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# A preliminary study on the preparation of metallic copper by direct hydrogen reduction of CuS slurry

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**Abstract** A preliminary study demonstrated that CuS in the acid or basic slurry could be reduced to a certain extent by hydrogen in an autoclave. The reduction mechanisms in the two systems are probably different. The reduction of CuS in the basic slurry of pH 12.0 reached 92% under the hydrothermal conditions, such as 2.5MPa of partial hydrogen pressure, 220 ºC for 3 h and adding 95% of stoichiometric ZnO.

## Introduction

Covellite (CuS) is one of important copper sulfide minerals in nature. The recovery of copper from copper sulfide minerals involves the extraction process of pyrometallurgy or hydrometallurgy [1]. Because of deepening environmental consciousness, hydrometallurgy has made good progress, although pyrometallurgy is still the main method of recovering copper from its sulfides minerals [2, 3]. Up to now, acid leaching or ammonia leaching is always necessary for hydrometallurgical processes, normally as the beginning step of handling copper sulfide minerals, by which copper in minerals dissolves completely in solution in the form of ions or complex ions and then are recovered by electrolysis or hydrogen reduction after solution purification and separation [4–6]. For example, a process on the recovery of copper from aqueous ammoniacal ammonium sulfate solutions containing copper ions by hydrogen reduction has been developed [7]. To our knowledge, there is no report on the preparation of metallic copper by direct hydrogen reduction of CuS slurry. An attempt has been made by authors to prepare Cu by direct hydrogen reduction of $Cu_2S$ slurry [8]. In this paper, a preliminary study on the preparation of metallic copper by direct hydrogen reduction of CuS slurry has been reported. The thermodynamic possibility of the reduction reaction and some important factors influencing the reduction of copper sulfide to copper have been investigated. This provides an alternative route of recovering Cu from copper sulfide minerals by the novel hydrothermal process of hydrogen reduction.

Hydrogen reduction experiments were carried out in a 2-L stainless steel autoclave equipped with an electric heater and an agitator having a 6 cm diameter four-blade marine type impeller. The autoclave was charged with 1000 mL of a slurry obtained by mixing 20 g of CuS, distilled water and a little of $H_2SO_4$ or NaOH solution for adjusting pH. The autoclave was purged with $N_2$ gas three times after sealing and heated up to 220 °C, then $H_2$ gas was introduced into the autoclave to total pressure of 5.4 MPa. The pressure began to decrease as the reaction started. After a certain period of time the pressure remained unchanged, which indicated the end of the reaction. And after the completion of the reaction, the powder was obtained by filtration, then washed with distilled water, ethanol and acetone, and dried in an oven at 50 °C. The chemicals used for the study were reagent-grade in purity. The crystalline phases of powder were determined by X-ray diffractometer (XRD, Rigaku RINT2000) with a copper target. A scanning electron microscope (SEM, JEOL JSM-35CF) was used to observe the morphology of powder. The Cu transformation from CuS was calculated

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according to the chemical reaction equilibrium and the chemical phase analyses.

CuS is one of the difficult soluble compounds with the K*sp* value of $3.5 \times 10^{-38}$. It is impossible to dissolve in neutralized or basic solution, but it could partially be dissolved in an acid solution to form some copper ions. It is known from the Eh-pH diagram of metals and hydrogen that the copper ions can be reduced by hydrogen in solutions of any pH values, and from the potential of CuS and hydrogen that it is also possible to reduce CuS by hydrogen in basic slurry although without copper ions. Thus the hydrogen reductions of CuS in acid and basic slurries were attempted, and the results were shown in Table 1. It can be seen that CuS can be reduced by hydrogen in the two slurries, but the reaction mechanisms seem to be different.

In the acid slurry, the solution after reaction showed light blue color, which indicated some $Cu^{2+}$ ions existed in the solution. Together with the powder composition of CuS and Cu, it was considered that the hydrogen reduction process was probably via the following reactions:

$$CuS = Cu^{2+} + S^{2-} \tag{1}$$

$$Cu^{2+} + H_2 = Cu + 2H^+ \tag{2}$$

The essence of the reaction was the hydrogen reduction of $Cu^{2+}$ ions dissolved in the solution, and it was generally considered as a homogenous reaction.

