Study on Preparation of Nano-porous Copper by Dealloying Method

Zhiwei Wang, Mingyu Li* and Qingxuan Zeng
Beijing Institute of Technology, Beijing, China
*Email: mingyuli@163.com

Abstract. Nano-scale mixed powder composed of oxalate copper and oxalate manganese was prepared by chemical synthesis method, after tabletting, it was sintered at high temperature in a tube furnace under the protection of nitrogen to obtain nano-level Cu-MnO alloy. The Mn is removed by corrosion to obtain nanoporous copper. The solid copper-manganese oxalate was analyzed by TG/DTG. The specific surface area and composition of porous copper before and after sintering and dealloying were analyzed and characterized by using automatic specific surface area analyzer and ICP-OES. The results show that the specific surface area of the copper-manganese alloy can be greatly improved by controlling the sintering temperature so that it is not completely decomposed. The specific surface area of porous copper obtained when the Mn element is 14% (mole fraction) is the largest. After hydrochloric acid corrosion, the specific surface area of porous copper will be significantly reduced, and hydrochloric acid dealloying is a continuous process. If the corrosion concentration and time are too small, the purity of the porous copper will be lower. Conversely, if they are too large, the porous copper structure will collapse and the specific surface area will quickly decrease. Nano-porous copper with a specific surface area of 75.9 m$^2$/g can be obtained by etching in 0.5 mol/L HCl for 4 h.

1. Introduction
As a special porous material, nano-porous metal has a large number of interconnected pores. The microscopic size of metal particles is at the nanoscale. Due to the high specific surface area and special interface characteristics of nano-porous metal, it has unique physical and chemical properties. It is widely used in catalysis, filtration, sensing and spectrometer[1-4], it is a functional material that is developing rapidly at present.

The dealloying method is currently a common method for preparing nanoporous metals. This method uses the difference in the activity of different alloy metals. The electrochemically active metal elements in the alloy are chemically or electrochemically corroded. It is selectively dissolved to form interconnected nano-porous structures composed of inert metal elements[5]. This method is simple to operate and easy to repeat, so it has received more and more attention[6]. In addition to its unique physical and chemical properties, the copper element is retained as an element in the binary system as its lower cost than other precious metals. The current research on the preparation of nanoporous metals by dealloying mainly focuses on the control of the conditions for the formation of NPC structures, as well as the study of the micromechanism of its dealloying process. The study found that by adjusting the composition of the alloy precursor, the corrosion solution[7], the corrosion time and post-treatment, it is easy to control the microstructure of the nanoporous metal such as the pore size. For some preparation processes using NPC as a precursor, the specific surface area, pore volume and pore size of NPC are important influencing factors, but there are relatively few studies in this area.

The method of preparing nano-porous metal alloy is arc smelting. In this paper, nano-copper and manganese oxide are prepared by chemical synthesis and high-temperature sintering method. The
manganese oxide is removed by chemical corrosion to obtain nano-porous metal copper, which improves the preparation efficiency and reduces corrosion. Difficulty. The specific surface area of the nanoporous copper and oxide and the nanoporous copper after the removal of manganese oxide was analyzed using an automatic specific surface area analyzer. At the same time, the NPC was measured at different manganese oxide content, sintering temperature, corrosion solution concentration and time. The influence of specific surface area was studied, which provided a new idea for the preparation of NPC with higher specific surface area.

2. Materials and Methods

2.1. Instruments and Reagents
Micromeritic ASAP 2460 automatic specific surface area analyzer (American Micromeritics); Japanese SEIKO Exstar SII 6300 thermal analyzer (Japan Seiko).
Copper nitrate, Beijing Tongguang Fine Chemical Company, analytically pure; manganese nitrate, Tianjin Yongda Chemical Reagent Co., Ltd., analytically pure; oxalic acid, Tianjin Fuchen Chemical Reagent Factory, analytically pure; ethanol, Tianjin Yongda Chemical Reagent Co., Ltd., analytically pure; deionized water, self-made.

