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# HYDROGEN REDUCTION BEHAVIOR AND MICROSTRUCTURE CHARACTERISTICS OF $WO_3$-NiO-CuO POWDER MIXTURE

The characteristics and hydrogen reduction behavior of W-0.8 wt% Ni-0.4 wt% Cu powder synthesized from $WO_3$-NiO-CuO composite powder have been investigated. The metal oxide powder mixtures were prepared using a ball milling process. XRD analysis and HR-TEM revealed that the oxide powders are changed to W and CuNi alloy powders with an average particle size of about 100 nm by hydrogen reduction. To understand the reduction behavior of oxide powders, TG analysis was performed, and the reduction kinetics was evaluated by the amount of peak shift with heating rates. The activation energies for the reduction of $WO_3$-NiO-CuO, estimated by the slope of the Kissinger plot, were measured as 60.6-114.4 kJ/mol depending on reduction steps.

*Keywords:* W-Ni-Cu alloy; Oxide powder mixture; Hydrogen reduction behavior; Microstructure

## 1. Introduction

Tungsten (W) is a promising high temperature material that exhibit high melting point, low thermal coefficient, and high temperature strength [1]. However, a major drawback for its use is the inherent high ductile-brittle transition temperature, poor ductility and low sinterability due to high melting point [2]. Meanwhile, much attention has been paid to the fabrication of W heavy alloy (WHA) consisting of W particles embedded in a ductile matrix phase with lower melting point elements up to 10~20 wt% such as Ni, Fe, and Cu. Due to the unique combination of high density, high strength and ductility, good machinability, and thermal conductivity, WHA is employed in many engineering applications such as radiation shields, vibration dampers, kinetic energy penetrators and rocket nozzles [3,4]. The powder mixture of WHA is usually prepared by high energy ball milling of elemental metal powders. However, this process induced contamination by impurities and formation of coarse aggregates in the milled powders that is harmful to fabrication of homogeneous powder mixture [5].

To overcome these problems, a mechanochemical processing that consists of ball milling of metal oxides instead of metal powders and a subsequent hydrogen reduction has been used [6]. Considering that metal oxide powder is more brittle than metal powder, WHA can be fabricated finer and more homogeneous by ball milling using metal oxide powder as a raw material. In this process, understanding of the reduction behavior of metal oxides and microstructure control are important for the fabrication of alloy powders having required properties. We have attempted to find a new processing route for fabricating W-Cu-Ni alloy powders by ball milling and hydrogen reduction of $WO_3$-NiO-CuO powder mixtures. The reduction behavior of ball-milled mixtures is evaluated by thermogravimetric analysis with different heating rates in $N_2$-10% $H_2$ atmosphere. Moreover, we discuss the effect of the powder processing condition on the microstructure of synthesized alloy powders. This will help to optimize the powder synthesis process and to understand the hydrogen reduction behavior.

## 2. Experimental

Tungsten trioxide ($WO_3$, 99.9%, 0.2 μm), nickel oxide (NiO, 99%, <44 μm), and cupric oxide (CuO, 99.9%, 1 μm) were used as starting powders. Weighed oxide powders, corresponding to W-0.8 wt% Ni-0.4 wt% Cu, in the final alloy, were ball-milled in a 3D mixer for 5 h using high purity yttria-stabilized zirconia balls instead of metal-based alloy balls to minimize metal im-

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purities. The ball-to-powder weight ratio was 5:1. The powder mixtures were heated at 800°C in hydrogen atmosphere for 2 h to reduce the oxides to W-Ni-Cu alloy.

The reduction behavior of $WO_3$-NiO-CuO powders was measured by thermogravimetric analysis (TGA) method with different heating rates of 2, 5, 10, and 20°C/min in $N_2$-10% $H_2$ atmosphere. Phase identification of the powders was determined by X-ray diffraction (XRD, Miniflex 300, Rigaku Denki). The morphology of the powders was observed by field emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL). High resolution transmission electron microscopy (HR-TEM, NEO ARM, JEOL Ltd.) were used for microstructure analysis.