In the basic slurry, the solution after reaction showed no color, but black precipitate was formed when a little $CuSO_4$ solution was added. This indicated some $S^{2-}$ ions existed in the solution. Together with the powder composition of CuS and Cu, it was considered that the hydrogen reduction reaction might be performed as follows:

$$CuS + H_2 + 2OH^- = Cu + 2H_2O + S^{2-} \tag{3}$$

**Table 1** Reduction of CuS slurries by $H_2$ at two pH values

| PH of the end solution | 2.8 | 12.0 |
|---|---|---|
| $H_2$ consumption | 0.1 MPa | 0.2 MPa |
| Powders obtained after reduction | Copper red colored powder was found on the stirrer, the cooling pipe and the wall of the autoclave. The rest of powders remained black. | Copper red colored powder was found on the stirrer, the cooling pipe and the wall of the autoclave. The rest of powders were black with some copper red colored powder in it. |
| Component of the powder detected by XRD | CuS, Cu | Cu, CuS |
| Color of the solution | Light blue | Colorless |
| Adding $CuSO_4$ solution into the end solution | No precipitate | Black precipitate |

The essence of the reaction was the hydrogen reduction of CuS solid particles, and it was generally considered as a heterogenous reaction occurring on the surfaces of the particles.

Figures 1–3 showed the SEM micrographs of CuS and the powders obtained by the hydrogen reduction of CuS in acid and basic slurries. It can be seen from Fig. 1 that the morphology of CuS particles before reduction was irregular with difference particle sizes. Partial dissolution of CuS in the acid slurry might occur and those $Cu^{2+}$ ions dissolved in the solution were reduced by hydrogen. Thus, the morphology of the powder after reaction in Fig. 2 was obviously different from that of CuS powder in Fig. 1.

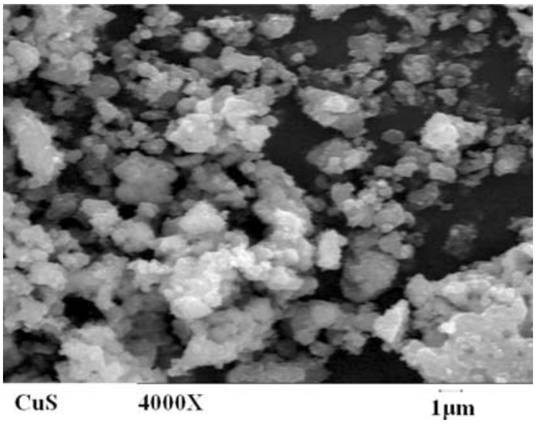

**Fig. 1** SEM micrograph of CuS powder

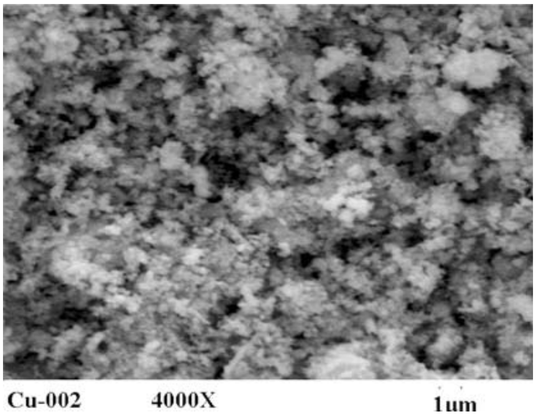

**Fig. 2** SEM micrograph of the powder obtained by hydrogen reduction of CuS slurry at pH 2.6

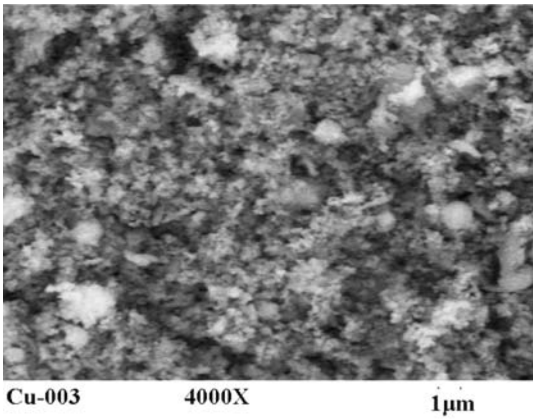

**Fig. 3** SEM micrograph of the powder obtained by hydrogen reduction of CuS slurry at pH 12.0

However, it was impossible to dissolve CuS in the basic slurry. It seemed that the reduction reaction of CuS was carried out between the solid particle and the activated hydrogen by a collision. Thus the powder had the particle shapes something like their original but became loose before reduction reaction completed due to the partial reduction in situ. This can be observed by comparison of Fig. 3 and Fig. 1.

