Materials Chemistry and Physics 172 (2016) 47–53

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Enhanced reduction of copper oxides via internal heating, selective heating, and cleavage of Cu–O bond by microwave magnetic-field irradiation

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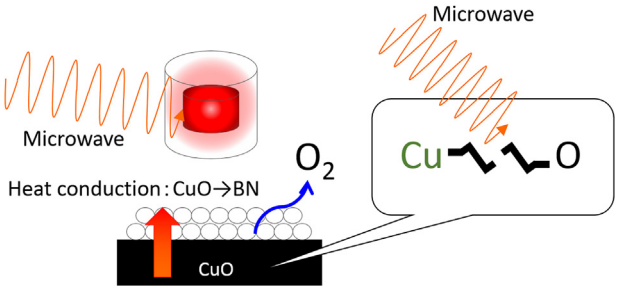
HIGHLIGHTS

- Microwave H-field irradiation is effective reduction method of CuO to Cu metal.
- Microwave H-field couples to the Fermi level electrons of CuO.
- Internal heating by MW resulted in a unidirectional diffusion of oxygen.
- Selective heating prevented the oxidization of the BN powder near the CuO pellet.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 May 2015
Received in revised form
12 November 2015
Accepted 27 December 2015
Available online 7 January 2016

Keywords:
Oxides
Copper oxide
Powder metallurgy
Powder diffraction
Band-structure

ABSTRACT

The reduction behavior of copper (II) oxide (CuO) covered with boron nitride (BN) powder under microwave H-field irradiation was investigated to understand the mechanism of enhanced reduction of CuO in microwave processing. Internal heating using microwave irradiation resulted in a unidirectional diffusion of oxygen from inside the CuO pellet to its outside, and selective heating prevented the oxidization of the BN powder near the CuO pellet. A quantum chemical interpretation of this phenomenon revealed that the microwave H-field couples to the Fermi level electrons of CuO, and the copper-oxygen bond may be cleaved by both microwave energy and thermal energy. As a result, microwave H-field irradiation resulted in a more effective reduction of CuO to copper metal compared to conventional heating.

1. Introduction

Copper metal is widely used for electric devices owing to its high electrical conductivity. A recent study has indicated that copper can be used as a catalyst for the conversion of carbon dioxide to liquid fuels, such as methanol, through intermediate carbon monoxide (CO) via an electrochemical route [1]. This study pointed out that the reduction method is important to create a large number of grain boundaries, which is integral for an efficient catalysis. Various reduction methods of copper (II) oxide are reported, including hydrogen reduction [2,3], CO reduction [4], plasma reduction [5], carbothermal reduction [6], and UV irradiation reduction [7]. In these methods, copper oxides obtain reduction energy through the surface by thermal convection, plasma or UV light. On the other hand, microwave irradiation method for the

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http://dx.doi.org/10.1016/j.matchemphys.2015.12.057
0254-0584/

reduction of transition-metal oxides was reported [8–12]. One of the features of the microwave heating is an internal heating. Microwave electromagnetic energy is absorbed from inside of the materials and the feature isn't seen in other kinds of reduction methods. Thus, the microwave method is expected to be one of the innovative methods for the reduction of copper oxides.

The mechanism of microwave reduction of copper oxides is until under discussion. A previous study reported that solid copper with an oxidized surface in boron nitride (BN) powder was deoxidized by multimode microwave irradiation, whereas the oxidized surface was retained with a conventional heating method [13]. This study does not focus on the reduction mechanism of CuO; therefore, it is unclear why a deoxidization reaction occurs by microwave irradiation but not by conventional heating. In addition, the authors indicated that the rate of the reduction reaction of CuO was enhanced with microwave irradiation compared to a conventional heating method in a vacuum [14]. The authors also revealed that the reduction of CuO was more pronounced during microwave H-field irradiation than during E-field microwave irradiation. However, CuO was reduced to Cu_2O, *i.e.*, metallic copper was not obtained. Nevertheless, the study was conducted in an ultra-high vacuum condition, which requires expensive devices. It is also unknown whether or not the non-thermal enhancement occurs in a non-vacuum, *i.e.*, in an air condition, such as in the previous study [13]. Elucidation of the mechanism of the microwave H-field effect for deoxidizing CuO to metallic copper in air is required to develop a simple and effective reduction process to obtain metallic copper.

In the current study, the reduction behavior of CuO in microwave H-field irradiation was investigated in detail, and the mechanism of enhanced reduction by the Cu–O bonding state, which is affected by the microwave magnetic field, is discussed.

