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SIZE CONTROL OF TUNGSTEN POWDER SYNTHESIZED BY SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS PROCESS

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ABSTRACT

Tungsten powder was prepared by self-propagating high temperature synthesis (SHS) from a mixture of WO_3 and Mg. The MgO in the product was leached with an HCl solution. The complete reduction of WO_3 required a 33% excess of magnesium over the stoichiometric molar ratio Mg/WO_3 of 3. The tungsten product had a purity of 99.98%, which was higher than that of the reactants. The high purity resulted because the impurities in the reactants were volatilized during the highly exothermic reaction and dissolved during leaching of the product. Size distribution and the shape of the tungsten particles produced was affected by compaction pressure on the green pellet. *© 2000 Elsevier Science Ltd*

KEYWORDS: A. metals, A. oxides, B. chemical synthesis, C. X-ray diffraction, D. thermodynamic properties

INTRODUCTION

Tungsten has the useful characteristics of high melting point (3410°C), high-temperature strength, and electrical conductivity. There are many applications in the fields of illumination, electronics, electrical contact, and heat-resistant structure using its good properties. It is also the main raw material for the ultra-hard alloys used in cutting tools, anti-friction tools, and high-speed steels [1]. Currently, tungsten is produced by the reduction of WO_3 at 1000 to 1100°C with carbon, H_2, or calcium, or by the hydrogen reduction of WF_6 at high

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temperature [1]. Many pure substances have been prepared by self-propagating high temperature synthesis (SHS) [2–4]. This process can be used to prepare a fine powder of high-temperature materials at 2000 to 4000°C, using their high exothermic heats of reaction. High-purity W powder has been produced by SHS, using Mg powder as a reducing agent [5]. This process is relatively simple and rapid without requiring a large external heat supply [6,7]. However, it is necessary to control the particle size in order to commercialize the product by the SHS process. The SHS reaction is very difficult to control because the combustion rate is too fast and the reaction mechanism is not yet completely understood.

In this study, as a preliminary work to commercializing W powder by SHS, the effects of the cooling rate, compaction pressure, and molar ratio of reducing agent to WO_3 on the microstructure of W powder were investigated.

EXPERIMENTAL

Predetermined amounts of the reactants were mixed in an alumina ball mill and pressed into pellets of 30 mm diameter and about 30–40 mm height under various compaction pressures. The pellets were placed in a SHS reactor under argon and ignited by a tungsten wire connected to a power supply. Temperature profiles were measured by C-type thermocouples (W–5%Re vs. W–26%Re, 0.5ϕ) connected to a data logger (DASTC). The product was very porous, and a substantial amount of magnesium and zinc oxide dust was generated. The product mixture, which was easily broken in a mortar, was leached with 10 to 6.5 M HCl solution at 80°C for 40 min to remove MgO and ZnO, and then dried in a drying oven at 70°C for 24 h. The powder thus produced was analyzed by X-ray diffraction (XRD) to determine its crystal structure and by scanning electron microscopy (SEM) to determine its microstructure. Its chemical composition was determined by inductively coupled plasma spectrometry (ICP).

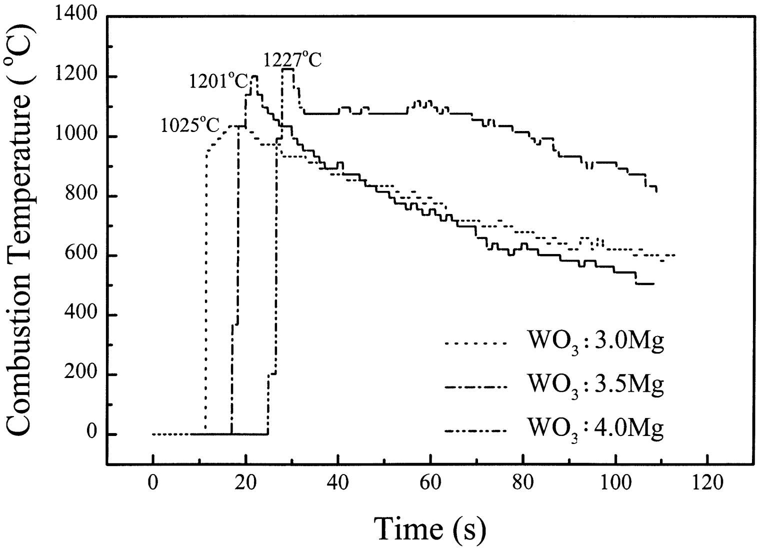

FIG. 1

Temperature profiles of combustion reaction (Ar atmosphere).

