Investigation of Submicron Powder Fabricated Cr50Cu50 Alloys Using Various Vacuum Hot-Press Sintering Temperatures

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The aim of this study is to explore the two different constituents of submicron-sized copper and chromium powders as Cr50Cu50 alloy materials. The research imposes various vacuum hot-press sintering temperatures (950°C, 1000°C, 1050°C and 1100°C) and pressures maintained at 12 MPa for 1 h, respectively. The experimental results show that the optimal parameters for the hot-press sintering of Cr50Cu50 alloys are 1050°C at 12 MPa for 1 h. The relative density reaches 96.09% and the apparent porosity decreases to 0.12%. Moreover, the hardness and TRS (transverse rupture strength) values increase to HV0.2 198.82 (HRB 91.07) and 910.04 MPa, respectively. The results of this study also indicate that the closed pores are effectively reduced and the mechanical properties of the Cr50Cu50 alloys are dramatically improved by increasing the temperature of the hot-press sintering process. Moreover, the optimal hot-press sintered Cr50Cu50 alloys also possess a dense microstructure and good electrical conductivity. The resistivity is decreased to 5.89 × 10⁻⁸ Ω·cm and the ICAS is enhanced to 29.27%.

Keywords: submicron powder, Cr50Cu50 alloy, hot-pressed sintering, transverse rupture strength (TRS), resistivity

1. Introduction

Nanomaterials have received many recent attentions because they are expected to be used in various applications based on their excellent and unique optical, electrical, magnetic, catalytic, or mechanical properties. Presently, the use of nano and submicron-structured powders for producing materials with finer microstructures represents one of the most active fields of research in the alloy industry, because the nano and submicron-structured alloys possess more excellent mechanical properties such as high hardness, strength and toughness.1,2)

Since Cr-Cu alloys have high strength, good electrical conductivity, excellent arc erosion and welding resistance, due to the exclusive combination of properties of the two constituents, they are employed as the best contact materials for medium-voltage, high-vacuum interrupters. Most of the production methods of this component initiates with a powder mixture of Cr and Cu.3,4) The properties of Cr-Cu alloys mainly depend on the microstructure, such as compositional distributions and grain sizes. With the decreasing of the grain size, the chopping current and the breakdown field of the Cr-Cu materials could be improved significantly.5)

Powder metallurgy (P/M) is the conventional process for the production of Cr–Cu alloys. Typically the alloys are produced by blending, pressing, vacuum sintering, and further compact the sintered pieces, when Cr content is in the range 25–40% by weight.3,6–8) On the other hand, hot-pressed sintering technique as a common technique was performed to fabricate the bulk bodies of the alloys. The hot-pressed sintering is another special P/M technology, which directly pressed and sintering the material through a graphite mold to transmit the pressure to the powders. Whereby, it can obtain the dense material at relatively lower sintering temperature.9–11)

As the application of Cr50Cu50 requires long-term stability and reliability, this study aims to use hot-press sintering technology to produce the optimal Cr50Cu50 alloys. The effect of submicron structured powders on the alloy properties is also a chief concern. In this work, a series of experiments using the hot-press sintering process was carried out to explore the sintering behavior and properties of Cr50Cu50 alloys. The effects of the microstructure features on the mechanical and electrical properties of the alloys were of particular interest. In addition, the feasibility of commercially manufacturing Cr50Cu50 alloys by means of the hot-press sintering process was evaluated.

2. Experimental Procedure

In this work, the Cr50Cu50 alloys produced via vacuum hot-press sintering of P/M technology; 99.95% submicron-size particles of reduced chromium and gas-atomized copper powders were mixed and pressed to produce Cr50Cu50 alloys. A Microtrac X 100 laser was used to analyze the particle size of the submicron-size powders. The morphology of the chromium and copper powder particles is shown in Fig. 1. The shape of the reduced chromium powder was irregular; there was no smooth undulating surface, as shown in Fig. 1(a). The mean particle size was about 650 ± 43 nm. In addition, the morphology of the gas-atomized copper powder showed obvious round shapes, as shown in Fig. 1(b). The gas-atomized powders possessed an excellent forming
mechanism and sintering characteristics because the particles had a relatively smooth surface; the mean size was 350 ± 48 nm. Figure 1(c) shows the clear cold welding morphology under the effect of mechanical alloying by ball milling for 1 h. The mixed alloy powders produced many secondary particles, and the mean particle size was enhanced to 876 ± 63 nm.