2. Experimental

Copper oxide (CuO) powder of 99% purity, with particle diameters of approximately 5 μm (Kojundo Chemical Lab. Co., Ltd., Saitama, Japan) was palletized to ϕ 6 mm and was put into a fused silica test tube that was transparent to 2.45 GHz microwaves. The weight of CuO was 300 mg, and the pellet was covered with BN powers (0.15 g and 0.20 g were under and on top of the pellet, respectively). Felt of alumina-silicate sealed the test tube, and the height of the BN powder was kept constant throughout the reduction process to maintain the contact density between the pellet and BN powder. The test tube was set into the microwave cavity as shown in Fig. 1 (a). A single-mode cavity was used for microwave irradiation. Fig. 1 (b) shows the simulation results of the microwave field in the TE_{102} cavity. The arrow around the center of the cavity indicates the point of maximum strength in the microwave magnetic field (H-field). Points from an iris to $\lambda/2$ indicate the maximum points in the H-field. On the other hand, this point is the minimum point of the microwave electric field (E-field). In this study, the sample was irradiated with microwaves at the maximum point of the H-field. The microwave power and the plunger were manually controlled, and we attempted to keep the sample at 800 °C for 2 min at various microwave powers. The temperature of the sample was measured using an infrared pyrometer. After irradiation, the sample was rapidly cooled in air because there was no insulator. In the conventional heating method, the sample was heated at the rate of 40 °C/min by using an electric furnace (SPM 100-17, Marusho Electro-Heat Co., Ltd., Hyogo, Japan) and was maintained at various temperature conditions for 2 min before being quenched in air. The sample setting was the same as mentioned above. The microwave-irradiated or heated sample and BN powder around the pellet were analyzed by powder X-ray diffraction (XRD) method using Cu-Kα monochromator (Rigaku, RINT-2000).

3. Results and discussion

3.1. Reduction behavior of CuO by microwave irradiation

Fig. 2 shows pictures of the sample heated up to 1000 °C by H-field irradiation and up to 1200 °C by conventional heating as well as a schematic illustration of a cross section of samples. The pictures in the left column show the samples just after H-field irradiation and conventional heating. The samples were covered with an oxide shell, and the surface colors of the sample after H-field irradiation and conventional heating were brownish-red and black, respectively. As the colors of Cu_2O and CuO are brownish-red and black (or brownish-black), respectively, the outermost surface of the sample heated by an electric furnace was supposed to be CuO. On the other hand, the outermost surface of the sample after H-field irradiation was supposed to Cu_2O. This result confirms the results from the previous work, which stated that the sample irradiated with microwaves was deoxidized on the surface [13]. After conventional heating, the shape of the sample was spherical and the sample looked like melt. The melting point of CuO was 1201 °C; thus, the sample was melted in conventional heating due to a slight overshoot of the furnace temperature. The metallic parts appeared from inside the sample. The melting point of copper is

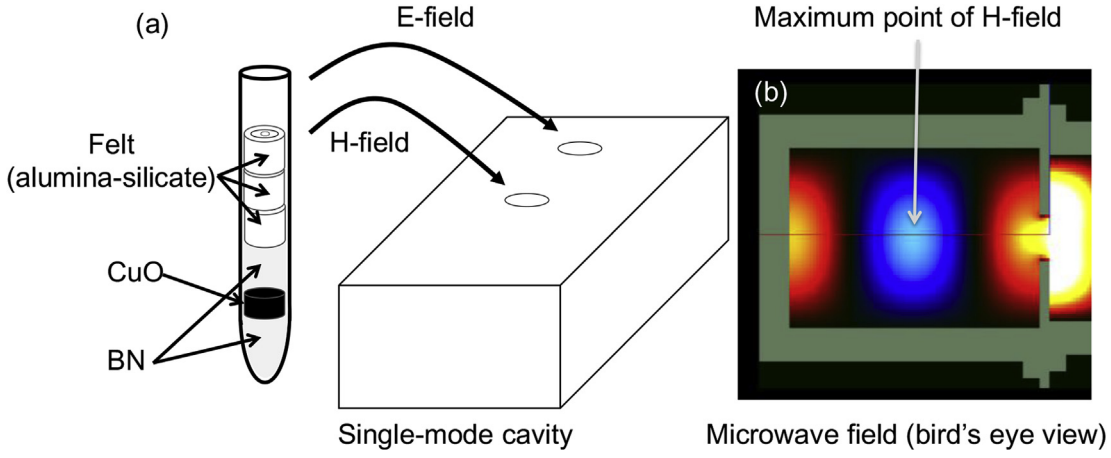

Fig. 1. (a) Sample setting in microwave H-field irradiation. (b) Simulation result of the microwave electromagnetic field in the TE_{102} cavity.