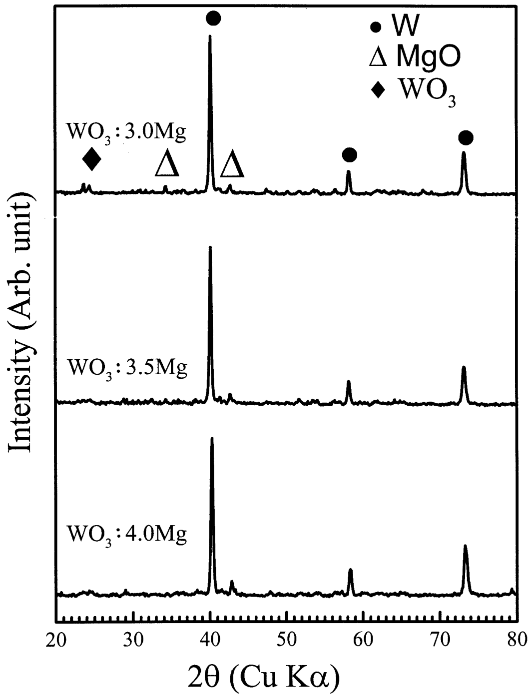

FIG. 2
X-ray diffraction patterns of reaction products with different molar ratios (before leaching).

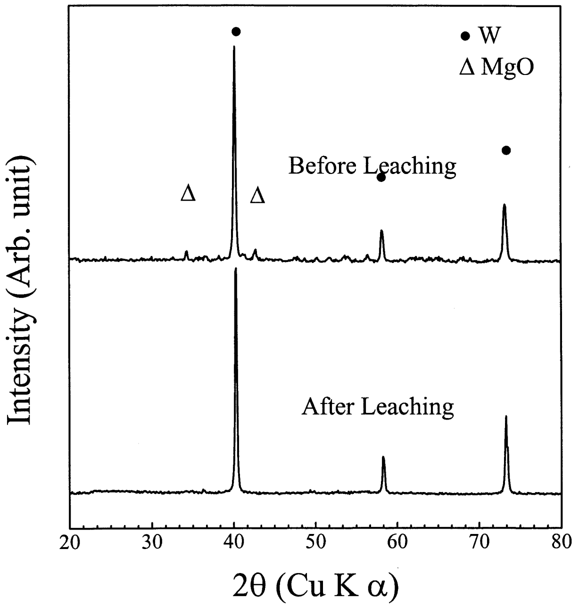

FIG. 3
Effect of leaching with 6.5 M HCl solution at 80°C for 40 min (WO_3:2.4Zn:0.9Mg system).

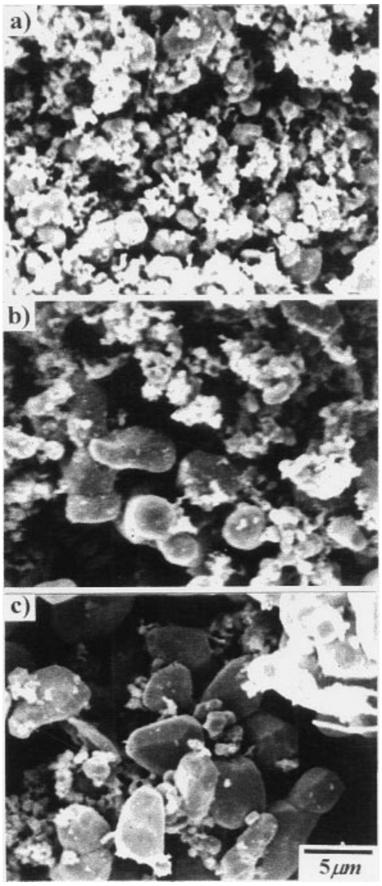

FIG. 4
SEM photomicrographs of combustion-synthesized W with different molar ratios of Mg/WO_3 (in Ar atmosphere, at 480 MPa): (a) 3.0, (b) 3.5, and (c) 4.0.

