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Original Research Paper

Effect of yttrium on properties of copper prepared by powder metallurgy

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A B S T R A C T

In this paper, Cu–Y composite materials containing different content of Y were prepared with optimized hot-press and cold-press forming process based on L_9 (3^4) orthogonal experiment and their physicochemical and mechanical properties including relative density, conductivity, oxidation resistance and hardness were been tested. The results indicate that the optimum preparation condition was: sintering temperature 800 °C, sintering time 3 h, pressure 30 MPa, Y-doping concentration 0.5 wt.% for hot-press forming and sintering temperature 880 °C, sintering time 3 h, pressure 600 MPa, Y-doping concentration 0.5 wt.% for cold-press forming. The addition of yttrium can improve the hardness and oxidation resistance of copper significantly and has the opposite effect on conductivity. The overall performances and process conditions of samples prepared by hot-press forming were significantly superior to those of cold-press forming.

1. Introduction

Copper alloys have excellent performance including high temperature strength, good temperature stability, high electrical and thermal conductivity [1–4], and they are commonly used as electrical conductivity and thermal conductivity materials in industry areas, especially being applied in resistance welding electrodes, lead frames, accelerators and electrical contact materials. Currently, the materials that own the vast majority of electrical contact materials are Ag-based composites [5,6]. However, due to the limited resources and valuableness of Ag, it is necessary to find an alternative material, such as copper, which has a similar conductivity to Ag [7], and it is more cheaper. The use of Cu instead of Ag as the substrate to make the electrical contact materials has great economic significance [8–10]. But, when used as the composite material substrate, Cu has a softer texture than Ag, and the electrical conductivity will rapidly decline when added with the strengthening phase. Is easily to surfer oxidation [11,12], resulting in the formation of CuO, Cu_2O or the mixture of them, and leading to the decline of conductivity, which consequently does harm to the stability of instruments and service life of electrical components. So it is generally difficult to use Cu or Cu alloy as the electrical contact materials in the air atmospheric environment.

The addition of rare earth lanthanum and cerium in the Cu and Cu alloys has been reported [13,14]. Both the addition of lanthanum and cerium can improve the strength of Cu, and lanthanum can also enhance the corrosion resistance of Cu. But due to the complexity of the Cu alloy as well as the limit and difficulty of characterizing the effect of rare earth, no complete theories are available to guide the design of this type due to the lack of research on it. Powder metallurgy is a commonly used method of preparing the electrical contact materials which can meet the requirements of the overall performance. Hot-press forming, known as process of the powder sintering to prepare products under the combined pressure and temperature condition simultaneously, has been applied in preparing Cu–Al_2O_3, Cu–W, Cu–C composites [15–18] that have been developed and applied earlier in the powder metallurgy technology. Compared with cold-press process forming, the powder sensitivity for hot-press forming process is lower and it is also true to the sintering temperature and pressure. That is to say compared with cold-press process forming, when the powder have a larger size range or a more irregular shape, the properties of the samples prepared by hot-press forming will be better. And the sintering temperature and pressure changed smaller, the properties of the samples prepared by hot-press forming will have a bigger change. The products with high density, homogeneous microstructure and no deformation can be obtained by hot-press forming, resulting in the excellent properties of products. In this

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paper, the cold-press forming vacuum and hot-press forming process were applied to prepare Cu–Y composites to study the effect of yttrium on the microstructure and properties of Cu and the different parameters between the two kinds of processes, aiming to give some contribution in the field of Cu–Y composites manufacturing by powder metallurgy.

2. Experiment

The particle size of both copper powder (degree of purity: 99.8%) and yttrium powder (degree of purity: 99.7%) are 200 mesh. The mixing time of the pre-mixing powder was 30 min by XQM type planetary ball mill. The zinc stearate was used as dispersant and added by an amount of 0.4 wt.%. The hot-press forming process is: mixing by ball mill → charging → preloading (10 MPa) → vacuum pumping → heating → boosting → holding temperature and pressure → cooling → pressure relief at 500 °C → cooling to room temperature → sampling. The cold-press forming process is: mixing by ball mill → Cold-pressing → compacts → vacuum sintering → cooling to room temperature → sampling. The VVPgr-80-2200 type vacuum hot pressing furnace was been used. Vacuum sintering was used by the GSL-1600 type vacuum furnace.

Density was measured by buoyancy method. Hardness was measured by brinell hardness sclerometer. The electric conductivity test was carried out with 4-electrode system. And antioxidant was measured by material gaining weight, in which the samples were oxidized under atmospheric ambience for 20 h at 380 °C in the GSL-1600 type vacuum furnace. The microstructure morphology of samples was characterized by the EVOMA 10 scanning electron microscopy (SEM). The crystal structures were studied by X-ray diffraction (XRD, D8-ADVANCE, Germany) with Cu Kα radiation.

