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FABRICATION OF ULTRAFINE ALLOYED POWDERS BY SODA REDUCTION PROCESS

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Abstract. Ultrafine powders of tungsten-based alloy (W-Ni-Fe) and zirconium carbide (ZrC) were synthesized by a soda reduction process, which is newly proposed in this study. Ultrafine-sized tungsten alloy powders were synthesized with ammonium metatungstate (AMT), iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), and nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) as source materials and sodium tungstate dehydrate ($Na_2WO_4 \cdot 2H_2O$) as a reductant. In the preparation of mixtures, the amounts of the source components were chosen to obtain a composition of 93W-5Ni-2Fe. Nano-sized zirconium carbide (ZrC) powders were fabricated by source materials of zirconium(IV) chloride ($ZrCl_4$) and carbon black, and a reductant of sodium bicarbonate ($NaHCO_3$). ZrC powders with about 150 nm in size were successfully obtained after heat treatment at 1637K.

1. INTRODUCTION

Tungsten heavy alloys consisting of tungsten (W) as a main phase along with Ni, Fe, Co, and Cu have been studied for many years due to unique properties such as high density, high elastic stiffness, improved mechanical properties, good corrosion resistance, and easy machining [1]. There are several conventional methods for the fabrication of tungsten heavy alloys such as mechanical alloying, electro-deposition technique [2], and metal injecting molding [3].

Zirconium carbide (ZrC) is emerging as a candidate for ultrahigh temperature applications because of its high melting temperature (~3805K), solid-state phase stability, good thermo-mechanical and thermo-chemical properties, and other desirable properties including high hardness and wear resistance [4]. Several possible methods for fabricating ZrC powder have been studied such as direct carbonization using pure zirconium and carbon [5], and carbothermal reduction of zirconia [6]. In this study, novel reduction methods to fabricate ultrafine alloyed powders using cost-effective source materials were investigated in detail.

2. EXPERIMENTAL PROCEDURES

Ammonium metatungstate (AMT), iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), nickel(II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) used as source materials and sodium tungstate dehydrate ($Na_2WO_4 \cdot 2H_2O$) chosen as a reducing agent were mixed together to obtain an alloy having a composition of 93W-5Ni-2Fe. The mixture dissolved in distilled water was dried and then heated at 773K for 2 hours in air for decomposition and formation of oxide phases. The products were washed out from soluble components in water, and the oxide phases were finally reduced by H_2 gas at 1073K for 2 hours.

An excess of 6 moles of sodium bicarbonate ($NaHCO_3$) mixed with 1 mole of zirconium chloride ($ZrCl_4$) was ball-milled for 5 hours in argon atmosphere, and then the mixture was heated at 773K

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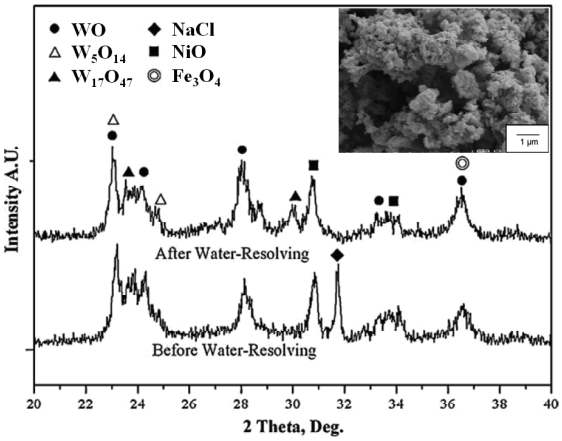

Fig. 1. X-ray diffraction patterns and FESEM image of the precursor.

