is the cobalt binder. A solid solution or “mixed crystal” of WC in TiC (TiC is almost insoluble in WC) retains the anti-cratering property to a great extent.¹⁻⁴

The mechanical properties of the hard metals depend not only on the chemical composition but also on their microstructure.¹ The hardness, fracture toughness and wear properties of the hard metals were strongly influenced by the size of the carbide particles, the degree of homogeneity of the microstructure and purity of the initial powders. These mechanical properties increased simultaneously with decreasing particle size and increasing homogeneity. To manufacture high performance hard metal with an ultra fine microstructure, raw powder materials with an ultra fine particle size should be used. Recently, several methods have been proposed for the synthesis of ultra fine particles.⁵⁻¹⁰ In the case of WC and TiC, it was possible to synthesize the WC/Co and TiC/Co composite powders with an average particle size under 100 nm and 200 nm, respectively.⁸⁻¹⁰ These composite powders were manufactured by the combination of spray conversion and carburization processes. For the other carbides (TaC, NbC and (Ti,W)C, etc.), however, no commercial process has been established for the synthesis of such ultra fine particles.

Titanium-tungsten carbide, (Ti₁₋ₓ,Wₓ)C, has been used as a dispersed particle in the WC/TiC/Co system hard metals for increasing high temperature hardness and decreasing the reaction with steel alloy during machining. Generally, titanium-tungsten carbide was commercially manufactured by carbothermal reduction using metallic tungsten powder, titanium dioxide powder and carbon black as the raw materials.¹ This process requires a temperature range of 2073–2473 K for the commercial production of the titanium-tungsten carbide with a solid solution or mixed-crystal, because of the difficulty of reduction of titanium dioxide. Therefore, it is difficult to produce fine particles using this process due to the agglomeration of the particles at the high synthesis temperature. Recently, a new mechano-chemical process was proposed for the synthesis of ultra fine WC/TiC/Co composite powder.¹⁰ This process could be used to synthesize ultra fine WC/TiC/Co composite powder at about 1673 K by the combination of spray conversion and direct carburization processes using a metallic salts solution as the raw material. However, this process has an environmental pollution problem due to the chemical processing based on the spray conversion of the metallic salts, especially titanium chloride. The titanium chloride, TiCl₃, dissolved into titanium and chloride ions in distilled water during preparation of the starting solution for spray conversion. The chloride ions in the solution were transformed into chlorine gas during spray conversion. It become generally known that this chlorine gas causes serious environmental pollution problems. Recently, we proposed a new carbothermal reduction process for the synthesis of ultra fine TiC and TiC/Co powders.⁹⁻¹¹⁻¹² Because this new process used ultra fine titanium dioxide powder instead of chloride as the titanium source, it could possibly decrease the environmental
pollution problem. Also, it decreased the reduction temperature of the titanium dioxide and titanium carbide formation temperature compared to the conventional processes.

In the present study, the focus is the synthesis of titanium-tungsten carbide powder by the carbothermal reduction process to investigate the synthesis possibilities of ultra fine titanium-tungsten carbide using titanium dioxide powder as the titanium source without the chemical processing based on the spray conversion of the chloride solution.

2. Experimental Procedure

The starting slurry was prepared by suspending the titanium dioxide powder (an average particle size of 50 nm and an anatase structure) in an aqueous solution of ammonium metatungstate (AMT, (NH₄)₂(H₂WO₄)·4H₂O), to obtain a target composition of 60 mass% TiC-40 mass% WC, i.e., (Tiₐ₈₃Wₐ₁₇)C. Drying was performed using an ultrasonic generator with a frequency of 20 kHz at about 358 K. The precursor powder obtained by the drying was decomposed at 1073 K for 7.2 ks in air to remove the salt components and form a titanium-tungsten-oxygen-based composite oxide powder. The calcined composite oxide powder was mixed with carbon black (mean particle size: 0.5 μm) for 86.4 ks using a tumbler-ball mill with a ball-to-powder mass ratio of 10:1. The mixture was placed in a graphite crucible and then heated in the temperature range from 823 K to 1673 K for 1.8 ks in a tube furnace under a flowing stream of argon atmosphere. After heat treatment, the samples were analyzed by X-ray diffraction using Cu-Kα radiation and observed by SEM. The changes in the thermal gravity of this powder mixture during heat treatment from room temperature to 1673 K in flowing argon was recorded by TG-DTA at a heating rate of 8.3 × 10⁻² K/s.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the dried precursor powder and calcined powder. The diffraction peak of the precursor powder prepared by the drying method shows only the anatase-TiO₂ phase. There are no visible X-ray diffraction peaks related to tungsten. This means that the dried powder from the starting slurry has a homogeneously mixed state of the titanium dioxide, tungsten-based salt and moisture. However, the calcined powder shows diffraction peaks of anatase-TiO₂ and WO₃. By heating the precursor powder in air atmosphere, the volatile components (such as NH₃, NOx, and H₂O) were evaporated by decomposition of the tungsten-based salt. The anatase-TiO₂ phase was less stable than the rutile-phase-structured one. In general, titanium dioxide of the metastable anatase phase transforms into the stable rutile phase during heating. In this study, the phase transformation of the titanium dioxide was not found during calcination at 1073 K for 7.2 ks. No chemical reaction occurred between the titanium dioxide and the tungsten component during calcination.