2.2. Fabrication of Nanocopper-manganese Oxalate
In the experiment, a chemical synthesis method was used to prepare the copper oxalate precursor. A mixed ethanol solution of copper nitrate (mass fraction ≥99.9%) and manganese nitrate (mass fraction ≥99.9%) with a total amount of 1 mol was used. The solution react with oxalic acid (mass Fraction ≥99.9%) (reaction temperature 50°C, stirring speed 500r/min) to obtain a mixed powder containing copper oxalate and manganese oxalate.

2.3. Fabrication of Nanocopper-manganese Oxalate
Using a tablet press, the mixed powder is compressed into a cylinder with a diameter of 13.3 mm (pressure = 2 MPa), which is sintered at high temperature in a tube resistance furnace. The sintering process is completed in an N2 atmosphere at a heating rate of 3°C/min to get a series of different Mn Content of copper-manganese alloy flaky solids. The obtained alloy flake solids were corroded in hydrochloric acid solutions of different concentrations, and MnO was easily dissolved in the acid solution. The Mn element and other residual substances in the flake solids were removed by the alloy removal method, and finally the higher purity was obtained. The sheet-shaped NPC was washed with ethanol solution and tested.

The main reactions involved in the test are the following:

\[ \text{Cu(NO}_3\text{)}_2 + \text{H}_2\text{C}_2\text{O}_4 \xrightarrow{\Delta} \text{CuC}_2\text{O}_4 \downarrow + \text{HNO}_3 \]  

\[ \text{Mn(NO}_3\text{)}_2 + \text{H}_2\text{C}_2\text{O}_4 \xrightarrow{\Delta} \text{MnC}_2\text{O}_4 \downarrow + \text{HNO}_3 \]  

\[ \text{CuC}_2\text{O}_4 \xrightarrow{\Delta} \text{Cu} + 2\text{CO}_2 \uparrow \]  

\[ \text{MnC}_2\text{O}_4 \xrightarrow{\Delta} \text{MnO} + \text{CO} \uparrow + \text{CO}_2 \uparrow \]

TG/DTG analysis was performed on the obtained copper-manganese oxalate powder material using a thermal analyzer, and the weightlessness of copper manganese oxalate powder material with different manganese contents during heating was analyzed and tested. The specific surface area, pore volume, pore size, etc. of the copper oxalate-manganese oxalate mixed powder, copper-manganese alloy and the NPC sheet material finally obtained during the experiment were analyzed using an automatic specific surface area analysis tester.
3. Results and Discussion

3.1. TG Analysis of Copper-manganese Oxalate Mixed Powder

Figure 1 is the thermal decomposition curve of the nano-copper oxalate powder; Figure 2 is the thermal analysis curve of the nanocopper-manganese oxalate mixed powder with Mn content of 25%; Figure 3 is the nanocopper-manganese oxalate mixed powder with different Mn content thermal analysis curve.

![Figure 1. TG/DG of nano copper oxalate](image1)
![Figure 2. TG/DTG of mixed powder (25%Mn)](image2)
![Figure 3. DTG of mixed powder](image3)

It can be seen from Figure 1 that the thermal decomposition curve process of the nano-copper oxalate powder can be divided into two stages, a small amount of weightlessness before 250°C and a significant weightlessness peak occurs at 250~290°C. The previous stage of weightlessness is because the sample contains excessive oxalic acid and a small amount of water; the latter is caused by the decomposition of copper oxalate. From Figure 2 and Figure 3, we can know that the decomposition process of nano copper-manganese oxalate powder can be divided into three stages: (1) a small amount of weightlessness before 250°C, two of the samples have small peaks at 180~200°C, indicating that they contain more oxalic acid. (2) At 250~350°C, the DTG curve shows two obvious weightlessness peaks, one at 290°C, which is caused by the decomposition of copper oxalate, and one at 340°C, which is caused by the decomposition of manganese oxalate. (3) After 350°C, the sample mass remain unchanged at this stage, because copper-manganese oxalate has been completely decomposed.

