

## BRIEF COMMUNICATION

# Improvement of Oxidation Resistance of Ultrafine Copper Powders by Phosphating Treatment

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Ultrafine copper powders with mean diameters of about 0.05 and 1  $\mu\text{m}$  were prepared by the chemical reduction method. The powders were treated with phosphating solution to improve their oxidation resistance. Nanometer-sized copper powders are unstable in air at room temperature and the treated nanometer-sized powders have an oxidation temperature of about 220°C, which is very stable in air. The treated micrometer-sized copper powders have an oxidation temperature of about 350°C, 100°C higher than that of untreated micrometer-sized copper powder. The phosphating mechanism of copper powders also suggested that insoluble phosphates are deposited on the surface of copper particles and that the surface corrosion of copper powders is carried out by  $\text{NO}_3^-$  under acidic conditions.  $\text{H}^+$  ions were provided by phosphoric acid and dihydrogen orthophosphate in the phosphating solution. © 1997 Academic Press

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### 1. INTRODUCTION

Different-sized copper powders have different uses (1). When the copper particles are ultrafine, their surfaces are very active. Nanometer-sized copper powders would be oxidized by oxygen in air at room temperature. Oxidation of nanometer-sized copper powders greatly limited their reservation and utilization. Therefore, the improvement of oxidation resistance is a key issue for ultrafine copper powders. However, there is little information about techniques for the oxidation improvement of the ultrafine copper.

Phosphating treatments have been used to prevent iron products from corroding. Iron products were put into phosphating solutions to form an insoluble phosphating film on the surfaces of the iron products (2–4). The mechanism was that dihydrogen orthophosphate or phosphoric acids ionize with  $\text{H}^+$  in water, the  $\text{H}^+$  reacts with iron, and then an insoluble phosphating film is formed.

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The aim of this paper is to employ phosphating treatment to retard the oxidation of ultrafine powders.

### 2. EXPERIMENTAL PROCEDURES

#### 2.1. Preparation of Nanometer-Sized and Micrometer-Sized Copper Powders

All chemicals used were reagent grade. Sodium hypophosphite (2.0 g) and gelatins (1.5 g) were dissolved in deionized water (60 ml). This solution was added to a 400-ml reaction vessel. Later, copper sulfate solution (0.625 mol/L, 100 ml) and sodium hypophosphite solution (1.25 mol/L, 100 ml) were made in two vessels. These three solutions were all maintained in a water bath at 85°C. Finally, the copper sulfate solution and the sodium hypophosphite solution were added to the reaction vessel at the same speed under agitation. At the end of the reaction, copper powder was washed with deionized water four times and kept in deionized water for later use.

For comparison, micrometer-sized copper powder was also prepared by the following steps: Copper sulfate (8.0 g) and glucose (7.0 g) were dissolved in deionized water (50 ml). This solution was added to a reaction vessel. Sodium hydroxide solution (1.25 mol/L, 100 ml) and ascorbic acid solution (0.57 mol/L, 50 ml) were made in another two vessels. These three solutions were maintained at 90°C.

Sodium hydroxide was added drop by drop to the reaction vessel under agitation. After 20 min, the ascorbic acid solution was added to the reaction vessel. At the end of the reaction, the copper powder was washed with deionized water four times and dried at 40°C.

#### 2.2. Phosphating Treatment of Ultrafine Copper Powders

Zinc dihydrogen orthophosphate (10 g), zinc nitrate (30 g), and appropriate amounts of phosphoric acid were dissolved in 250 ml deionized water at 60–70°C. Then the

copper powders were added to the solution and treated for 20 min under agitation. Finally, the powders were washed with deionized water four times and dried at 40°C.

