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MICROSTRUCTURE AND HYDROGEN-REDUCTION BEHAVIOR OF HIGH ENERGY BALL MILLED CuO-SnO_2 POWDER MIXTURE

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Abstract. The CuO and SnO_2 powders with the mean powder size of approximately 2 mm were mixed and ball-milled at a rotation rate of 800 rpm for 5 h, their microstructure and reduction characteristics were investigated. The mixed powder size became smaller to approximately 0.7 mm after milling, which consisted of the nano-sized particles with approximately 45 nm in diameter. In the milled mixture, there existed the CuO and SnO_2 phases. The reduction reactions of CuO and SnO_2 powders occurred at about 250 and 545 °C respectively. However, as-milled CuO-SnO_2 powder mixture showed three reduction reactions at around 250, 500, and 545 °C, which related to the reactions of CuO $\rightarrow$ Cu, SnO_2 $\rightarrow$ SnO and SnO $\rightarrow$ Sn, respectively.

1. INTRODUCTION

Ceramic materials with grain sizes of the submicrometer (<0.5 μm) have received a great interest due to their special properties. Among them, CuO has wide industrial applications such as solar cells, gas sensors, optical technology, antiwear systems and nanofluids [1]. And SnO_2 has been also used in nanoparticles, nanotubes, nanowires, nanorods and hollow microspheres [2]. In particular, SnO_2 nanomaterials with unique structure were expected to have improved electrochemical performance. Especially, the CuO-SnO_2 nanocomposites have been studied as gas sensor materials [3] or electrochemical materials [4].

High energy ball milling is a process of mechanical alloying (MA) that starts with the powder along with the grinding medium (STS balls), then mills for the desired length of time at very high speed [5]. Due to very high rotation rate, the collision energy supplied to the powders is very high, resulting in very fast process and obtained fine powder than normal ball milling.

In this study, therefore, we focused on fabricating the powder mixture consisting of CuO and SnO_2 powders by the high energy ball milling, and investigated the microstructure and hydrogen-reduction characteristics.

2. EXPERIMENTAL PROCEDURE

The CuO-SnO_2 powder mixture was ball-milled under a high purity argon atmosphere using 5 mm stainless steel balls. The weight ratio of ball to powder was 20:1 and the mixed powders were ball milled at a rotation rate of 800 rpm for 5 h. Milled powder

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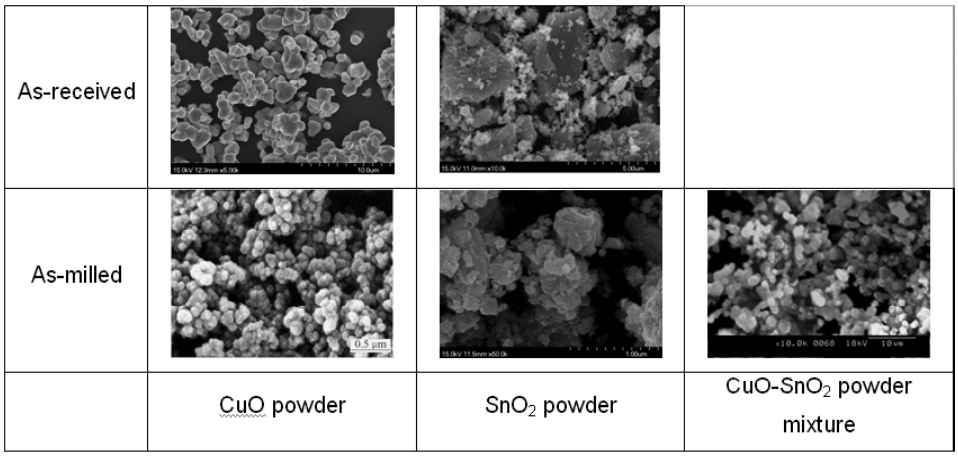

Fig. 1. SEM images showing as-received and as-milled CuO, SnO_2 powders, and CuO-SnO_2 powder mixture.

mixture was collected in the glove box filled with argon gas. Microstructure of the milled CuO-SnO_2 powder mixture was characterized by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The powder and particle size were investigated by an image analysis. The identification of the phases was carried out by an X-ray diffractometer (XRD). The as-milled CuO-SnO_2 powder mixture was reduced during heating up to 1100 °C with a heating rate of 10 °C/min under the hydrogen atmosphere.