RESULTS AND DISCUSSION

The reactions involved in the experiments are as follows:

$$WO_3 + 3Mg \rightarrow W + 3MgO \tag{1}$$

$$WO_3 + xZn + xMg \rightarrow W + xZnO + xMgO \tag{2}$$

Zn powder was added to control the combustion temperature and rate. The combustion reactions of eqs. 1 and 2 are governed by the molar ratio of Mg/Zn. Hence, experiments to study the effects of the stoichiometric molar ratio of MgZn/WO_3 and compaction pressure on particle size were carried out. Figure 1 shows the combustion temperature of products with different Mg concentrations. As the molar ratio of Mg/WO_3 increased, the combustion temperature was increased. The cooling rate of the specimen with 4.0 mole of Mg was slower than that of the other samples. The maximum combustion temperature, 1227°C, was recorded

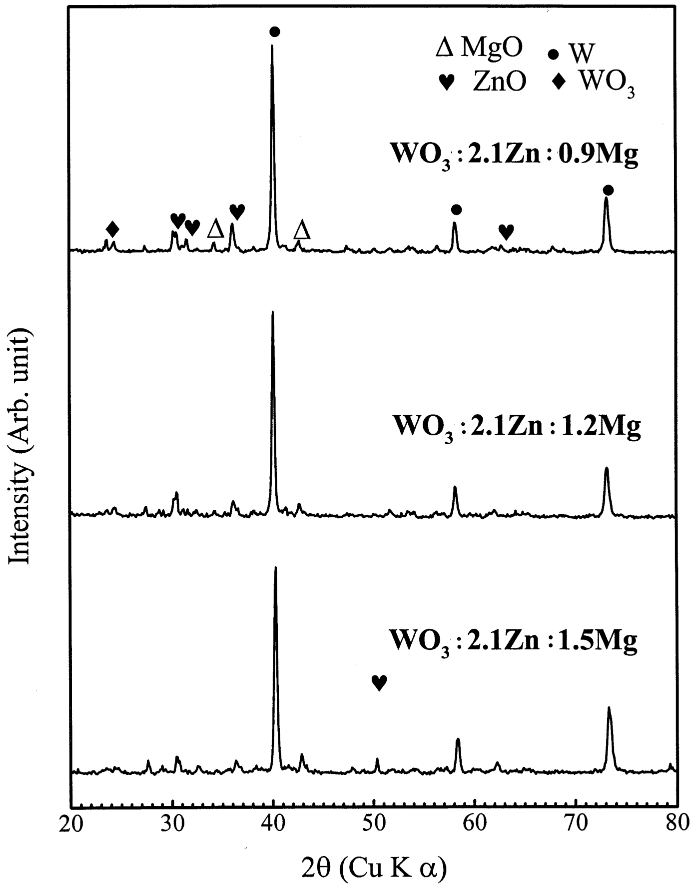

FIG. 5
X-ray diffraction patterns of the reaction products with various concentrations of Mg in the WO_3:2.1Zn:xMg system.

for the sample with 4.0 mole of Mg. However, there was a large deviation in the measured combustion temperature from a theoretical adiabatic temperature, approximately 14,000°C. This may be because the reaction was explosive, so the instantaneous reaction could not be measured exactly.

Figure 2 shows the XRD patterns of products with different Mg concentrations before leaching. W and a small quantity of MgO were dominant phases. As the Mg concentration increased, the amount of unreacted WO_3 decreased. All WO_3 was eliminated at 4.0 mole of Mg. In the case of a stoichiometric molar ratio of Mg/WO_3 (i.e., 3), some WO_3 remained unreduced because of incomplete contact and Mg loss during the rapid SHS reaction, which generates a high temperature. The concurrently formed MgO in the product was easily removed by leaching with 100 ml of 6.4 M HCl solution at 80°C for 40 min (Fig. 3).

Figure 4 shows SEM photographs of combustion-synthesized W with different Mg concentrations after leaching. The W particles consist of irregular and spherical types from under