### 2.3. Test of the Characterization of the Powders

Characterization of the particles was achieved through different techniques. The shapes and grain size of the powders were observed by transmission electron microscope (TEM, Model JEM-1200EX II, Japan) and scanning electron microscope (SEM, Model S-250, England). The phase composition of the powders was measured by X-ray diffraction (XRD, Model Rigaku D/max  $\gamma$  B, Japan). UV absorption of solutions was measured with a UV-750 spectrometer and oxidation resistance of the powders was determined by TG analysis.

## 3. RESULTS AND DISCUSSION

### 3.1. Stability of Nanometer-Sized and Micrometer-Sized Copper Powders

Figures 1 and 2 respectively show the copper powders with mean diameters of about 50 nm and 1  $\mu$ m.

The bottom spectrum in Fig. 3 is the XRD spectrum of 50 nm copper powder after drying at room temperature. Characteristic peaks of both copper and cuprous oxide are shown in the figure: copper,  $d = 1.807$  (1.808\*), 1.278 (1.278\*) (see ① in Fig. 3); cuprous oxide,  $d = 3.021$  (3.020\*), 2.466 (2.465\*), 2.314 (2.135\*), 1.742 (1.743\*), 1.509 (1.51\*) (see ② in Fig. 3), where the lattice distance values with \* are cited from the *Standard Powder Diffraction File of the ASTM*. This figure indicates that nanometer-sized copper powders are unstable in air; the powder can be oxidized by oxygen in air at room temperature. SEM pictures of treated 50 nm copper powder are shown in Fig. 4; spherical grains have diameters of about 250 nm.



FIG. 1. TEM of nanometer-sized copper powder.



FIG. 2. TEM of micrometer-sized copper powder.

In the XRD spectra of 1  $\mu$ m copper powders stored for 1 year (see the middle spectrum in Fig. 3) there are only characteristic peaks of copper,  $d = 2.088$  (2.088\*), 1.807 (1.808\*), 1.278 (1.278\*) (see ① in Fig. 3), and no peaks of CuO or Cu<sub>2</sub>O. This indicates that 1  $\mu$ m copper powder is stable in air. Figure 5 shows the TG curve of 1  $\mu$ m copper powder. We learn that the powder was oxidized at about 250°C. This indicates that micrometer-sized copper powders are very stable in air.

### 3.2. Oxidation Resistance of Nanometer-Sized and Micrometer-Sized Copper Powders after Phosphating Treatment

The top spectrum in Fig. 3 is the XRD spectrum of dried nanometer-sized copper powders after phosphating treatment. There are characteristic peaks of copper,  $d = 2.088$  (2.088\*), 1.807 (1.808\*), 1.278 (1.278\*) (see ① in Fig. 3), and no peaks of CuO or Cu<sub>2</sub>O in this figure.

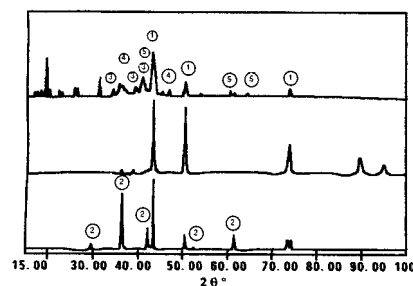


FIG. 3. XRD spectra of the powders. (Top) 50 nm copper powder after phosphating treatment. (Middle) 1  $\mu$ m copper powder stored for 1 year. (Bottom) 50 nm copper powder after drying in air at room temperature.

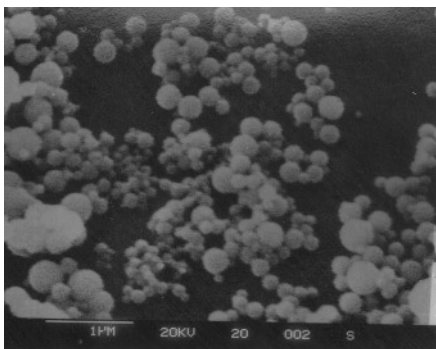


FIG. 4. SEM of treated nanometer-sized copper powder.