In addition, a series of hot-press sintering (950°C, 1000°C, 1050°C and 1100°C maintained at 12 MPa for 1 h, respectively) treatments was performed in order to investigate the effects on the mechanical properties, microstructures and electrical behaviors of the Cr50Cu50 alloys. The hot-press sintering process directly pressed and sintered the material through graphite mold to transmit the pressure onto the powders. As a result, it can obtain the more dense material at relatively lower sintering temperature. Moreover, sintering is a method for manufacturing parts from powders, by heating the material until its particles adhere to each other. The size of hot-press sintering compact was 40 mm × 40 mm × 5 mm. To evaluate the sintered characterization of the Cr50Cu50 alloys via hot-pressed sintering (Yu Tai Vacuum Co., Ltd. HPS-1053) processes, the porosity, hardness, transverse rupture strength (TRS) tests, electrical tests and microstructure inspections were performed. Microstructural features of the specimens were examined by X-ray diffraction (XRD, Rigaku D/Max-2200) and scanning electron microscopy (Hitachi-S4700). Porosity tests followed the ASTM B311-08 and C830 standards.

The hardness of the specimens was measured by Rockwell indenter (HRB, Indentec 8150LK) with loading of 981 N, which complied with the ASTM E18-08b standard methods. In addition, the hardness also measured by Micro-Vickers (HV, Matasuzawa MMT-X) with loading of 2 N, which complied with the ASTM E92. The Hung Ta universal material test machine (HT-9501A) with a maximum load of 245 kN was used for the TRS tests (ASTM B528-05). Meanwhile, \( R_{\text{bm}} \) was the transverse rupture strength, which determined as the fracture stress in the surface zone. \( F \) was maximum fracture load, \( L \) was 30 mm, \( k \) was chamfer correction factor (normally 1.00–1.02), \( b \) and \( h \) were 5 mm in the equation \( R_{\text{bm}} = \frac{3FLk}{2bh^2} \), respectively. The specimen dimensions of the TRS test were 5 mm × 5 mm × 40 mm. Moreover, it needs to slightly grind the surface of the specimen and tests at least three pieces. A four-point probe (LRS4-TG2) was used to measure sheet resistance. Besides, resistivity was calculated according to the following formula:

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\rho = \frac{V}{I} C \cdot t \text{ (mΩ-cm)}
\]

where the \( \rho \) is resistivity, \( V \) is voltage, \( I \) is current, \( C \) is a constant, and \( t \) denotes the thickness of the test sheet.

### 3. Results and Discussion

Vacuum hot-press sintering is a complex method that combines sintering and pressing processes. In this process, the material is directly pressed and sintered through a graphite mold to transmit the pressure onto the powders, as shown in Figs. 2(a) and 2(b). As a result, it is possible to obtain a denser material at a relatively low sintering temperature. Figure 3 shows the XRD patterns of the Cr50Cu50 alloys following hot-press sintering at different temperatures. The major diffractions appeared in the Cr (110), (200) and Cu (111), (200), (220) planes, respectively. Due to the crystal structure dependence on the XRD diffraction intensity, \( 6,7 \) it was reasonable to suggest that all Cr50Cu50 alloys possessed a good crystalline property after hot-press sintering under the different temperatures. Significantly, the two thermodynamically immiscible metals of chromium and copper produced no alloy phases after the hot-press sintering processes; only the pure chromium and copper peaks appeared in the XRD patterns, as shown in Fig. 3.
Increasing the temperature of the hot-press sintering (950°C → 1000°C → 1050°C → 1100°C) slightly increased the intensity of the Cr diffractions (110); or rather the X-ray counts of Cr (110) increased from 4546 (950°C) to 4601 (1000°C), 4650 (1050°C) and 4985 (1100°C), respectively. In addition, the relative intensity of the Cu diffractions (111) also increased slightly before 1100°C hot-press sintering. The X-ray counts of Cu (111) increased from 5548 (950°C) to 5627 (1000°C) and 5675 (1050°C), but declined to 5350 at 1100°C. When the sintering temperature was raised to 1100°C, the high angle offset phenomenon of the copper was reduced. It was reasonable to surmise that the copper generated a lot of liquid interfaces, which caused the rearrangement of the pressurized crystal grains.

