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Study on the preparation and properties of ultrafine copper powder

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Abstract: In the study, the common copper powder is used as sample, the ultrafine copper powder is researched by a new process of high energy ball milling. The influence of the milling time, the milling intensity, the milling medium, the ratio of ball to material, the dry milling and the wet milling on copper powder size are studied and the rule of every factors influencing properties of copper particle size and specific surface area under the best experimental conditions are acquired. By the regressive analysis of experimental results under the best conditions, the characteristic equation of copper particle prepared by high energy milling is confirmed.

Key words: copper powder; ultrafine; high energy ball mill; nanometer

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1 Introduction

As an important raw material of powder metallurgy products, copper powder plays a vital role in industrial fields. There are many methods for preparation of copper and copper based powder as follows[1−5]: electrolytic technique, gas-reduction technique, atomization machanical smashing, permutation, high-pressure hydrogen reduction, microbe lixiviation, and so on. Recently, high energy ball milling is used widely in preparation and sythesis of materials such as dispersion intensified alloy materials, magnetic materials, supersaturated solid solution materials, diversified amorphous materials, high polymer and high polymer/ceramic composite materials, ultraconductive alloy, and intermetallic compound[6−8].

2 Experimental raw materials and equipments

In this study, the common metal copper powder is used as experimental raw material with purity of 99.8%, and its maximum partical size and median diameter is 50 μm and 27.8 μm, respectively. The ananlysis of raw material particle size is showed in Table 1.

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The high energy milling equipment used in the experiment is experimental vibrating milling machine. Its structure properties are as follows: a horizontal central circular pipe is equipped in the center of the stainless steel, it can not only eliminate "central inert area" showed in the center of milling pipe, but also activates the movement of milling medium in order to increase the impactive energy of milling medium and the milling efficiency.

Table 1 Analysis of copper particle size

Size/μm	Mass percent /%	Accumulative mass percent/%
0−10	1.5	1.5
10−15	8.6	10.1
15−20	13.2	23.3
20−25	25.7	49.0
25−30	19.2	68.2
30−35	15.7	83.9
35−40	4.6	88.5
40−45	7.6	96.1
45−50	3.9	100.0

3 Results and discussion

3.1 Influence of milling time on partical size

The stainless steel balls (10 mm) are used as ball milling medium, the ratio of ball to material is 25:1. The changes of particle (<100 nm) content under different milling time is showed in Fig. 1. From Fig. 1, the influence of milling time on copper partical size is obvious. At the beginning, the partical size decreases sharply with the milling time prolonging, nanometer particle content increase fastly. After the milling time reaches 80 h though the milling time is prolonged, the particle size of products decreases lenitively, the increasing speed of the nanometer particle content tends lenitively. Different sample has different ball milling time. The results of the monofactor experiment show that the best milling time of copper particle is near to 80 h.

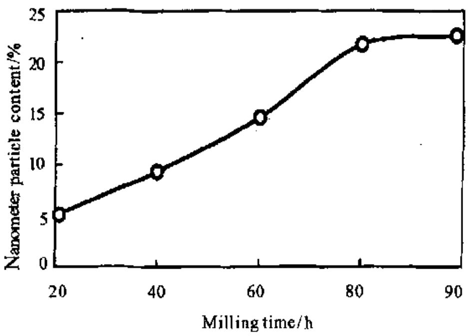

Fig. 1 Influence of milling time

3.2 Influence of ball milling intensity on copper particle size

Recently, the main equipments of high energy milling ars as follows: planetary mill, stirring mill and vibrational mill, and so on. The milling intensities of these milling machine are different. If the ball milling intensities are different, the particle distribution of final products are different in the same milling time. The experiment indicats that the energy by collision transfer and collision frequency has the important influence on the product particle size. In order to compare vibrational milling intensity with common milling intensity influenting on comminution of sample, experimental conditions are as follows: the milling medium is the stainless steel (D10 mm), the ratio of ball to material is 25:1, and the milling time is 80 h. The experimental results indicated that the effect of vibrational mill(the content of nanometer partcle is 21.7%) is better than that of common mill (the content of nanometer partcle is 0.8%), that is to say, an increase in the milling intensity makes for forming nanometer particle.

3.3 Influence of ball milling medium on partical size

During the high energy ball milling process, acid-resistant stainless steel or cemented carbides ball is usually used as ball milling medium, the ceramic ball can also be used in order to prevent the ball diaelectric from polluting the sample. The stainless steel balls (D10mm) and the ceramic balls (D10mm) are used respectively as the milling medium during experiment. The ball milling time is 30 h, the ratio of ball to material is 30:1. It can be found that nanometer particle content in the milling products prepared by use of the stainless steel ball is 13.1% and that in the milling products prepared by use of the cemented carbides ball is 7.8%. That is because impactive intensity produced on the sample porticles by using the stainless steel ball as the milling medium is higher than by using ceramic ball.

3.4 Influence of the ratio of ball to material on copper particle size

The ratio of ball to material is also an importent parameter of influencing the copper particle size. The stainless steel balls(D10 mm) are chosen as milling medium, ball milling time is 40 h, a series of experiments are made under different ratio of ball to material. The results show that nanometer particle content in the sample is ascending trend with the ratio of ball to material increasing under the same experimental conditions. From Fig. 2, the throughput of ball mill and the effect of ball mill will be reduced under the excessive ratio of ball to material. Therefore, the ratio of ball to material is not very high and not very low.