3. RESULTS AND DISCUSSION

The typical SEM photographs of as-received and as-milled CuO, SnO_2, and CuO-SnO_2 powder mixture are shown in Fig. 1. The as-received CuO and SnO_2 powders were irregular in shape and had an average size of approximately 2 μm. After milling, the powders were changed to nearly spherical shape and were agglomerated. The size of as-milled CuO and SnO_2 powders were approximately 0.1 and 0.2 μm, respectively. However, the CuO-SnO_2 powders in the mixture showed the size of approximately 0.7 μm.

Fig. 2 shows the XRD patterns for the as-received and as-milled CuO, SnO_2 powders and CuO-SnO_2 powder mixture. The CuO and SnO_2 phases were detected in the as-received CuO and SnO_2 powders, respectively, the as-milled CuO-SnO_2 powder mixture was composed of a mixture of CuO and SnO_2 phases. These results indicate that there was no formation of new phases between CuO and SnO_2 during milling.

Fig. 3 shows the TEM photographs of as-milled CuO, SnO_2 and CuO-SnO_2 particles after milling for 5 h. The as-milled CuO and SnO_2 powders were composed of nano-sized particles with approximately 20 and 25 nm in a diameter, whereas the

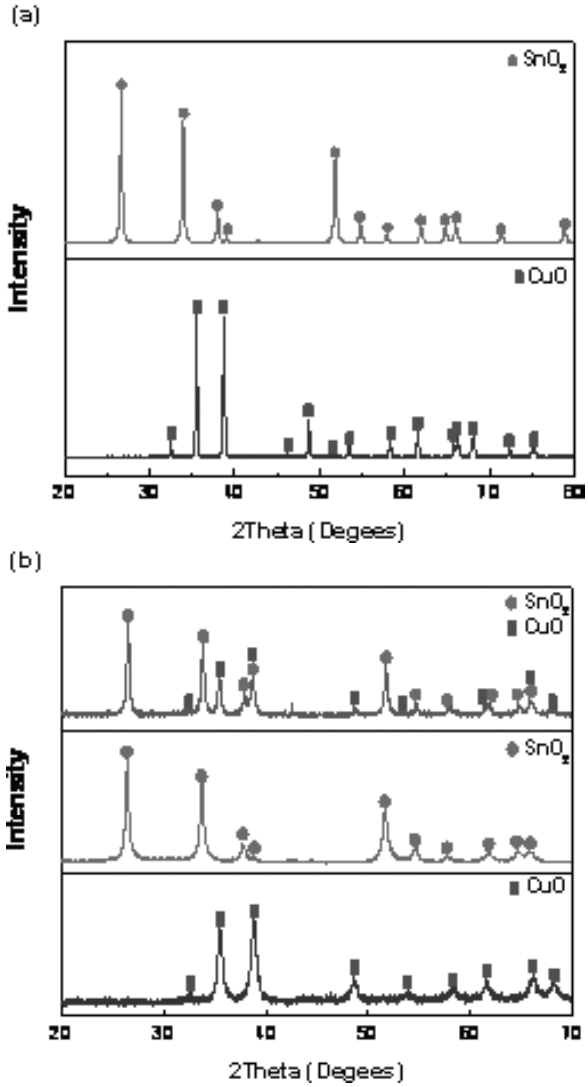

Fig. 2. XRD patterns of powders; (a) as-received and (b) as-milled.

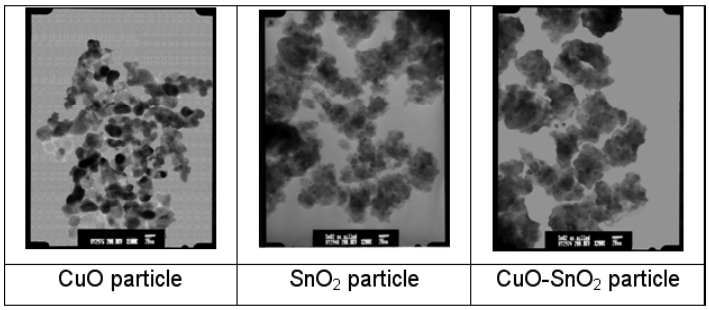

Fig. 3. TEM images of as-milled CuO, SnO_2, and CuO-SnO_2 particles.