Figure 4 shows a comparison of the relative density and apparent porosity of Cr50Cu50 alloys by hot-pressed sintering at different temperatures. The experimental results indicated that the relative density of the Cr50Cu50 alloys was slightly lower (92.78%) and the apparent porosity slightly higher (0.57%) after hot-press sintering at 950°C for 1 h. However, when the hot-press sintering temperature was raised to 1050°C, the relative density rapidly increased to 96.09%, while the apparent porosity decreased to 0.12%. Generally, it is difficult to achieve a high density (> 95%) of the Cr-Cu alloys for solid-phase sintering (SPS) under an atmospheric pressure.11,12) The characteristics of the hot-press sintering are that the mixed powder is synchronously heated and pressed into the shape of a graphite mold. However, when hot-pressed sintering entered the sintering stage, the assistance in high compressing stress led to effective atomic diffusion, plastic deformation and compaction results. In this research, hot-press sintering was effective in providing the driving force of the sintering mechanism and helping the atomic diffusion due to external pressure (12 MPa). Therefore, the Cr50Cu50 alloys could achieve a good sintering effect at a relatively low temperature (1050°C) as compared with our previous vacuum sintering study7) (the optimal vacuum sintering temperature of Cr50Cu50 alloy is 1270°C). When the hot-press sintering temperature was increased to 1100°C, the relative density and apparent porosity showed no obvious change. However, the liquid binding phase (copper) could more easily fill the pores between the two grains and provide much higher energy for the particles to move and diffuse. Consequently, the dissolution and re-precipitation effects resulted in a slight reduction in porosity. Besides, the liquid-phase produced under a high pressure (12 MPa) easily generated the melting and gravity segregation phenomenon between the alloy and graphite mold, which is not conducive to fabricate Cr50Cu50 alloys by hot-press sintering.

Figure 5 shows the OM morphology observations of the Cr50Cu50 alloys by hot-press sintering at different temperatures; while the white parts are the chromium grains and the gray parts are the copper, both uniformly dispersed in the microstructure. The existence of residual black pores was obvious after hot-press sintering at 950°C for 1 h, as shown in Fig. 5(a). The pores decreased as shown in Fig. 5(b). When the sintering temperature was raised to 1050°C, the copper quickly filled the pores between the chromium grains due to the SPS effects; few internal pores of the Cr50Cu50 hot-press sintering specimens remained in the sample. Moreover, the refined particles of the chromium tended to coarsen slightly
due to the solid diffusion of the high temperature (1050°C) and high pressure (12 MPa), as shown in Fig. 5(c). In this study, the melting temperature of copper is 1085°C. Therefore, the solid diffusion of hot-pressed sintering was generated below 1050°C, and the mean grain size of the chromium increased from 4.98 µm (950°C) to 5.87 µm (1050°C). On the other hand, the liquid phase sintering (LPS) effect should appear at 1100°C. Figure 5(d) shows the obvious LPS effects after the high-temperature (1100°C) and high-pressure (12 MPa) sintering, i.e. the grain coarsening (the mean grain size of the chromium was 6.33 µm) and the agglomeration phenomena. Particularly, the volume ratio of copper and chromium phase after solid-phase sintering at 1050°C 1 h was 34.6 ± 0.1 and 62.9 ± 0.1% respectively (Fig. 5(c)). However, the volume ratio of copper and chromium phase after liquid-phase sintering at 1100°C 1 h was 46.6 ± 0.1 and 50.8 ± 0.1% respectively (Fig. 5(d)). In addition, the literature has indicated that rapid grain growth during the early stage of sintering has been found in many nano and submicron material systems.13,14) Significantly, the Cr50Cu50 powders seemed to lose their submicron-scale characteristics after sintering, as is the case for most submicron-size powders, due to the extremely rapid grain growth during the high-temperature and high-pressure sintering. The mechanism of rapid grain growth needs further examination.