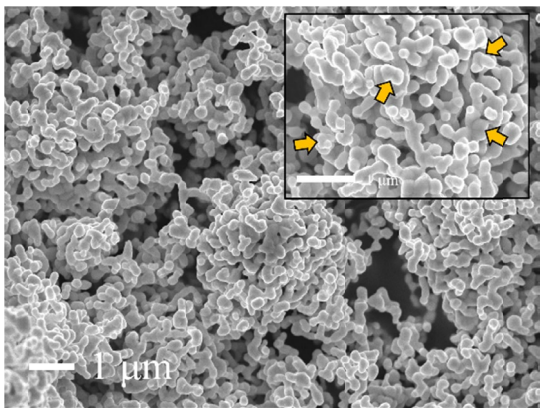


Fig. 2. Powder mixture after hydrogen reduction at 800°C for 2 h. Regions showing neck growth are indicated by arrows

### 3. Results and discussion

Typical SEM images of starting $WO_3$, NiO and CuO powders are shown in Fig. 1(a-c), respectively. $WO_3$ and CuO powders had aggregates of nano-sized particles, and NiO exhibited a relatively large particle size. After ball milling for 5 h, the powder mixture showed a homogeneous agglomerates consisting of refined starting powders, as shown in Fig. 1(d). Microstructure of hydrogen-reduced powder mixture is shown in Fig. 2. As clearly seen in magnified image, fine particles of about 100 nm in size with partially grown necks (arrowed) were observed in the reduced powder mixture.

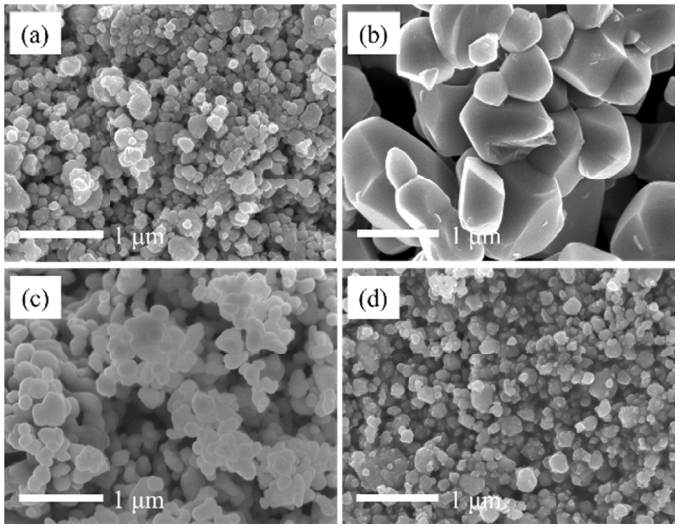


Fig. 1. SEM morphologies of (a) $WO_3$, (b) NiO, (c) CuO raw powders, and (d) ball-milled $WO_3$-NiO-CuO powders

Fig. 3 shows the XRD profiles for the ball-milled and hydrogen-reduced powders. As shown in Fig. 3(a), the diffraction lines corresponding to $WO_3$, NiO and CuO can be observed in the ball-milled powders. After hydrogen reduction at 800°C for 2 h, the powder mixture was composed of W, CuNi and Si phase for baseline correction in which CuNi peak represented weak intensity because of low content of CuO and NiO (Fig. 3b). This result is suggested that during the hydrogen reduction of the powder mixtures, all oxide powders were reduced, and Ni and Cu formed a solid solution. For further characterization of reduced microstructure, HR-TEM analysis was performed. As shown in Fig. 4, the selected area electron diffraction (SAED) pattern reveals the existence of W and CuNi, corresponding to XRD profile in Fig. 3(b). Also, $(1\bar{1}0)$ plane of body-centered cubic W and $(\bar{1}11)$ plane of face-centered cubic CuNi are detected in fast Fourier transform (FFT) pattern [7,8]. These results suggested that a novel synthesis, ball milling of oxide powders and subsequent hydrogen reduction process, is one of the useful routes for producing the powder mixtures of W and CuNi alloy phases.

