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Preparation and properties of ultra-fine-grained and nanostructured copper alloy with the addition of P

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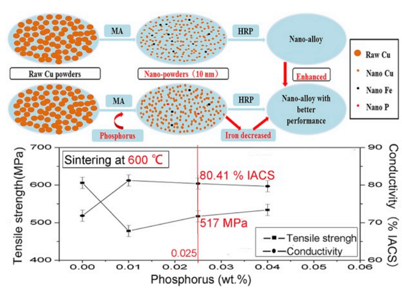
HIGHLIGHTS

- Nanoscale Cu-Fe-P powders with grain size of about 8 nm were fabricated.
- Nanostructured product can be obtained in a short time and at a low temperature.
- The content of Fe is reduced by P and thus the properties can be highly improved.
- The product exhibits excellent properties than most existing Cu-Fe-P alloys.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, the high performance Cu-Fe-P alloys with ultra-fine grain and nanocrystalline structure were successfully prepared by mechanical alloying (MA) and reactive hot-pressing (RHP). Then the combined effects of sintering temperature and phosphorus content on microstructure and properties were investigated. The results showed that phosphorus had a positive effect on the performance of Cu-Fe-P alloy. It could reduce the content of iron doped in the Cu matrix rather than forming precipitates such as Fe_3P or Fe_2P. Moreover, the ultra-fine grain and nanocrystalline structure had a great effect on performance of the alloys. The crystallite size of the Cu-Fe-P alloys exhibited average value of 10 nm after milling for 4 h by TEM. The lower sintering temperature was better to retain the size of nanoparticles and achieve excellent performance. Consequently, the best performance was achieved by the Cu-Fe-0.025P sintered at 600 °C and ball-milled for 4 h. The electrical conductivity reached 80.41% IACS with the tensile strength of 517 MPa which was much better than the conventional Cu-Fe-P alloy.

1. Introduction

Copper is widely used in the field of electronic appliances because of its good conductivity and fatigue resistance [1]. However, high mechanical strength is also a necessary condition for the Cu alloys' further application. So Cu-Fe-P alloys are widely concerned in the lead frames of integrated circuit because of their excellent electrical conductivity, good combination of mechanical and physical properties, ease of manufacture, and low cost [2–6]. It accounts for more than 65% of the total amount of lead frame materials. It has been frequently reported that Cu−Fe−P alloys are strengthened by precipitation hardening. Though the iron doped in the alloy can increase the tensile strength, it will also lead to a decrease of the conductivity. Therefore, it is very important to reduce as much iron in the copper matrix as possible [7].

Adding other alloying elements may be one way to reduce the content of iron in copper and improve the conductivity of the Cu alloys. P is a comparatively cheaper alloying element (compared with Ag, Ni, etc) in industry. And some studies found that Fe and P

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Table 1
The main components of the mixed powder (ICP).

Sample	Addition of P wt.%	Cu wt.%	Fe wt.%	O wt.%	C, Cr, Zr, Si wt.%
S1	0	> 98.66	1.330	1.000×10^{-3}	$< 1.000\times 10^{-3}$
S2	1.000×10^{-2}	> 98.83	1.150	1.100×10^{-3}	$< 1.000\times 10^{-3}$
S3	2.500×10^{-2}	> 98.85	1.120	1.300×10^{-3}	$< 1.000\times 10^{-3}$
S4	4.000×10^{-2}	> 98.99	0.9600	1.000×10^{-3}	$< 1.000\times 10^{-3}$

can form precipitates such as Fe_3P or Fe_2P during aging, which increases the strength and conductivity [5]. Despite all this, the contents of Fe and P should be limited to a very low level to maintain a high conductivity, which will result in low volume fraction of precipitates in the matrix and therefore low response to precipitation strengthening [3]. So many investigations of assisted enhancement methods have been conducted to increase the mechanical strength with a relatively high conductivity such as cold working and fine particles strengthening methods [8].