As regards the OM observations, the results showed that the internal pores of the Cr50Cu50 alloys slowly decreased as the sintering temperature increased under the same hot-press pressure (12 MPa). Figure 5(a) illustrates the many larger and dispersed pores in the specimen (porosity 0.57%). When the temperature increased, the larger pores apparently became smaller, as shown in Figs. 5(b) (porosity 0.24%), 5(c) (porosity 0.12%) and 5(d) (porosity 0.11%). Due to the compaction effects of the hot-press pressure, the original pores of the Cr50Cu50 alloys gradually decreased and led to the lower amount of pores. This result, when compared with Fig. 4, shows that the relative density increased to 96.09% and the apparent porosity rapidly decreased to 0.12% after hot-press sintering at 1050°C at 12 MPa for 1 h. The high density (> 95%) of the Cr-Cu alloys for SPS can be acquired.

Figure 6 shows the hardness tests and relative density of the Cr50Cu50 alloys by hot-pressed sintering at different temperatures. Both HV0.2 and HRB tests for the specimens exhibited a similar hardness trend (HV0.2 is a representative hardness of specimens), as shown in Figs. 6(a) and 6(b). Significantly, the hardness values of the Cr50Cu50 alloys were similar after sintering at 950°C, 1000°C and 1050°C, respectively. The hardness of the 1050°C-sintered specimens reached HV0.2 198.82 and HRB 91.07, while the hardness of the 1100°C-sintered specimens showed a rapid decline (HV0.2 181.22 and HRB 87.44). As seen in Fig. 6, there was no relationship between the relative density and the hardness. LPS is a process for forming high performance, multiple-phase components from powders. It involves sintering under conditions where solid grains coexist with a wetting liquid. In addition, the main densification mechanism of hot-pressed sintering included the initial diffusion creep of high temperature and plastic deformation during the SPS step. When hot-pressed sintering entered the sintering stage, the assistance in high compressing stress led to effective plastic deformation and compaction results. It seemed reasonable to suggest that the main difference in the hardness resulted from the LPS and SPS effects, and that the hot-press LPS of the Cr50Cu50 alloys clearly resulted in a relative instability. The result could be further compared with Fig. 5, while also noting that the increase in relative density was advantageous to the hardness. The grain-coarsening phenomenon also appeared in the 1050°C-sintered specimens (Fig. 5(c)) and was disadvantageous to the hardness. As a result, there were no significant variations in hardness as a result of the SPS process (950°C, 1000°C and 1050°C).

The interface numbers are calculated by the overall interface numbers of cross chromium/copper alloys in the unit length of BEI images. The previous literature indicated that a structure with more interface numbers has a better microstructure.5) Figure 7 shows the interface numbers and transverse rupture strength tests of the Cr50Cu50 alloys by hot-press sintering at different temperatures. Increasing the hot-press sintering temperature to 1050°C significantly increased the interface numbers of the Cr50Cu50 alloys. The highest value (487.83) of interface numbers appeared in the 1050°C-sintered specimens. However, the interface numbers (348.16) rapidly declined at 1100°C, as shown in Fig. 7(a). It is reasonable to state that the 1050°C-sintered specimens possessed the more meticulous microstructure, which was advantageous to the mechanical property. Conversely, the 1100°C-sintered specimens had lower interface numbers due to the LPS effect. A large amount of liquid copper was
covered with the chromium grains after the LPS process; consequently, the lowest hardness appeared in the 1100°C hot-press sintering specimens.