To determine the oxidation temperature of nanometer-sized and micrometer-sized copper powders, we heated the treated powders to a certain temperature. Then the powders were measured by X-ray diffraction to show whether the copper powders were oxidized by oxygen. The results are given in Table 1. From the results, we can draw the conclusion that the treated nanometer-sized copper powders have an oxidation temperature of about 220°C, which is very stable in air. The treated micrometer-sized copper powders have an oxidation temperature of about 350°C, 100°C higher than that of untreated micrometer-sized copper powder.

These experimental facts indicate that the oxidation resistance of both nanometer-sized and micrometer-sized copper powders was greatly improved by the phosphating treatment.

### 3.3. Mechanism of Phosphating Treatment for Copper Powders

When the copper powders were treated for a long time, the phosphating solution appeared to be light blue, indicating that there were  $\text{Cu}^{2+}$  ions in the solution. Similar to the phosphating treatment for iron, some Cu atoms “dissolved” in the solution.

The composition of the treated copper powder can be analyzed by its XRD spectrum (top in Fig. 3). There are

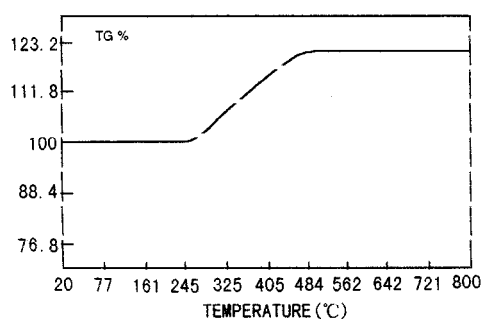


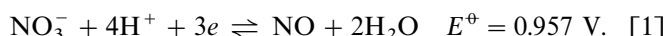
FIG. 5. TG curve of 1 μm copper powder.

TABLE 1  
Oxidation Resistance of Copper Powders after Phosphating Treatment

Diameter	Temperature (°C)	Oxidization	Conclusion <sup>a</sup>
50 nm	180	No	Stable
50 nm	220	No	Stable
50 nm	240	Yes	Unstable
1 μm	320	No	Stable
1 μm	350	No	Stable
1 μm	380	Yes	Unstable

<sup>a</sup> Identified through X-ray diffraction.

characteristic peaks of  $\text{Cu}_3(\text{PO}_4)_2$ ,  $d = 2.649$  (2.65\*), 2.288 (2.29\*), 2.156 (2.15\*) (see ③ in Fig. 3);  $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ,  $d = 2.268$  (2.269\*), 1.939 (1.941\*) (see ④ in Fig. 3);  $\text{Zn}_3(\text{PO}_4)_2$ ,  $d = 2.288$  (2.29\*), 2.131 (2.13\*), 1.507 (1.51\*), 1.45 (1.45\*) (see ⑤ in Fig. 3); and no peaks of  $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  or other chemical substances. Therefore, the phosphating film was mainly composed of  $\text{Cu}_3(\text{PO}_4)_2$ ,  $\text{Zn}_3(\text{PO}_4)_2$ , and  $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ . This showed that some Cu atoms were “dissolved” from the copper particles. The  $\text{Cu}^{2+}$  ions reacted with  $\text{PO}_4^{3-}$  and insoluble  $\text{Cu}_3(\text{PO}_4)_2$  was formed. Because there was  $\text{NO}_3^-$  in the phosphating solution,  $\text{H}^+$  ionized by  $\text{H}_3\text{PO}_4$  and  $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  raised the electrode voltage value of the half-reaction

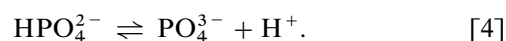
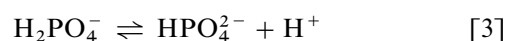
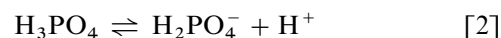


The electromotive force of the oxidation–reduction reaction was increased by this means and the reaction carried out very slowly. Light blue  $\text{Cu}^{2+}$  and tiny bubbles were seen in the treatment process. To verify that there were light blue  $\text{Cu}^{2+}$  ions in the solution, we measured the copper sulfate solution and the phosphating solution with the UV-750 spectrometer (see Fig. 6). We can see from the figure that two UV absorption curves exhibit the same maximum absorption peak at 290 nm. This confirms that there were  $\text{Cu}^{2+}$  ions in the phosphating solution which dissolved from the copper particles.