Figure 2 shows an SEM micrograph of the ball-milled mixture of calcined composite oxide powder and carbon black. The synthesized starting composite oxide powder from the drying had an irregular morphology with an average particle size of about 2 μm. After milling, the particle morphology changed to a globular shape, and the average particle size decreased to below about 0.5 μm. The composite oxide particles were homogeneously mixed with carbon black, and there were no visible differences in the X-ray diffraction patterns of the powder before and after the ball-milling.

Figure 3 shows the mass change in the mixture of the calcined composite oxide powder and carbon black as a function of the temperature during heating in the flowing argon gas. The theoretical quantities of the carbon for the carbothermal reduction of the calcined composite oxide powder are estimated by:

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\text{WO}_3(s) + \text{TiO}_2(s) + 6\text{C}(s) \rightarrow (\text{Ti}, \text{W})\text{C}(s) + 5\text{CO}_2(g)
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In this study, 10% excess carbon was used for the reaction. The theoretical mass fraction of the reaction was 58.83% after complete carbothermal conversion of the titanium-tungsten-oxygen-based composite oxide powder of 60 mass% TiC-40 mass% WC target composition by the reaction. As shown in Fig. 3, the value of the mass fraction of the mixture at 1673 K was higher than 58.83%, which means that the present titanium-tungsten-oxygen-based oxide in the mixture could not be completely converted to titanium-tungsten carbide during the analysis by TG-DTA. The mass...
of the mixture powder started to decrease around 1123 K and showed a first remarkable decrease in the mass fraction at about 1203 K. A second significant mass loss occurred at about 1273 K, and the mass fraction continuously decreased with increasing temperature until the heat-treatment temperature reached about 1513 K. These mass losses mean that the carbothermal reactions remarkably occur at these temperatures.

Figure 4 shows the X-ray diffraction patterns of the mixture of the calcined composite oxide powder and carbon black heat-treated in the tube furnace under a flowing stream of argon at a specified temperature for 1.8 ks. The heat-treatment temperature was determined from the TG curve (Fig. 3). Below 1073 K, the X-ray diffraction patterns showed anatase-TiO₂ and WO₃ phases as the calcined composite oxide powder. The diffraction pattern changed to the mixed state of the anatase-TiO₂, rutile-TiO₂ and W₁₈O₄₉ phases at 1123 K. At 1223 K, there were two kinds of phases in the heat-treated powder; i.e., the rutile-TiO₂ and W. This means that the titanium dioxide had undergone phase transformation from the metastable anatase phase structure to the stable rutile phase structure above 1073 K. The WO₃ in the calcined powder was preferentially reduced to tungsten below 1223 K. Therefore, this indicates that the first remarkable decrease in the mass fraction at about 1203 K is the preferential carbothermal reduction of the WO₃ in the calcined composite oxide powder by the solid carbon. The X-ray diffraction pattern of the heat-treated powder at 1273 K showed the coexistence of W₂C, W and magneli phases. The magneli phase is the lower oxide in the Ti-O system, which is written as Ti₄O₈₋₃₋₁ (n > 3). This means that the carburization of the tungsten and reduction of the titanium dioxide simultaneously occurred at about 1273 K. Therefore, the second significant decrease in the mass fraction at about 1273 K indicates the reduction of the titanium dioxide in the calcined composite oxide powder. At 1473 K, there were four kinds of phases in the diffraction pattern: Ti₃O₅, W₂C, W and Ti₂O₃. The X-ray diffraction pattern of the heat-treated powder at 1573 K showed W₂C, W, Ti₃O₅ and (Ti₁₋ₓWₓ)Cₓ. The titanium-tungsten carbide, (Ti₁₋ₓWₓ)Cₓ, is a solid solution of TiC and WC with a maximum solubility of about 72 mass%WC. In the case of the carbothermal reduction of pure titanium dioxide powder by solid carbon, the titanium dioxide was carbothermally reduced to TiC through three steps; i.e., reduction of TiO₂ to form TiₙO₂ₙ₋₁ (n > 3) phases, formation of titanium oxy carbide and deoxidization of the titanium oxy carbide to titanium carbide. The titanium oxy carbide, TiCₙOₙ, is a solid solution of TiC and TiO₂. Generally, the initially formed carbide from the titanium dioxide by the solid carbon is not pure titanium carbide. Thermodynamic calculation predicts that the initial composition of TiCₙOₙ is dependent on the temperature and partial pressure of CO and will be between TiC₉O₅ and TiC₅O₃. However, no diffraction peaks related to the titanium oxy carbide are found in the Fig. 4. At 1673 K, there were two kinds of phases in the heat-treated powder; i.e., the (Ti₁₋ₓWₓ)Cₓ and a small amount of W₂C. No different oxide phases were found in the cases of heat-treated powders below 1573 K. The diffraction peaks related to tungsten almost disappeared in the diffraction pattern compared to other X-ray diffraction patterns below 1573 K. However, the diffraction peaks related to titanium-tungsten carbide more clearly appeared in the diffraction pattern. This means that the tungsten carbide and/or tungsten dissolved into the carburized titanium phase.