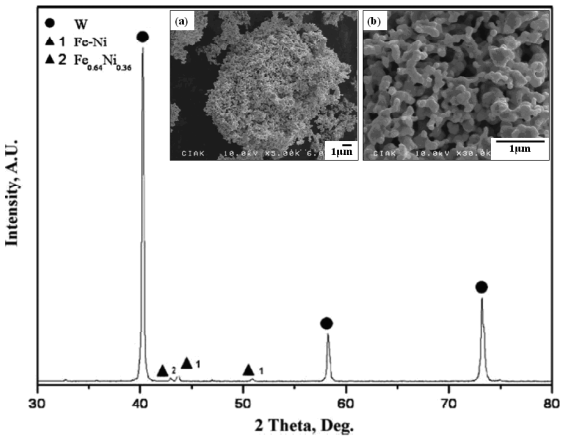

Fig. 2. XRD patterns and FESEM images of the composite powder synthesized at 800 °C for 2 hrs under flowing H_2 gas: (a)×6,000 and (b)×30,000.

under the same condition. The mixture prepared with 1 mole of $ZrCl_4$, 6 moles of $NaHCO_3$, and 4 to 8 molar factions of carbon black was ball-milled again and then heated at the temperature range from 1473 to 1673K in argon atmosphere. After heat treatment, an undesirable NaCl or other Na-containing compounds was removed by washing them out using distilled water. The two different powders synthesized were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), and field emission microscope (FESEM). The chemical composition of each powder was also identified by energy dispersive X-ray analysis (EDX).

3. RESULT AND DISCUSSION

The synthesis to fabricate ultrafine powders of the tungsten based alloy (W-Ni-Fe) was conducted at two reduction stages. The first stage was to decompose the precursor to obtain oxide phases. Fig. 1 shows the X-ray patterns of the precursor after decomposition at 773K in air. The major reflections corresponded to tungsten oxides with different phases, and NaCl was found to be completely removed by washing the mixture out using water owing to its good solubility in water. The microstructure of the precursor was examined by FESEM, and the composite powder agglomerated was observed with an average size of 0.1~0.5 μm. The second stage was the hydrogen reduction of the precursor at 1073K for 2 hours. According to Lassner and Schubert [7], the reduction of WO_3 can be divided into two steps: (i) oxygen transport by solid state diffusion ($WO_3 \rightarrow WO_{3-X}$ in Eqs. (1) and (2)) and (ii) tungsten transport by chemical vapor transport ($WO_{3-X} \rightarrow W$ in Eqs. (3) and (4)):

$$WO_3(s) + H_2(g) \rightarrow WO_{3-\chi}(s) + \chi H_2O(g), \quad (1)$$

$$WO_{3-\chi}(s) + H_2(g) \rightarrow W(s) + (3-\chi)H_2O(g), \quad (2)$$

$$WO_{3-\chi}(s) + (1-\chi)H_2O(g) \rightarrow WO_2(OH)_2(s) + \chi H_2(g), \quad (3)$$

$$WO_2(OH)_2(g) + 3H_2(g) \rightarrow W(s) + 4H_2O(g). \quad (4)$$

During the reduction process, it might be assumed that nickel and iron components were previously reduced before the tungsten due to the low reduction temperature of them.

Fig. 2 demonstrates X-ray diffraction patterns and FESEM images of the composite powder reduced at 1073K for 2 hours in H_2 gas, and it was observed that the main phase of BCC structured W-rich phase was detected, and small amounts of Fe-Ni phases were observed as well. The microstructure of the synthesized composite powder was found to be strongly agglomerated with an average size of 5-10 μm in Fig. 2a, and the composite had relatively dense net-shaped structure of the grains with different size less than 0.5 μm having macro-pores observed in high magnification in Fig. 2b.

The chemical composition of the synthesized powder was analyzed by EDX, and the distribution of the particles in the alloy matrix was also examined using a mapping technique shown in Fig. 3. Quantitative EDX analysis showed that W-Ni-Fe composite was made up of about 93.5 mass.%W - 4.6 mass.%Ni -1.9 mass.%Fe, which is very close to the preferred composition of 93W-5Ni-2Fe. The

