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Synthesis of WC–20 wt. % Cu composite powders by co-precipitation and carburization processes

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WC/Cu composite powders were synthesized by co-precipitation and subsequent reduction-carburization process. The precipitates contained W-Cu compounds fabricated using a chemical procedure from a mixture of copper nitrate and ammonium paratungstate in distilled water. In order to synthesize the WC-Cu composite powders, dried precipitates were calcined at 823 K in air and then reduced and carburized by carbon monooxide (CO). The non-isothermal mechanism of reduction-carburization of the calcined powders in carbon monoxide was investigated by thermogravimetry, differential thermogravimetry and X-ray diffraction analyses. The optimum reduction-carburization temperature was determined as 1065 K. The microstructures of the powders were characterized by the scanning electron microscopy.

Keywords: *WC-Cu composites; reduction; carburization; thermogravimetry*

1. Introduction

Electrical contact materials should be characterized by a good combination of electrical conductivity, wearing qualities and resistance to erosion and welding [1]. WC-Cu contacts have high thermal conductivity as well as high electrical conductivity, because of their copper content. They also have high wear resistance, because of the hardness of tungsten carbide. WC-Cu contacts are therefore used in oil switches and wiping shoes in power transformers [2]. These kinds of materials, due to excellent wetting characteristics between tungsten carbide and copper as well as the limited solubility of tungsten in copper, are composites rather than solid solutions [3, 4].

A conventional method to synthesise these kinds of materials is infiltration of copper into a tungsten carbide skeleton, but infiltration does not result in a homogene-

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ous microstructure and is not a net shape process, being unsuitable for mass production [5, 6]. Other than infiltration, WC-Cu metal matrix composites could be prepared by a powder metallurgy process, namely by blending and sintering WC and Cu powders [7]. However, it has been shown that by using composite powders instead of blending the constituents, the densification of the composite increases significantly. For these kinds of powders, the effectiveness of sintering can be enhanced by improving the homogeneity and decreasing the particle size of the starting powders. This is especially true for a liquid phase sintering system, such as for WC-Cu materials [8, 9].

In this study, in order to prepare WC-Cu composite powders, a new co-precipitation method, followed by calcination of the precipitates, was used to obtain a homogeneous mixture of W-Cu oxide powders. Subsequently, the oxide powders were reduced and then carburized by carbon monoxide. The mechanisms of reduction and carburization of oxide powders were investigated by TG, DTG and XRD analyses.

2. Experimental

Blue coloured copper nitrate ($Cu(NO_3)\cdot 3H_2O$), >99% purity, Merck, Germany) and white coloured ammonium paratungstate ($H_{42}N_{10}O_{42}W_{12}\cdot xH_2O$, >99% purity, Riedel-de Haen, Germany) were used as precursors.

In order to synthesise the initial precipitates with the desired weight proportion of copper and tungsten carbide (equal to 4), a predetermined mixture of ammonium paratungstate and copper nitrate in distilled water was heated to 358–368 K. In order to adjust pH to 3–4, ammonia solution was added to the mixture dropwise. The process was continued for 3 h. Then the precipitates were washed, dried and calcined at 823 K for 2 h in air. Thermogravimetry and differential thermogravimetry (Netzsch STA 409 PC/PG) analyses were carried out in carbon monoxide (CO) atmosphere with the heating rate of $7.5\ K\cdot min^{-1}$ and $50\ cm^3\cdot min^{-1}$ gas flow up to 1273 K. In order to characterize the weight loss stages revealed by thermogravimetry (TG) analyses, oxide powders reduced/carburized by carbon monoxide in a tube furnace were examined by the differential thermogravimetry method (DTG). The heights of the bed powders were 1 mm. The powders were characterized by X-ray diffraction (XRD-Jeol 8030, CuK_{α}) and scanning electron microscopy (SEM, Cambridge S360).

3. Results and discussion

3.1. Characterization of the initial and calcined precipitates

Figure 1 shows the XRD pattern of initial precipitates. According to this pattern, the precipitates consisted of APT and another chemical compound which cannot be identified by XRD patterns. Based on the applied chemical process, the latter compounds should contain W, Cu, NH_3 and H_2O. It may be believed that due to the heating of the solution which contained $Cu(NH_3)_4(H_2O)^{2+}{}_2$ complex ions, NH_3 evaporated and was replaced by para A ($HW_6O_{21}^{5-}$) or para B ($H_{10}W_{12}O_{46}^{10-}$) ions which existed in the media because of a low solubility of APT in distilled water. The SEM micrograph of the initial precipitates is shown in Fig. 2. This figure shows the morphology of the dried precipitates: they have granular shapes and are of submicron size.