No chemical reaction occurred between the titanium and tungsten components during reduction of the oxide phases in the calcined composite oxide powder. It was considered that the reduction reactions of the titanium oxides and tungsten oxides in the titanium-tungsten-oxygen-based composite oxide powder by the solid carbon occurred independently.
The carburization reaction of the tungsten component occurred at lower temperature than that of the titanium component. The dissolving reaction of the tungsten carbide in the titanium component simultaneously occurred with the carburization reaction of the titanium component. Contrary to the titanium-oxygen-based oxide powder, no titanium-oxide carbide, TiC$_2$O$_y$, was found. It was considered that the carburization of the titanium component and the formation of (Ti$_{1-x}$W$_x$)$_y$C$_y$ simultaneously occurred above 1473 K. For verification of the reaction mechanism during heat treatment, however, fundamental research is needed concerning the crystal structure and chemical composition in the future.

Figure 5 shows the change in the relative intensity of the XRD peaks of the W$_2$C to that of (Ti$_{1-x}$W$_x$)$_y$C$_y$ in the samples heated at 1573 K and 1673 K. The peak intensities for the W$_2$C and (Ti$_{1-x}$W$_x$)$_y$C$_y$ corresponding to the (102) and (111) reflections, respectively, are used. As shown in Fig. 5, the amount of the retained W$_2$C decreased with the increasing heat treatment time. In spite of 21.6 ks heat treatment, a small amount of W$_2$C still remained in the case of the 1573 K sample. At 1673 K, however, no diffraction peak related to the W$_2$C phase was found above the heat-treatment time of 10.8 ks. The heat-treatment time needed for complete dissolution of the tungsten carbide. The synthesized particles, however, fundamental research is needed concerning the lattice constant and chemical composition in the future.

4. Conclusion

The present study focused on the synthesis of titanium-tungsten carbide powder by a carbothermal reduction process using a titanium-tungsten-oxygen-based composite oxide powder. This composite oxide powder with a target composition of 60 mass%TiC-40 mass%WC (or (Ti$_{0.83}$W$_{0.17}$)C) can be synthesized by the combination of drying and calcination processes using titanium dioxide powder and an aqueous solution of ammonium metatungstate. The synthesized composite oxide powder has a mixed phase structure of anatase-TiO$_2$ and WO$_3$ phases with an average particle size of about 0.5 μm. This composite oxide powder is carbothermally reduced to the titanium-tungsten carbide through three steps with increasing temperature; i.e., the reduction of WO$_3$, the reduction of TiO$_2$ and formation of tungsten carbides, and the formation of titanium-tungsten carbide. The reduction reactions of the titanium and tungsten components in the composite oxide powder by the solid carbon occurred independently. The carburization of the tungsten component occurred at a lower temperature than that of the titanium component. The formation of the titanium-tungsten carbide occurred by the simultaneous reaction of the carburization of the titanium component and the dissolution of tungsten carbide. The synthesized (Ti$_{1-x}$W$_x$)$_y$C$_y$ powder at 1673 K for 10.8 ks has an average particle size of about 200 nm.

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