Considering the experimental facts, a phosphating process of copper powders in three steps is suggested:

Step 1: Ionization of phosphoric acid and dihydrogen orthophosphate in aqueous solutions.

Ionization of phosphoric acid:



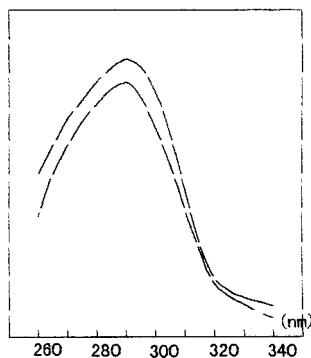
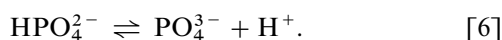
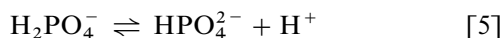
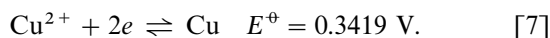


FIG. 6. UV absorption of copper sulfate and phosphating solution. (Top) UV absorption of copper sulfate, (bottom) UV absorption of phosphating solution.

Ionization of dihydrogen orthophosphate:



Step 2: "Dissolution" of Cu atoms. Because of the resulting  $\text{H}^+$ , which raised the electrode voltage value of reaction [1], the electromotive force of the oxidation-reduction reaction, which is made up of [5] and the negative pole half-reaction [7], was also raised. The overall reaction occurred very slowly:

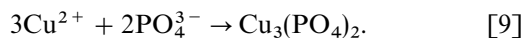


The overall reaction equation is



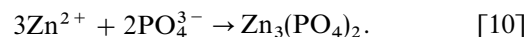
The concentration of phosphoric acid and the treatment temperature can change the electrode voltage of the half-reaction. Therefore, the surface corrosion speed of copper powders can be regulated by this means.

Step 3: Deposition of insoluble phosphate (formation of phosphating film).  $\text{PO}_4^{3-}$  ions react with the newly generated  $\text{Cu}^{2+}$  ions from copper particles and insoluble copper phosphates resulted. The reaction equation is



Because of the exhaustion of  $\text{H}^+$  in the solution, the concentration of  $\text{PO}_4^{3-}$  gradually increased, and therefore,

the soluble dihydrogen orthophosphate changed to insoluble phosphate. The reaction equation is



The existence of soluble  $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in the phosphating film is due to supersaturation and deposition of  $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ .

#### 4. CONCLUSIONS

1. The phosphating anticorrosion treatment is suitable for ultrafine copper powders as well as for iron products. On the basis of the size increase of nanometer-sized copper powders after surface phosphating treatment and XRD analysis, the existence of phosphate composite was identified. The oxidation resistance of copper powders was greatly improved by the phosphating film that formed on the surface of copper particles.

2. The micrometer-sized copper powders treated with the phosphating solution have an oxidation temperature of about  $350^\circ\text{C}$ ,  $100^\circ\text{C}$  higher than that of untreated micrometer-sized copper powder.

3. Nanometer-sized copper powders with a mean diameter of about 50 nm were very stable in air after the phosphating treatment. The oxidation temperature was about  $220^\circ\text{C}$ .

4. The mechanism of the phosphating treatment for copper powders is different from that for iron products. The surface corrosion of copper powders is carried out by  $\text{NO}_3^-$  and acidic conditions are optimal for the surface corrosion.  $\text{H}^+$  ions in the phosphating solution were provided by phosphoric acid and dihydrogen orthophosphate.

#### ACKNOWLEDGMENTS

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