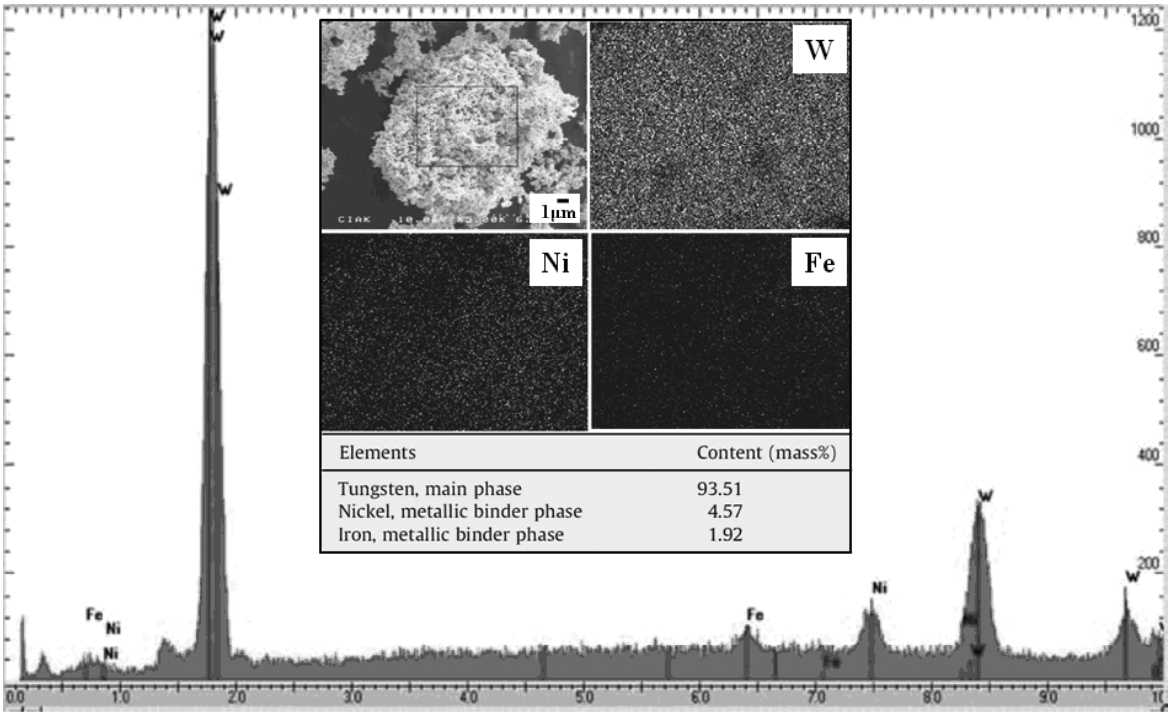

Fig. 3. Chemical composition of matrix phase and mapping analysis of the synthesized W-Ni-Fe examined by EDX.

result of mapping analysis revealed that all elements were uniformly distributed throughout the matrix of the synthesized ternary alloy system.

Fig. 4a indicates the XRD patterns of the initial materials (1 mole of $ZrCl_4$ and 6 moles of $NaHCO_3$) simply mixed. After ball-milling, the mixture was transformed into NaCl phase without any other crystal phases shown in Fig. 4b. It might speculate that zirconium and oxygen components exist as an amorphous phase. The XRD patterns of ball-milled powder heated at 773K in argon atmosphere were shown in Fig. 4c and the broadened peaks of ZrO_2 observed might indicate the typical amorphous profile. Such an amorphous phase of ZrO_2 may be kinetically more effective for carbonization into ZrC than stable zirconium oxide as the initial material.

XRD patterns of the powder heated for 4 hours at each temperature under argon atmosphere after stirring in water were shown in Fig. 5. It was found that Na-component was not detected, since the NaCl and Na_2O could readily dissolved in water. As temperature increased, the ZrC phase continually increased to reach the high content, while the ZrO_2 phase was shown to tend to disappear. Finally, the clean and full ZrC crystalline phase only appeared in the sample synthesized at 1673K. Final particles of the powder synthesized at 1673K were examined by FE-SEM to confirm the particle size. It was observed that almost spherical shape of ZrC particles was obtained with small crystalline sizes between 70 and 200 nm, which is one of the many advantages of low-temperature synthesis of ZrC.