It can be also seen from Eqs. 1–3 and Table 1 that the hydrogen reduction in acid or basic slurry could not be finished because of the accumulation of $H^+$ or $S^{2-}$ by the chemical equilibrium. Only by breaching the equilibrium, the hydrogen reduction could proceed to the end. $S^{2-}$ ions in solution can be removed by forming insoluble sulphide precipitate with the proper additive compound. Therefore, it was more reasonable to carry out the hydrogen reduction in a basic slurry system.

ZnO is an amphoteric oxide and the solubility product of $Zn(OH)_2$ ($2.0 \times 10^{-17}$) is greater than that of ZnS ($1.6 \times 10^{-24}$) [9]. Consequently ZnO is able to precipitate $S^{2-}$ ions. ZnS yielded cannot be reduced by hydrogen ($E^0_{Zn/ZnS} = -1.44V$) and has a density of 4.0 g/cm$^3$, which is obviously different from the density of metallic copper (10.49 g/cm$^3$). Thus, ZnS can be separated from Cu by flotation or gravitational separation, or can be also treated as a zinc concentrate and recovered by extractive metallurgy. Therefore, ZnO was considered as an ideal additive. The experimental results showed that 92% of Cu transformation from CuS was reached when 95% of stoichiometric ZnO was added into the CuS slurry of pH 12.0 and then reduced by hydrogen at 220 °C and 2.5 MPa of partial hydrogen pressure for 3 h. The effect of ZnO in the hydrogen reduction process on CuS in basic slurry can be expressed as follows:

$$CuS + H_2 + ZnO = Cu + ZnS + H_2O \tag{4}$$

Figures 4 and 5 show the SEM micrograph and the XRD pattern of the reduction products. It can be seen from Fig. 4 that the particles were no longer keeping their original morphologies and the particle sizes were relatively small by comparison with Fig. 1. Compared with Fig. 3 it can be seen that the powder had more clear shape. It was obvious that every CuS particle was disintegrated into several separated smaller Cu particles after completely reduced. In Fig. 5, the diffraction peaks indicated that Cu and ZnS are predominant in the product, while CuS and ZnO are only a few residues.

It should be pointed out that the present study only provides the preliminary results on the preparation of metallic copper by direct hydrogen reduction of CuS slurry. Additional studies have been undertaking to investigate the effect of some other factors, such as the particle sizes and the compositions of the raw materials on the reaction rate, yield and purity of the product. Furthermore, efficient separation of the metallic copper from the copper sulfide remained in the product will be also investigated.

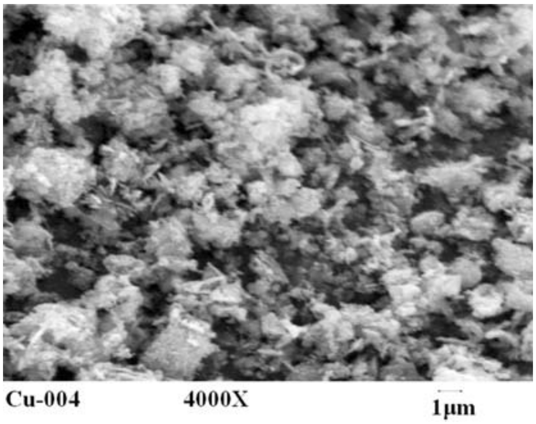

**Fig. 4** SEM micrograph of the powder obtained by hydrogen reduction of CuS slurry at pH 12.0 with adding ZnO

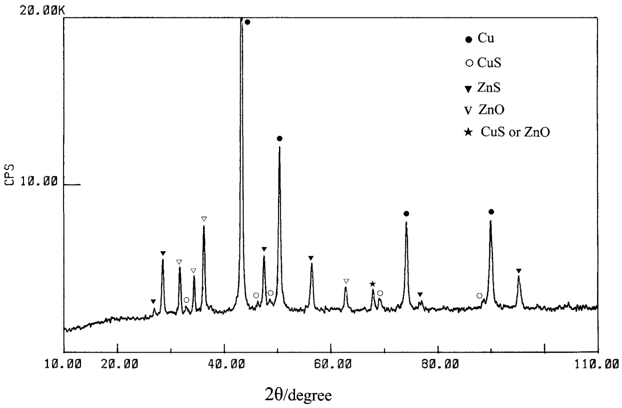

**Fig. 5** XRD patterns of the same powder as shown in Fig. 4

In conclusion, a preliminary study demonstrated that CuS in the acid or basic slurry could be reduced to a certain extent by hydrogen in an autoclave. The reduction mechanisms in the two systems are probably different. The reduction of CuS in the basic slurry of pH 12.0 reached 92% under the hydrothermal conditions, such as 2.5 MPa of partial hydrogen pressure, 220 °C for 3 h and adding 95% of stoichiometric ZnO.

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