From the curve of the second stage, we know that copper oxalate starts to decompose at 250°C, and the decomposition rate is maximum at 290°C, and it has been almost completely decomposed at 310°C, while manganese oxalate starts to decompose at the same degree, and reaches the maximum decomposition rate at 340°C. At 350°C, it has been substantially completely decomposed, and the sample mass will not change thereafter.

3.2. BET Characterization

3.2.1. Effect of sintering temperature on specific surface area of sample

From the TG/DTG diagrams in Figures 1 to 3, it is known that the temperature at which copper oxalate is completely decomposed is 310°C, while manganese oxalate is 350°C. Therefore, the samples of copper-manganese oxalate powder were sintered at 310°C and 350°C, and the specific surface area of the sintered product was analyzed and tested.
Figure 4 shows the specific surface area curves of the nanoporous copper and manganese oxide products sintered at different sintering temperatures. It can be seen that the specific surface area of the precursor of copper-manganese oxalate increases first and then gradually decreases with the increase of the manganese content in the mixture. The specific surface area of the precursor reaches the maximum when the amount of Mn element material is 6%. It is 103.9 m$^2$/g. When the sintering temperature is 310$^\circ$C, the specific surface area of the sintered product increases first and then decreases. When the amount of Mn element is 14%, the specific surface area of the nanoporous copper and manganese oxide. The maximum is 110 m$^2$/g. At this time, the copper oxalate in the copper-manganese oxalate mixture has been completely decomposed, but the manganese oxalate has not yet begun to decompose. A large amount of micropores are formed inside the powder material during the gas escape process of copper oxalate decomposition, thereby increasing its specific surface area. The specific surface area of the nanoporous copper and manganese oxide sintered at 350$^\circ$C gradually increases. The specific surface area is 42 m$^2$/g when the amount of Mn element is 20%. The main reason is that when manganese oxalate begins to decompose, the copper oxalate has been decomposed, and the microcrystalline copper constructed by nanocrystals gradually melts with the increase of temperature to become larger copper balls, destroying the microcrystalline copper particles constructed by nanocrystals, and forming larger copper microparticles balls, which causes its surface area to become smaller. Studies have shown that the sintering temperature of nanoporous copper in order to obtain a larger specific surface area during the decomposition of the copper-manganese oxalate powder material can not be too high, preferably not higher than 310$^\circ$C, at this time copper oxalate has been decomposed to form a nanocrystalline structure. For this kind of porous copper, manganese oxalate is not completely decomposed at this temperature. Subsequent considerations can use acid dissolution to remove manganese oxalate to obtain nano-porous copper. The sintering temperature is not higher than 310$^\circ$C in subsequent experiments.

3.2.2. Effect of corrosion solution concentration and corrosion time on surface area
Dealloying as the final step in the preparation of nanoporous copper materials, the concentration and time of the etching solution have an important effect on the change of the specific surface area of nanoporous copper. Figures 5 and 6 show the plot of specific surface area data of nanoporous copper obtained under different hydrochloric acid concentrations and immersion times.
As can be seen from Figures 5-6, the specific surface area of the nanoporous copper and manganese oxide material soaked in hydrochloric acid solution and then dried is significantly lower than that of the precursor material. After soaking in 0.2mol/L hydrochloric acid for 4h, the maximum specific surface area in the product was 100.1m²/g. After soaking for 12h, the maximum specific surface area was 61.4m²/g. After soaking for 24h, the specific surface area dropped sharply. The maximum specific surface area of the product obtained after soaking in 0.5mol/L hydrochloric acid for 4h is 75.9m²/g. The results of increasing the immersion time and the concentration of hydrochloric acid solution are not ideal. The specific surface area of nanoporous copper is directly reduced to single digits. Therefore, the solvation effect will greatly affect the specific surface area of the nanoporous copper. This is also because the nanomaterials have the characteristic of surface area shrinkage in the solvent. Therefore, the contact time between the nanoporous material and the solvent needs to be considered when preparing the nanoporous material by the alloy removal method.