In addition to the particle size, the carbon content in synthesized ZrC powder was also an important factor to minimize the free carbon. Fig. 6 dem-

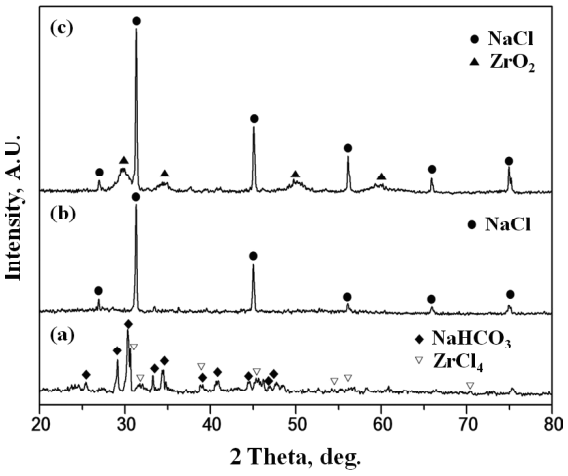

Fig. 4. X-ray diffraction of the powder at each step: (a) Simply mixed with $ZrCl_4$ and $NaHCO_3$; (b) Ball-milled powder; (c) Heat-treat ball-milled powder at 773K in Ar gas.

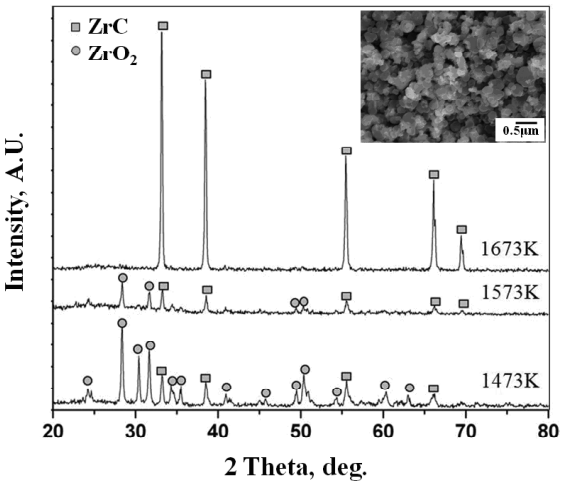

Fig. 5. X-ray diffraction pattern of the powder synthesized at each temperature and FESEM image of ZrC powder synthesized at 1673K.

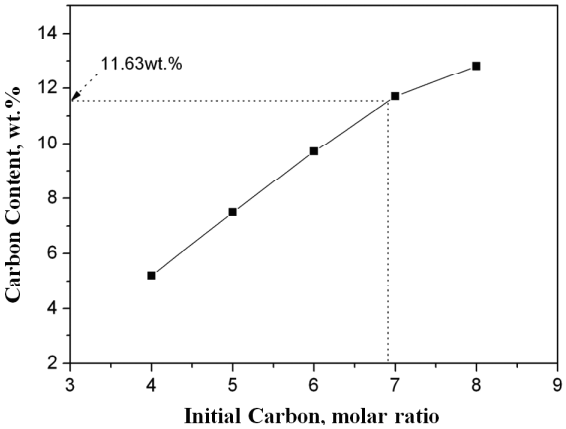

Fig. 6. Carbon content in synthesized powder as a function of the initial molar ratio.

onstrates a plot of the carbon content measured in the final traced powders as a function of the initial carbon. This plot indicates that addition 7 moles of initial carbon yielded 11.68 wt.% of carbon content, which is almost same as the stoichiometric carbon content of 11.63 wt.%.

4. CONCLUSIONS

The tungsten-based alloy powder with a chemical composition of 93W-5Ni-2Fe was successfully synthesized by a novel soda process. The decomposed precursor was found to be made up of oxide phases of W, Ni, and Fe along with small amounts of undesired NaCl phase, which was completely removed by washing in distilled water. Finally, the synthesized alloy powder of ternary system with 93.5mass% W-4.6mass% Ni-1.9%mass Fe was obtained under flowing H_2 gas at 1073K for 2 hours.

The ultrafine ZrC powder using $ZrCl_4$, carbon powder, and $NaHCO_3$ was successfully synthesized by a novel reduction process. It was found that final powders synthesized at 1673K consisted of the full ZrC phase, and an average crystalline size of this phase was about 150 nm. Compared to the carbothermal reduction of ZrO_2, this proposed process was very effective in fabricating ZrC powders with good stoichiometry at low temperature.

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