

Effect of Cu During Non-isothermal Hydrogen Reduction of MoO₃

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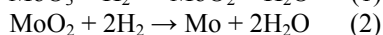
Abstract

The effect of Cu on the hydrogen reduction of MoO₃ powders was investigated by measuring the humidity change during a non-isothermal process of hydrogen reduction. The presence of Cu induced a shift in the reduction temperature and strongly affected the reduction processes of MoO₃→Mo₄O₁₁→MoO₂, which comprised the contained chemical vapor transport of MoO_x(OH)₂. This study suggests that the surface of the Cu grains acts as a nucleation site for the reduction of MoO_x(OH)₂ to MoO₂ particles from MoO₃ or Mo₄O₁₁. Such an activated reduction process results in the deposition of Mo and MoO₂ particles on the surface of the Cu.

Keywords : Molybdenum oxide, Hydrogen reduction, Chemical vapor transport

1. Introduction

The extraction of molybdenum metal involves a reduction of hydrogen from molybdenum trioxide. The reaction takes place in two distinct stages, viz.:



The first stage occurs via chemical vapor transport of MoO_x(OH)₂ [1]. This reduction process of molybdenum oxide is similar to that of tungsten oxide [1].

It has been reported that foreign elements can influence WO₃ hydrogen reduction by altering the reaction sequence and/or by changing nucleation and growth. Certain trace elements, such as Li, Na, K, Mn, Fe, Co, and Ni, enhance the reduction rate, while others, such as B, Al, and Cr, retard it [2]. Cu plays a role as a nucleation site for the hydrogen reduction of WO₂ during the chemical vapor transport [3,4]. Hydrogen reduction of molybdenum oxide at temperatures below 400 - 500°C is markedly accelerated by the use of an activating agent from the group VIII metals, in particular, palladium [5]. In this study, the effect of Cu on the hydrogen reduction behavior of MoO₃ powders was investigated by a non-isothermal analysis using an in situ observation of the reduction sequence.

2. Experimental and Results

There are two processes in the hydrogen reduction of MoO₃ powder. One is by chemical vapor transport (CVT)

and the other is by diffusion in the solid state (oxygen transport) [1]. The process of MoO₃→MoO₂ is dominated by CVT, while that of MoO₂→Mo is governed by oxygen transport [1].

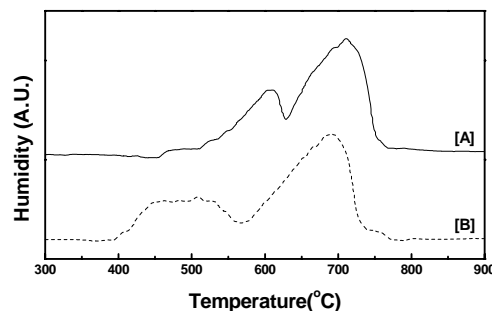


Fig. 1 Non-isothermal humidity curves obtained by heating MoO₃ [A] and a MoO₃-Cu mixture [B].

Fig. 1 shows the humidity changes during non-isothermal reduction processes of the MoO₃ powder [A] and MoO₃-Cu mixture [B]. As reported in the literature [1], the hydrogen reduction of the MoO₃ occurs in two stages. In Fig. 1, the first peak is observed in the reaction of MoO₃→MoO₂ which occur during CVT and the second, which occurs at high temperatures, is observed in that of MoO₂→Mo which occur during oxygen transport.

In this work, the first reduction process of the MoO₃ powder [A] took place in the temperature range from 460°C to 630°C, and the reaction increased with increasing temperature. The reduction of the MoO₃-Cu mixture [B]

steadily advanced from 400°C to 570°C. The second peak of [B] was similar to that of [A], but occurred at a lower temperature.

The microstructures of surfaces of copper grains were observed as depicted in Fig. 2. The morphology of the molybdenum oxide reduced at 450°C was nearly the same as the initial morphology of the raw powder as the reduction had not yet started. On the other hand, after hydrogen reduction occurred at 700°C and 800°C, the morphology changed because the CVT accompanies the microstructural change that the morphology change occurs.

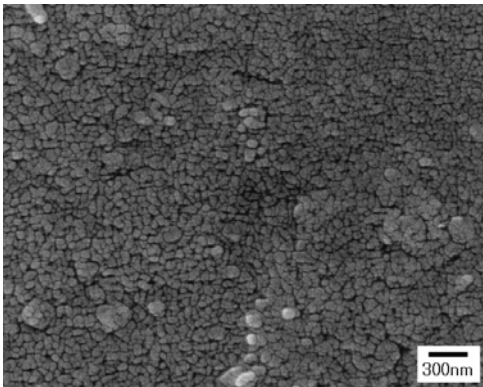


Fig. 2 Microstructures of the surface of copper grains during reduction in H₂ atmosphere at 450°C without a holding time.

During the reduction of the MoO₃-Cu mixture at 450°C (Fig. 2), 50-nm MoO₂ particles confirmed by XRD analysis in Fig. 2 were deposited onto the surface of the Cu grains for the CVT with MoO_x(OH)₂. The deposited MoO₂ particles were reduced on the surface of the Cu grain during the heating-up process. The particles grew to 100-200 nm at 700°C. At the reduction temperature of 800°C, the deposited molybdenum oxide particles were completely reduced as in the case of MoO₂ particles with the same size at 700°C. This result confirms that copper plays a role as a nucleation site for the hydrogen reduction of MoO₃ by chemical vapor transport.

Figure 3 shows the XRD patterns of Cu grains in the hydrogen reduced MoO₃-Cu mixture at a temperature of 450°C without a holding time. It was confirmed that the deposited material on the copper surface was MoO₂. As mentioned above, in the case of the MoO₃-Cu mixture, the reaction temperatures of MoO₃→MoO₂ shifted to lower temperatures. This phenomenon is due to the presence of nucleation sites for the molybdenum oxides on the surface of Cu during the CVT process. It is believed that this result is the evidence of activated reduction by Cu phase.

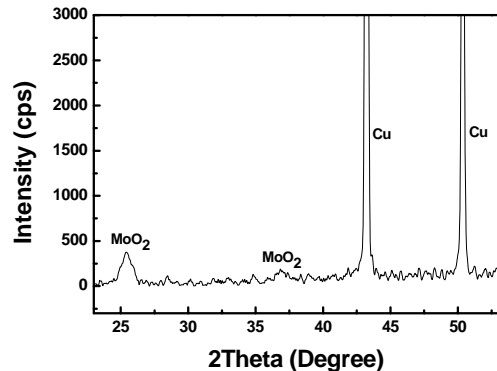


Fig. 3 The XRD patterns of the surface of copper after reduction in an H₂ atmosphere at 450°C without a holding time.

3. Summary

The hydrogen reduction behavior of MoO₃ and MoO₃-Cu mixtures was compared using an *insitu* humidity measuring system. The humidity peak for the reaction of MoO₃→MoO₂ in the MoO₃-Cu mixtures was shifted to lower temperatures. These results were attributed to the influence of the copper phase on the hydrogen reduction process of the molybdenum oxides during CVT. This was confirmed by microstructural observation of the Cu surface after the hydrogen reduction process. Molybdenum oxides were deposited on the copper surface during CVT. Consequently, it was confirmed that the Cu surface plays a role as a nucleation site for molybdenum oxide during the hydrogen reduction of MoO₃ by CVT.

4. References

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