3.5 Comparision of dry milling and wet milling

The stable ratio of ball to material is 30:1. The stainless steel balls (D10mm) are chosen as medium, the effect of dry milling is compared with that of wet milling under the same milling time. The dry milling is adopted in air and wet milling is adopted in water and ethanol. Experimental results are showed in Fig. 3.

Experimental results show that the effect of wet milling is better than that of dry milling, and the effect of ethanol is better than that of water during wet milling.

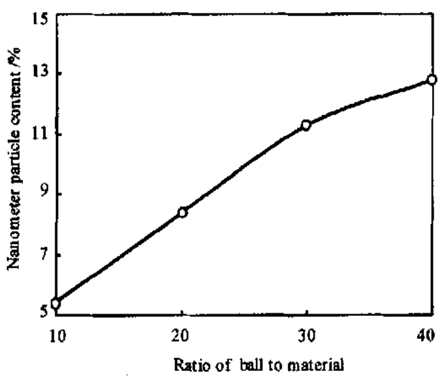

Fig. 2 Influence of ratio of ball to material

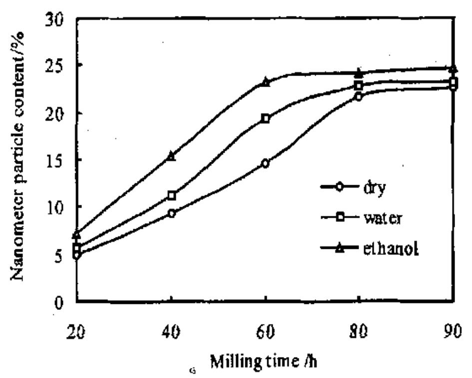

Fig. 3 Comparision of dry milling and wet milling

4 Properties of copper powder

4.1 Properties of copper particle size

By making an orthogonal experiment, the best conditions of preparing copper powder by vibrating milling (in ethanol) are found as follows: milling time is 60 h, the ratio of ball to material is 35 :1. The stainless steel balls (D10mm) are chosen as medium.

Under the best experimential conditions, the distributing characteristics of copper particle size is showed in Table 2, and its accummulative curve of particle size is showed in Fig. 4.

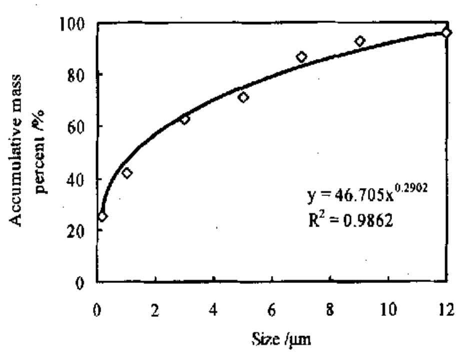

Fig. 4 Accumulative size distribution of copper powder

After the recursive ananlysis of the accumulative mass percent of every particle level is made, we reach that the distributive rule of copper particle size accords with the exponential function and the equation characteristic of copper particle is as follows:

$$y=46.705x^{0.2902}$$

correlative index R=0.9931

where y is the accumulative mass percent of particle size (%), x is the particle size(μm).

Table 2 **Analysis of copper particle size under the best conditions**

Size/μm	Mass percent /%	Accumulative mass percent/%
0—0.1	25.3	25.3
0.1—1.0	17.1	42.4
1.0—3.0	20.4	62.8
3.0—5.0	8.8	71.6
5.0—7.0	14.9	86.5
7.0—9.0	6.5	93.0
9.0—12.0	3.2	96.2
12—	3.8	100.0

4.2 Surface effect

Under the different millimg time, specific surface area of copper powder changes with different milling time as shown in Fig. 5. From Fig. 5, it is easy to find that the specific surface area increases with prolonging the milling time. A decrease in partical size increases the surface area and increases the surface atoms as well. These atoms have high activity and become instable because of these increased atoms and atoms with deficient proximate coordination numbers and high surface energy.

5 Conclusions

The milling time is one of the main factors affecting the effect of milling, any material has its own best milling time, the value is determined by certain experiment. The milling intensity is the direct factor affecting the particle size, if the high energy mill is used for preparing ultrafine copper powder, the properties of equipment are crucial. The milling medium and the ratio of ball to material can affect the fine partical content in products. The milling pipe and the ball are attrited by the crash and mill between balls and balls, balls and pipes, balls and materials, materials and pipes. The attrited substance is involved in the frayed raw material and become impurity. That is the maximal defect of ball mill. In order to prevend the impurity from being involed, the material of pipe is made of stainless steel, the cramic ball, the stainless steel ball or cemented carbides ball is often used as milling medium. And besides, the higher ratio of ball to material is used in order to acquire higher milling energy.

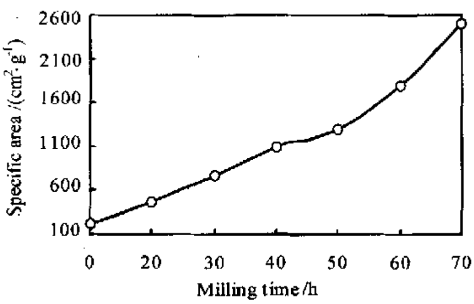

Fig. 5 Influence of the milling time on the specific surface area

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