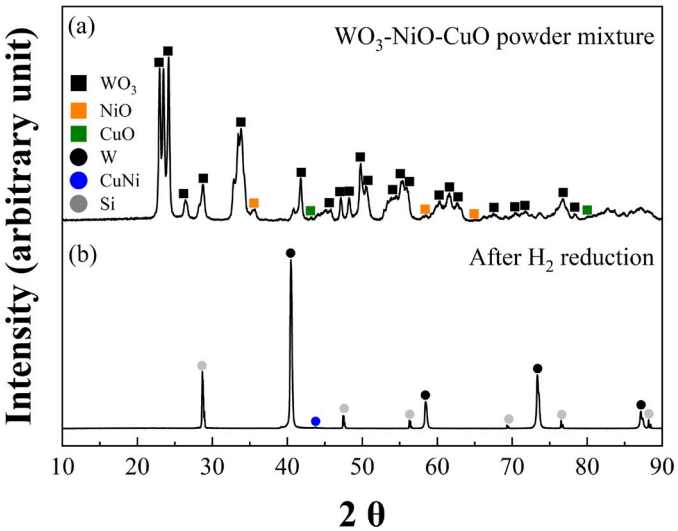


Fig. 3. XRD profiles of (a) ball-milled $WO_3$-NiO-CuO and (b) hydrogen-reduced powders

The hydrogen reduction behavior of $WO_3$-NiO-CuO powder mixtures was investigated by a non-isothermal analysis using TGA with different heating rates in $N_2$-10% $H_2$ atmosphere. Fig. 5(a) represents the relative weight during heat up of powder mixtures. The curves show that the powder mixtures undergo a weight loss in the three temperature ranges of 368-482°C (designated as $T_{m1}$), 393-535°C ($T_{m2}$) and 655-791°C ($T_{m3}$). Considering the reduction behavior of metal oxides reported in [9,10], it is proposed that the temperature range of $T_{m1}$ is related

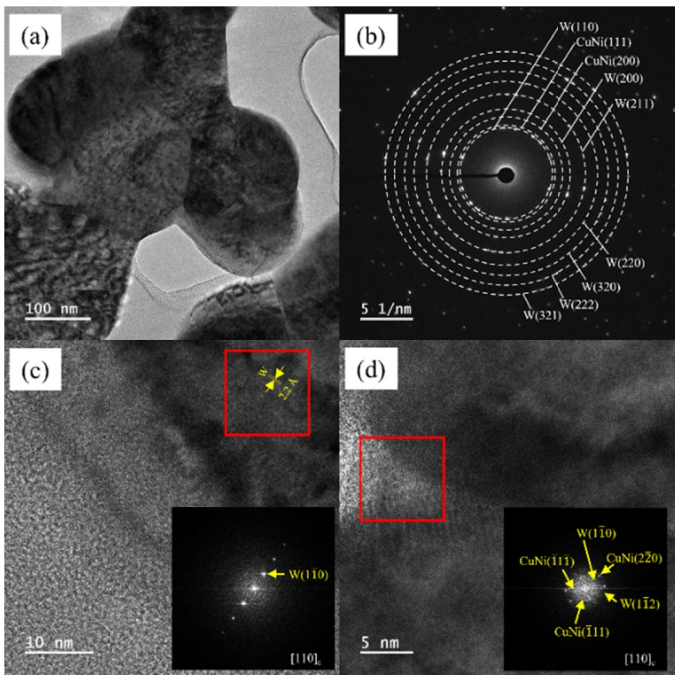


Fig. 4. HR-TEM analysis of the reduced powder mixture: (a) TEM image, (b) SAED pattern and (c, d) HR-TEM images (inset: FFT patterns) for W and CuNi phases

to the reduction of NiO, and the ranges of $T_{m2}$ and $T_{m3}$ is assigned to the reduction process of $WO_3$. However, in the case of CuO, no significant weight loss was observed in the TGA curve due to the small amount of addition of 0.4%.

Reduction kinetics of these powders were evaluated by the amount of peak shift with heating rates in TGA. As shown in Fig. 5(a), maximum peak temperature ($T_m$), obtained by differentiating the weight loss curve, shifts to higher temperature with increasing heating rate. In non-isothermal mode, the Kissinger method assumes that the reaction rate reached the maximum at peak temperature and determines the apparent activation energy [11]:

$$\ln\left(\frac{\beta}{T_m^{\,2}}\right) = -\frac{Q}{R}\cdot\frac{1}{T_m} + constant$$

where $\beta$ is heating rate, $T_m$ is the peak temperature, $R$ is the gas constant, and $Q$ is the activation energy. Thus, from a plot of $\ln(F/T_m^{\,2})$ versus $1/T_m$ as shown in Fig. 5(b), the kinetics constant and apparent activation energy for the reduction process could be obtained. The values of apparent activation energy calculated by Kissinger method are summarized in TABLE 1.