Fine-grain strengthening can be used as an assisting strengthening method because of its high response to strengthening and little harm on conductivity. And more attention has been paid to the ultrafine grain structure recently because it has much more potential to improve the mechanical properties than the coarse-grained materials [9–14]. Previous studies have shown that metallic oxide and alloys with ultra-fine grain and nanocrystalline structure can effectively improve the properties [15–21]. And for Cu-Fe-P alloys, the electrical conductivity is just slightly reduced with a significant increase in strength. The ultrafine grain structure can be obtained by mechanical alloying (MA) and reactive hot-pressing (RHP) [22,23]. Some researchers also use green synthesis methods to prepare nanomaterials [24–27].

MA is a solid powder processing technique in a high-energy ball mill which involves repeated welding, fracturing, and re-welding of powder particles. It can be used to produce nanocrystalline materials due to the remarkable deformation introduced into the powders and the low working temperature essential in keeping the nanocrystalline structure [28,29]. However, there will be iron introduced into the alloy during in the process of MA. So trace amounts of phosphorus were used to improve the performance. And as a sintering method, the advantages of reactive hot-pressing (RHA) lie in the short sintering time and low sintering temperature. So it could be used to prepare compact alloy block with ultrafine microstructure through inhibiting grain growth [30–36].

The main objectives of the present work are: (a) to synthesize Cu-Fe-P powders with ultra-fine grain by MA, (b) to sinter nanostructured Cu-Fe-P alloys by HRP, (c) to study the effect of trace addition of P, content of Fe and sintering temperature on the microstructures of Cu-Fe-P alloys, and (d) to obtain the optimum experimental conditions through analyzing the relationship between microstructure and performance.

2. Materials and methods

2.1. Preparation

Copper (48 µm, 99.9 wt.% purity) and phosphorus (3 µm, 99.9 wt.% purity) were used as raw materials. Then the powders were processed

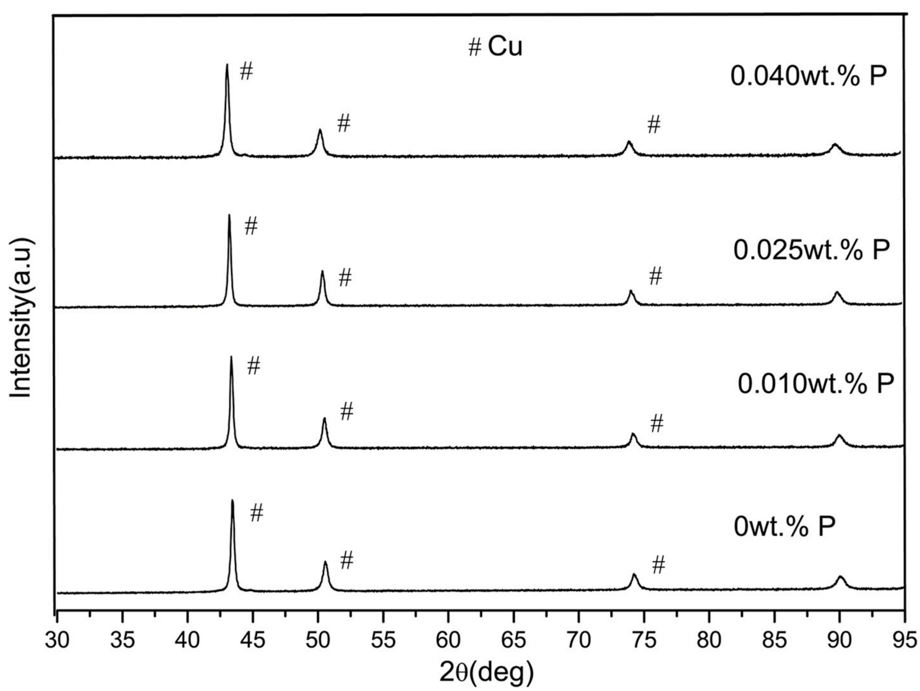

Fig. 1. XRD results of the powders with different P content.