The study found that the porosity of the nanoporous copper is mainly controlled by the composition of the pre-alloy, and the reaction of hydrochloric acid etching to remove the alloy is a continuous process. In this process, the Mn element is dissolved into the solution in the form of MnO and MnC₂O₄. The decomposition of manganese oxalate to generate CO₂ continues to create pores in the copper alloy, increasing its specific surface area, forming vacancies at the original surface position, driven by surface energy, the copper atoms diffuse to the surface, the microstructure of porous copper is changed, and coarsening occurs, And the pore size continues to increase, the specific surface area correspondingly becomes smaller. For low-concentration hydrochloric acid solution, it can only react with the Mn element on the surface of the porous copper, and it is difficult to enter the interior, so it has little effect on the specific surface area before and after corrosion and the residual Mn element content is large. As the concentration of hydrochloric acid solution increases and the corrosion time becomes longer, the skeletal of porous copper begins to be difficult to support, structural collapse occurs, and copper atoms begin to form clusters, thereby reducing the surface energy and causing the specific surface area of porous copper to have been reduced to single digits.

4. Conclusion

(1) The sintering temperature is that the decomposition of copper oxalate-manganese powder can increase the specific surface area of the nanoporous copper-manganese oxide product, in which the amount of Mn-containing material is 14%. The copper manganese oxalate powder is sintered at 310 °C to obtain nanoporous. The specific surface area of copper manganese oxide material can reach 110m²/g.

(2) Compared with the precursor material, the specific surface area of the copper alloy material after immersed in hydrochloric acid solution and dried is significantly lower than that of the precursor material. After soaking in 0.2mol/L hydrochloric acid for 4h, the maximum specific surface area in the product was 100.1m²/g. After soaking for 12h, the maximum specific surface area was 61.4m²/g. After soaking for 24h, the specific surface area dropped sharply. The maximum specific surface area of the
product obtained after soaking in 0.5mol/L hydrochloric acid for 4h was 75.9m$^2$/g, and the specific surface area of nanoporous copper increased to single digits by increasing the immersion time and the concentration of hydrochloric acid solution.

5. References

[1] Dong Changsheng, Zhong Minlin, Li Lin, et al. Fabrication and Functionalization of Tunable Nanoporous Copper Structures by Hybrid Laser Deposition and Chemical Dealloying [J]. Science of Advanced Materials, 2012, 4: 204-213.

[2] Tang Yong, Tang Biao, Qing Jianbo, et al. Nanoporous metallic surface: Facile fabrication and enhancement of boiling heat transfer [J]. Applied Surface Science, 2012, 258: 8747-8751.

[3] Bonroy K, Friedt J M, Frederix F, et al. Realization and Characterization of Porous Gold for Increased Protein Coverage on Acoustic Sensors [J]. Analytical Chemistry, 2004, 76(15): 4299-4306.

[4] Chen Luyang, Yu Jinshan, Fujita T, et al. Nanoporous Copper with Tunable Nanoporosity for SERS Applications [J]. Advanced Functional Materials, 2009, 19: 1221-1226.

[5] Q. Zhou, S.-J. Zang, B. Zheng. Effect of Mg-Cu alloy composition on morphology of nanoporous copper prepared by dealloying [J]. Materials Science and Engineering of Powder Metallurgy, 2015(04): 117-122.

[6] Wang Y, Liang S, Yang Q. Preparation of Nanoporous Coppers and Their Electrochemical Properties [J]. Rare Metal Materials And Engineering, 2014, 43(5): 1204-1208.

[7] Ding, Yi, Kim, Young Ju, Erlebacher, Jonah. Nanoporous gold leaf: "Ancient technology"/advanced material [J]. Advanced materials, 2010, 16(21): 1897-1900.