TABLE 1

Kinetic analysis by Kissinger plots

| | Temperature range (°C) | Activation energy (kJ/mol) | Reaction process |
|---|---|---|---|
| $T_{m1}$ | 368~482 | 69.6 | NiO → Ni |
| $T_{m2}$ | 393~535 | 60.6 | $WO_3$ → $WO_2$ |
| $T_{m3}$ | 655~791 | 114.4 | $WO_2$ → W |

The apparent activation energy calculated from the slope of Fig. 5(b) exhibits value of 69.6 kJ/mol for the peak temperature of $T_{m1}$. This value coincides with the reported activation energy for the reduction process of NiO to Ni which were obtained in non-isothermal heating in Ar-10% $H_2$ atmosphere [12]. Also, Table 1 shows that the activation energies for the peak temperature of $T_{m2}$ and $T_{m3}$ are 60.6 kJ/mol and 114.4 kJ/mol, respectively. It is reported that the reduction of $WO_3$ to $WO_2$ and $WO_2$ to W are characterized by activation energy values of 104-117 kJ/mol and 83-95 kJ/mol, respectively [13,14]. Considering that there are few studies on the reduction behavior of $WO_3$-NiO-CuO composite powders available in literature, it is difficult to explain the exact meaning of the measured values of activation energy in this study. Nevertheless, it is possible to explain that the difference between the measured and the reported activation energies is mainly attributed to the effect of pre-reduced Cu on the reduction process of $WO_3$ and the analysis conditions.

## 4. Conclusions

In this study, W-Ni-Cu composite powders were prepared by ball milling and hydrogen reduction of metal oxide powders, and the understanding the hydrogen reduction behavior and characterization of powder mixtures were conducted. Microstructure analysis revealed that the oxide powders could be completely reduced to metallic phases, resulting in the formation of W and CuNi alloy phases with an average particle size of about

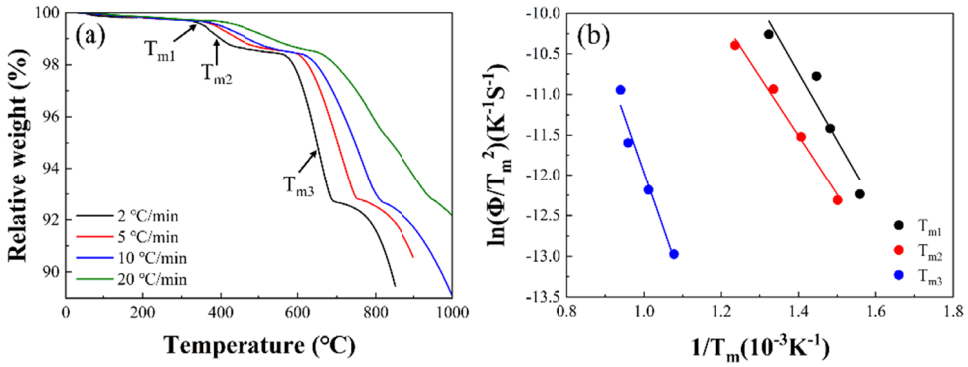


Fig. 5. (a) TGA curves for $WO_3$-NiO-CuO powder mixture, scanned at different heating rates in $N_2$-10% $H_2$ atmosphere, and (b) Kissinger plots for the reduction of powder mixtures from (a)

100 nm. The reduction behavior of oxide powder mixture was investigated by a non-isothermal analysis using TGA with different heating rate in $N_2$-10% $H_2$ atmosphere. The apparent activation energies, estimated by Kissinger method, had values of 69.6 kJ/mol for the reduction of NiO, 60.6 kJ/mol for the reduction of $WO_3$ to $WO_2$ and 114.4 kJ/mol for the reduction of $WO_2$ to W. A difference between the measured and the reported activation energies is explained by the effect of pre-reduced Cu on the reduction process of $WO_3$ and the analysis conditions.

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