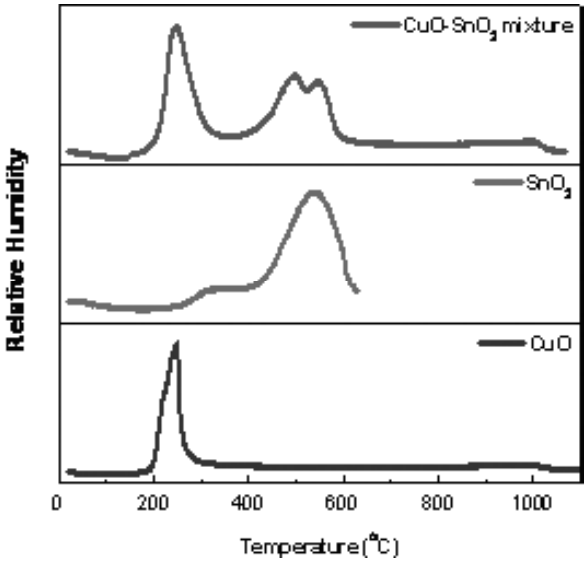

Fig. 4. Relative humidity curves of as-milled CuO, SnO_2 powders, and CuO-SnO_2 powder mixture.

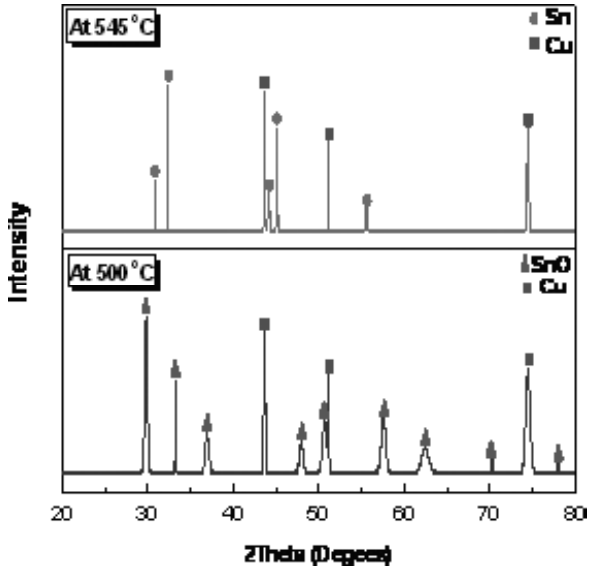

Fig. 5. XRD patterns of reduced CuO-SnO_2 powder mixture.

size of particles in the CuO-SnO_2 powder mixture was approximately 45 nm. On the other hand, the particle size increased to approximately 75 nm during heating up to 1100 °C with a heating rate of 10 °C /min under the hydrogen atmosphere.

Fig. 4 shows the non-isothermal humidity curve for hydrogen-reduction process of the as-milled CuO, SnO_2 powders and CuO-SnO_2 powder mixture. The CuO and SnO_2 powders showed the peaks at about 250 and 545 °C, respectively. The humidity peaks of CuO-SnO_2 powder mixture are largely divided into two parts. The first one at near 250 °C is related to the hydrogen-reduction process of CuO to Cu and second one in the temperature range of 450-600 °C is assigned to the hydrogen-reduction of SnO_2. In particular, the humidity curves of the SnO_2 powders were characterized by two small peaks at around 500 and 545 °C. Fig. 5 shows the XRD patterns of CuO-SnO_2 powder mixture reduced with heating up to 500 and 545 °C. The SnO phase was detected after reduction at 500 °C, and only Cu and Sn were detected after reduction at 545 °C. Based on this XRD results, accordingly, it is considered that two small peaks in the temperature range of 450~600 °C related to the reactions of $SnO_2 \rightarrow SnO$, which might be activated by the previously reduced Cu during heating, and $SnO \rightarrow Sn$.

4. CONCLUSIONS

The CuO-SnO_2 powder mixture was prepared by the high energy ball milling at 800 rpm for 5 h, and subsequently reduced under hydrogen atmosphere. The as-received CuO and SnO_2 powders were irregular in shape and had an average size of approximately 2 μm. After milling, the CuO-SnO_2 mixed powders became spherical in shape and had the size of approximately 0.7 mm, which was composed of nano-sized particles with approximately 45 nm in diameter. The as-milled CuO-SnO_2 powder mixture showed three hydrogen-reduction reactions at 250, 500, and 545 °C. This indicates that the reduction of the as-milled CuO-SnO_2 powder mixture was characterized by the reactions of $CuO \rightarrow Cu$, $SnO_2 \rightarrow SnO$ and $SnO \rightarrow Sn$ with increasing the temperature.

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