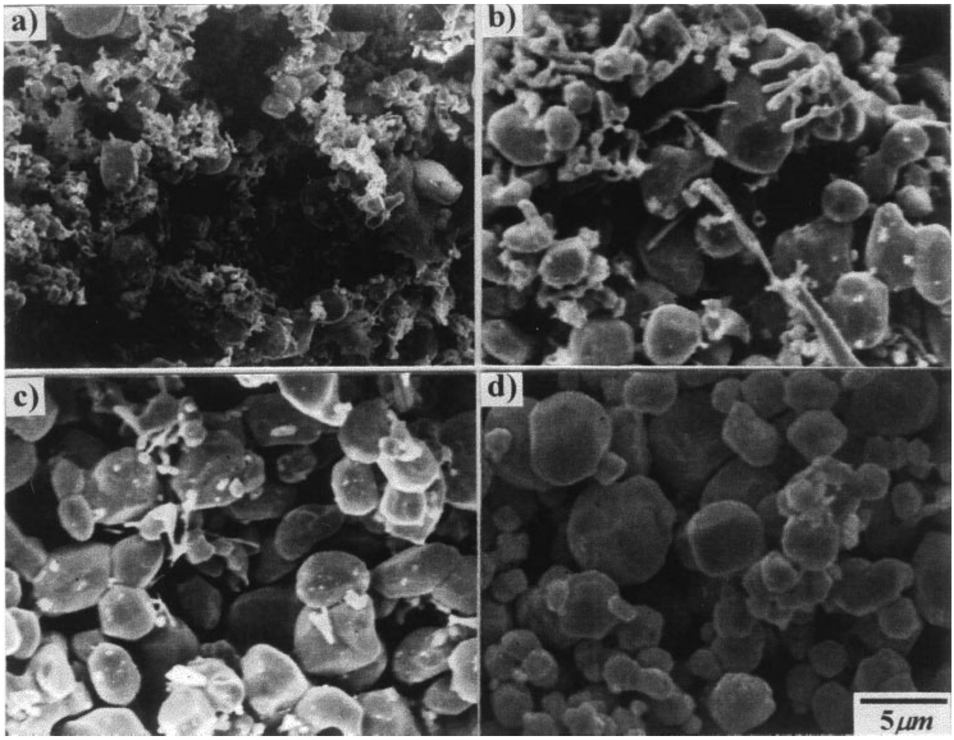

FIG. 6
SEM photomicrographs of combustion-synthesized W under different compaction pressures for WO_3:3.5Mg (spherical 70 mesh, Ar atmosphere): (a) 160, (b) 400, and (c) 640 MPa.

1 to 2 μm at the molar ratio Mg/WO_3 of 3.0, but at a higher molar ratio, 3.5–4.0, the tungsten particles produced had a spherical shape with a narrow size distribution.

Figure 5 shows XRD patterns of the products with various concentrations of Mg in the WO_3:2.1Zn:xMg system ($x = 0.9$, 1.2 and 1.5) before leaching. Complete reductions of WO_3 were achieved with Mg concentrations greater than 1.2; whereas unreacted WO_3 was detected with Mg concentration of 0.9, due to the relatively high free-energy of ZnO. It is believed that the Zn and Mg powders were lost during the explosive combustion reaction. As in the case of various Mg concentrations in the WO_3:2.1Zn:xMg system, similar results were obtained in the WO_3:xMg system. The W powder produced had irregular and spherical shaped particles with a mean particle size of 1–2 μm.

As shown in Figure 6, compaction pressure affected particle size. As the compaction pressure increased from 160 to 640 MPa, the W particle size increased from 1 to 5 μm. This may mean that the higher compaction pressure caused higher density of the green pellets and larger contact area among the reactants. In addition, better contact of the reactants can cause higher reactivity, which increases combustion temperature. Thus, we believe that the particle growth of the products under higher compaction pressure resulted from the higher combustion temperature.

The chemical composition of the W powder produced, as analyzed by ICP, is as follows (in wt%): 99.98 W, 0.0007 K, 0.003 Fe, 0.006 Na, 0.005 Mg, and 0.006 Al. Ca was not detected. The overall purity of 99.98% is greater than that of the starting materials. This is due to the vaporization of impurities at the high combustion temperature, which results from the high exothermic reaction as well as their dissolution in the leaching acid solution.

CONCLUSIONS

For the complete reduction of WO_3, an excess addition of Mg was necessary in the WO_3:xMg and WO_3:2.1Zn:xMg systems. The concurrently formed MgO and ZnO were easily eliminated by leaching the products in 100 ml 6.5 M HCl solution at 80°C for 40 min. Increased compaction pressure caused better contact among reactants and maintained the reaction heat in the samples for longer times and at higher temperatures. This made the products rounder and larger. It was possible to control the W particle size from 1 to 5 μm by varying the compaction pressure. The W powder produced had a higher purity than the reactant, because of the vaporization of impurities during SHS reaction and the dissolution by the leaching solution.

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