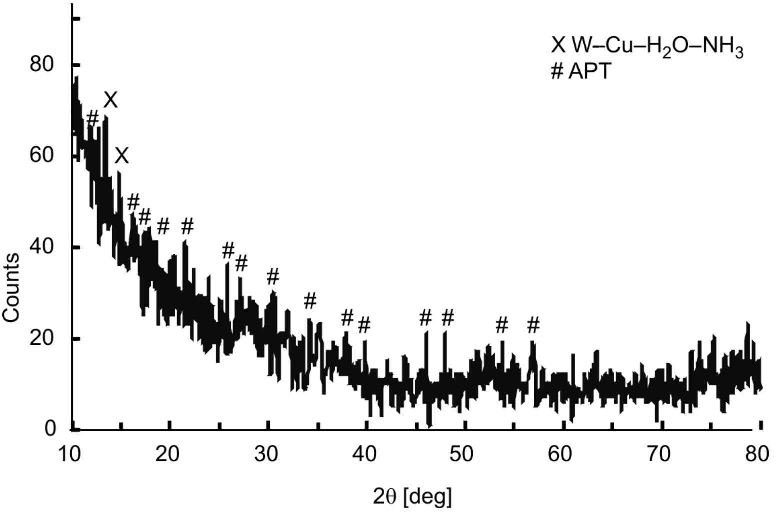

Fig. 1. XRD patterns of the initial precipitates

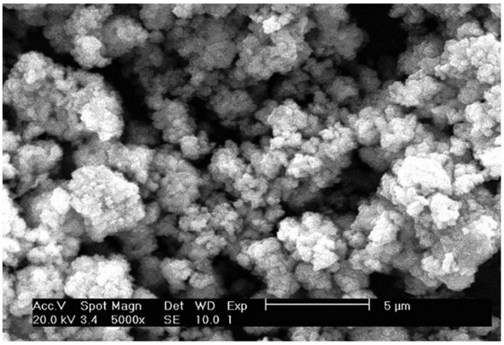

Fig. 2. SEM micrographs of the initial precipitates

The XRD pattern of the calcined powder is shown in Fig. 3. The calcined powders consisted of WO_3 and $CuWO_4$ phases. The SEM micrograph of the calcined powders is shown in Fig. 4. This figure shows that the particle sizes of the calcined powders have a wide distribution range and that the particles have spherical morphologies.

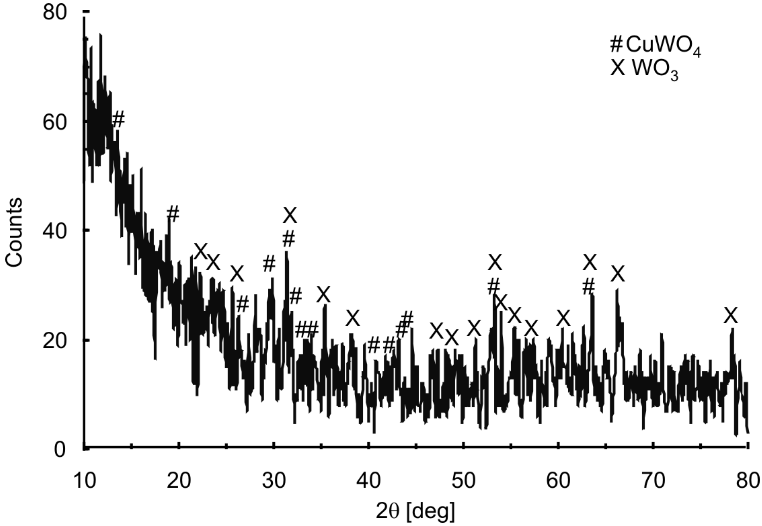

Fig. 3. XRD patterns of the calcined precipitates at 823 K

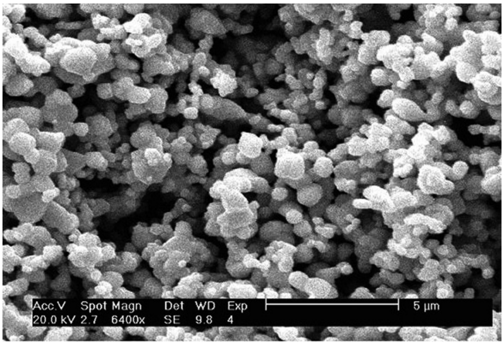

Fig. 4. SEM micrograph of the calcined powders at 823 K

3.2. Reduction-carburization of the oxide powders

3.2.1. TG/DTG analyses

Figures 5a (experimental curve) and 5b show TG and DTG curves of the oxide powders in carbon monoxide atmosphere. The TG curve shows two weight losses and one mass gain stages. These stages occur between 718 and 833 K, 928 and 1179 K and above 1179 K, respectively. The DTG curve exhibits two peaks at 756 K and 1065 K corresponding to the weight loss stages. The XRD pattern of the product of the first stage reaction is shown in Fig. 6. The first weight loss stage corresponds to reduction of CuWO$_4$. The reaction for the first weight loss stage is:

$$CuWO_4 + CO \rightarrow Cu + WO_3(WO_{2.9}) + CO_2 \tag{1}$$

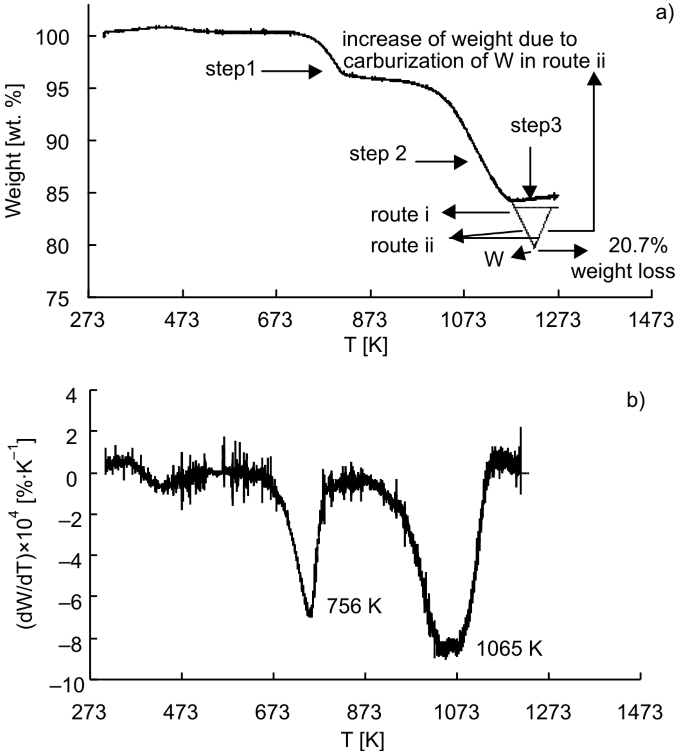

Fig. 5. TG (a) and DTG curves of oxide powder from room temperature to 1273 K in CO atmosphere

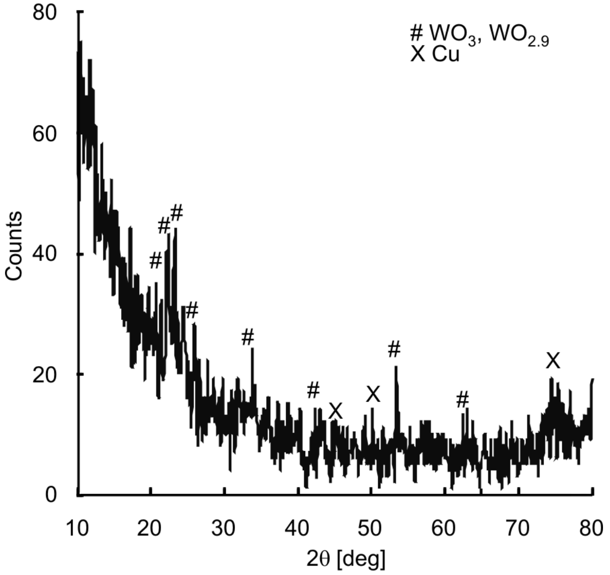

Fig. 6. XRD pattern of the reduced powder at 756 K for 1 h

It is worth noting that one or both of WO_3 ($WO_{2.9}$) oxide phases might have been formed, but according to the XRD observations the formation of WO_3 is the more probable. This result is due to the similar XRD pattern of these oxide phases. $WO_{2.9}$ is a simplified form of $W_{20}O_{58}$ oxide phase. According to the TG analysis, the corresponding weight loss of the first reaction is 3.85%. The theoretical weight loss for this step is 4% which is in agreement with experimental results.