Figure 7(b) shows the TRS tests of the Cr50Cu50 alloys by hot-press sintering at the different temperatures. The TRS values showed an increasing trend as the hot-press sintering temperature increased to 1050°C. The highest TRS value (910.04 MPa) appeared in the Cr50Cu50 alloys after hot-press sintering at 1050°C at 12 MPa for 1 h. Although the grain sizes showed a slight coarsening phenomenon in the 1050°C-sintered specimens, a small variation in grain size did not seem to affect the TRS value. When compared with Fig. 7(a), the results clearly showed that the interface numbers of the Cr50Cu50 alloys had a corresponding relationship with the TRS. It is reasonable to suggest that the effects of the LPS and SPS processes resulted in the differences in the mechanical property tests (hardness and TRS).

Figure 8 shows the fractographic observations of the Cr50Cu50 alloys by hot-press sintering at different temperatures; the white and black areas are the sintered copper and chromium phase, which are indicated by the arrows as shown in Fig. 8(b). It was found that both tough and brittle fractographs existed in the Cr50Cu50 alloys after the TRS tests, as shown in Figs. 8(a)–(c). The fracture mechanism was evidenced by the ductile copper producing the dimple fracture, and the brittle chromium generating the cleavage and transgranular fracture. When the deformation of a specimen exceeds its elastic limit, it will crack directly under the concentrated stress, causing the local chromium particles near the Cr-Cu interfaces to spread and expand rapidly, which is detrimental to the fracture resistance of the interface. In addition, it was also found that the more malleable and ductile copper surrounded the complete particles of chromium, and that the main fracture mechanism of the Cr50Cu50 alloys was generated by the brittle properties of the chromium, which showed obvious cleavage and transgranular fractures (Fig. 8(d)). It is possible to say that the more cleavage fractures appeared in the microstructures, which resulted in a decrease in TRS.

In order to study the effect of the hot-press sintering temperature on the resistivity of the Cr50Cu50 alloys, the resistivity was converted to the International Annealed Copper Standard (IACS). In general, alloys with a higher IACS (conductivity of specimen/5.8 × 10^6%) value have better conductive properties. As shown in Table 1, the highest IACS value (38.44%) of the Cr50Cu50 alloys occurred after LPS at 1100°C for 1 h. A lot of liquid copper surrounded the complete particles of chromium after the LPS, which was advantageous to the conductive properties. In addition, the SPS temperature (1050°C) possessed the higher IACS (29.27%) and relatively low resistivity (5.89 × 10^{-6} Ω·cm). Generally, the average distance that an electron travels before a collision is called the mean free path. The detailed explanation of the electron mean free path in metals is a major success of the modern theory of solids, and the mean free path is proportional to the relaxation time. A decrease in the mean free path of the electrons means “less moving”, and results in an increase in the resistivity. The high density (96.09%) of the 1050°C hot-sintered specimen resulted from a increase in the mean free path of the
electrons; thus, the resistivity of the Cr50Cu50 alloys decreased. According to the above results and discussion, the hot-press sintering parameters of 1050°C at 12 MPa for 1 h for the Cr50Cu50 alloys obviously possessed the optimal mechanical and electrical properties.

4. Conclusions

The sintered Cr50Cu50 alloys had better crystalline properties after the hot-press sintering treatment, in comparison with a conventional sintering treatment. Significantly, the two thermodynamically immiscible metals of chromium and copper produced no alloy phases after the hot-press sintering processes. Furthermore, the Cr50Cu50 powders lost their submicron-scale characteristics upon sintering, as is the case for most submicron-size powders, due to the extremely rapid grain growth during the high-temperature and high-pressure sintering processes.

The sintered Cr50Cu50 alloys possessed the optimal SPS at 1050°C and the optimal LPS at 1100°C for 1 h, respectively. Although the resistivity of the Cr50Cu50 alloys was effectively decreased after LPS at 1100°C, the LPS easily resulted in gravity segregation under a high-pressure condition. Therefore, achieving a high densification of Cr50Cu50 alloys by means of SPS becomes an important topic. In addition, the relative density of the Cr50Cu50 alloys reached 96.09%, the apparent porosity decreased to 0.12% and the TRS increased to 910.04 MPa after the optimal SPS treatment (1050°C at 12 MPa for 1 h). The resistivity decreased to $5.89 \times 10^{-6} \Omega \cdot \text{cm}$ and the ICAS was enhanced to 29.27%.

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