3. Results and discussion

3.1. Orthogonal experiment design

Orthogonal experiment is a kind of mathematical statistical method. With this method, the optimum experiment parameters and the influence law of each parameters can be obtained by minor experiments. The range analysis and variance analysis are adopted in the experiment to investigate the influence of the various parameters on the properties of samples. The range analysis can draw the level of the effect of various factors on the experimental results. And the data obtained from the analysis of variance are more accurate.

In the experiments, relative density, hardness, IACS and oxidation weight gain are taken as the examining indexes, in which, IACS represents the International Annealed Copper Standard, which annealed pure copper is 100% IACS. For the elaboration of experimental plan, the orthogonal method for four factors at three levels was adopted. The sintering temperature, sintering time, pressure and addition of yttrium were selected as the experimental factors. The studied factors and the assignment of the corresponding levels of hot-press and cold-press are listed in Tables 1 and 2; respectively. In Tables 1 and 2, the selections of the factors' levels of hot-press and cold-press forming are the same except for the pressures, so that it is expedient for the contrastive analysis of these processes.

Table 1
Assignment of levels to factors of hot-press forming.

Level	Sintering temperature (°C)	Sintering time (h)	Pressure (MPa)	Addition of yttrium (wt.%)
1	880	2	30	1
2	950	3	20	0.5
3	800	1	40	2

Table 2
Assignment of levels to factors of cold-press forming.

Level	Sintering temperature (°C)	Sintering time (h)	Pressure (MPa)	Addition of yttrium (wt.%)
1	880	3	600	1
2	950	1	500	0.5
3	800	2	400	2

3.2. Range and variance analysis of hot-press forming

Table 3 shows the orthogonal array L_9 (3^4), experimental results and the range analysis of hot-press forming. In Table 3, R represents the range in the range analysis, and the larger value of R, the greater effect of the factor. Table 4 shows the results of the variance analysis of hot-press forming. In Table 4, F represents the Fisher–Snedecor statistics. The degrees of freedom represent the effective sample size, all of which are 2 for the four factors in this orthogonal experiment design. In order to analyze the significance of the factors on the properties of compacts, the factor which has the minimum value of F is assigned to the reference. $F_{0.05}$ represents the ratio compared with the reference when the significance coefficient is 0.05, and $F_{0.01}$ is also true. In the variance analysis, for $F_{0.05} = 19.00$, $F_{0.01} = 99.00$, the influence of the factor is not significant when $F < F_{0.05}$, denoted by "/"; the effect of the factor is significant when $F \geqq F_{0.05}$, denoted by "$*$"; the effect of the factor is very significant when $F \geqq F_{0.01}$, denoted by "$**$".

3.2.1. Influence of addition of yttrium on properties

As shown in Table 3, the R values of the addition of yttrium express the maximum of 37.32, 16.19 and 1.07 for the hardness, IACS and gaining weight, respectively. In Table 4, the influence of the addition of yttrium on these properties of the samples is significant, especially for the very significant influence on the hardness, so the added amount of yttrium is the key factor in this experiment. In Table 4, the significant factors affecting the hardness are both the addition of yttrium and the sintering time, and the influences of other factors are not significant, so the sintering time can be fixed so that the addition of yttrium affecting the hardness could be researched, it is also true to the conductivity and gaining weight. Fig. 1 shows the addition of yttrium vs. hardness and conductivity on the sintering time of 3 h and the addition of yttrium vs. gaining weight under the sintering temperature is 800 °C. The results show that both the hardness and gaining weight of the samples increase with adding amount of yttrium, while IACS just the opposite. When the addition of yttrium is 0.5 wt.%, the value of IACS reaches maximum and gaining weight value is minimum. Therefore, the experiments determine preliminarily the optimal content of yttrium is 0.5 wt.%, taking into account the requirements of the electrical contact material for overall performance.

3.2.2. Influence of pressure on properties

In Table 3, the relative density of all the samples are above 98%, indicating that the preparation of hot-pressing forming process is effective to high density products. As shown in Table 3, the R value of pressure express the maximum for the relative density. In Table 4, the influence of pressure on the relative density of samples is significant, so the pressure is the key factor for the relative density. As shown in Table 3, when the amount of yttrium is 0.5 wt.%, the values of relative density are 99.18%, 99.56% and 98.84% under the pressure of 20 MPa, 30 MPa and 40 MPa, respectively. It is