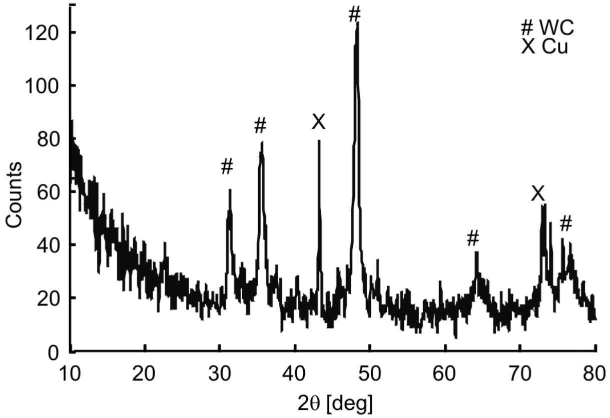

Fig. 7. XRD pattern of reduced and carburized powders at 1065 K for 6 h

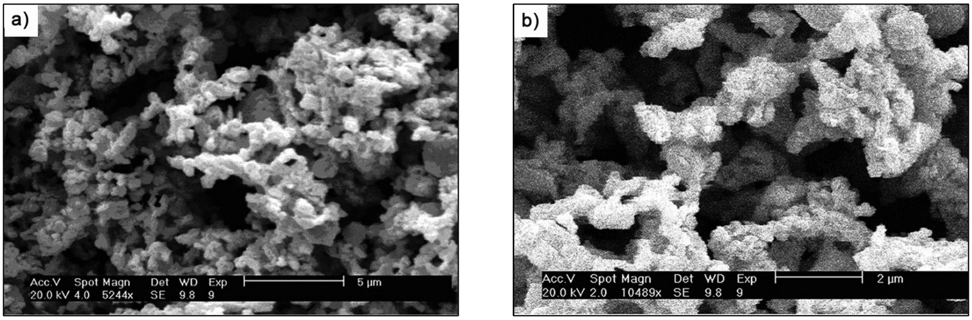

Fig. 8. SEM micrographs of reduced and carburized powders at 1065 K for 6 h in two magnifications (a, b)

The XRD pattern of the product of the second stage weight loss step is shown in Fig. 7. The product of the second reaction consisted of Cu and WC and. The SEM micrographs of the reduced and carburized powders at different magnifications are shown in Fig. 8. The images show that the agglomerates consist of several primary particles (~300–500 nm) having a worm-shape morphology.

The proposed reaction for this step is carburization of WO_3 ($WO_{2.9}$) to WC. The total weight loss of the reduction-carburization process is 15.9%. The theoretical weight loss after the second weight loss step is 16.47%. According to the results, the theoretical value is about 0.57% higher than the weight loss which has been determined by TG analysis. The reason for this difference between the experimental and theoretical values might be due to deviation of the results and deposition of carbon according to the following reaction [9]:

$$2CO \rightarrow C + CO_2 \tag{2}$$

Also, the mass gain in the third stage of the TG analysis may be considered to be associated with carbon deposition, corresponding to reaction (2) [9]. According to the above results, the optimum temperature for the reduction-carburization process is 1065 K. At this temperature, the oxide phases (WO_3 and $CuWO_4$) could be completely reduced to Cu and WC.

3.2.2. Carburization of WO_3 to WC

Carburization of WO_3 to WC has been investigated by other authors [9, 11]. According to the results of Venables et al., the carburization can proceed by the following routes [9]:

$$WO_3 \rightarrow WO_{2.9} \rightarrow WO_{2.72} \rightarrow WO_2 \rightarrow WC \tag{i}$$

$$WO_3 \rightarrow WO_{2.9} \rightarrow WO_{2.72} \rightarrow WO_2 \rightarrow \alpha\text{-}W \rightarrow WC \tag{ii}$$

$$WO_3 \rightarrow WO_{2.9} \rightarrow WO_{2.72} \rightarrow \alpha\text{-}W \rightarrow WC$$

$WO_{2.72}$ is a simplified form of $W_{18}O_{49}$ oxide phase.

The difference of the two routes is that in the former one WO_2 directly converts to WC, and in the latter one WO_3 was reduced completely to W and then W carburized to WC. According to the TG curve in this study (Fig. 5a), the dominant mechanism of the non-isothermal carburization of WO_3 with CO is the first one. The reason for this conclusion is the formation of W in the reduction process of the second route. In other words it can be shown that although at the end of the two routes WC forms and the total weight losses of the both processes differ only by 0.57% from the experimental value, the curve of the weight versus temperature of route (ii) has a minimum peak because of the formation of W and then shows an increase in weight due to carburization of this agent. This profile is not in a good agreement with the experimental curve. However, the aforementioned minimum weight loss peak does not exist in route (i), and the reduction/carburization curve is similar to the experimental one (Fig. 5a).

4. Conclusion

WC-Cu composite powders were synthesized by the co-precipitation and a subsequent reduction-carburization method. The process consisted of precipitation of the initial powder using ammonium para-tungstate and copper nitrate as raw materials, calcination the precipitates and reduction of the calcined powders by carbon monoxide. The reduction-carburization process of WO_3 and $CuWO_4$homogeneous mixture in CO atmosphere proceeded as:

$$CuWO_4, WO_3 \rightarrow Cu, WO_3(WO_{2.9}), WO_3 \rightarrow Cu, WC$$

The optimum reduction-carburization temperature of the mixture was 1065 K.

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