Journal of Alloys and Compounds 509S (2011) S361–S363

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Non-equilibrium copper-based crystalline alloy sheet having ultrahigh strength and good electrical conductivity

Haruko Miura [a,*], Nobuyuki Nishiyama [a], Akihisa Inoue [b]

[a] RIMCOF Tohoku Univ. Lab., The Materials Process Technology Center, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[b] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

ARTICLE INFO

Article history:
Received 30 June 2010
Received in revised form 25 January 2011
Accepted 27 January 2011
Available online 2 February 2011

Keywords:
Nano-composite
Mechanical properties
Electrical conductivity
Rapid-solidification
Quenching

ABSTRACT

To develop an alternative material to Cu–Be alloys, $Cu_{93.5}Zr_{5.5}Ag_1$ non-equilibrium alloy sheets were prepared through the simple production process of die-casting, annealing and cold rolling. The developed sheets exhibit ultrahigh tensile strength of 1530 MPa, plastic elongation of 1.2% and good electrical conductivity. These results suggest that the developed sheets have excellent properties and constitute an alternative material to Cu–Be alloys.

1. Introduction

To make our daily life more convenient, most of goods, devices and transportation are supported by electric power. Electrical connectors have an important role for transmitting the power with high reliability and low loss. Cu-based alloys such as phosphorus bronze and Corson (Cu–Ni–Si) alloy are conventionally used as electric conductive materials. According to the recent progress of miniaturized and sophisticated digital electronics such as cellular phones, car navigation systems or mobile TV, there is an increasing need for high strength and good conductivity materials. Due to such requirements, Cu–Be alloys are the most used materials because of their well-balanced properties of strength, elongation and conductivity. However, alternative materials to Cu–Be alloys are strongly required because of the future environmental regulations for beryllium use. In addition, the development of conductive materials with higher performance is also required for making electrical connectors with low height and fine pitch.

Besides Cu-based bulk metallic glasses [1], a number of Cu-based crystalline alloys have been produced by heavy working and age-hardening of supersaturated solid solutions [2,3] or by rapid solidification of hypereutectic Cu-based alloys [4] designed by the glass-forming rules [5] for stabilization of undercooled liquid. An alloy satisfying the glass forming rules in low or medium solute concentration range up to 7 at.% can be easily undercooled, leading to the formation of fine and disordered structure. By subsequent heavy working, various non-equilibrium phases with long-periodic hexagonal structures [6] or nano fibrous structures consisting of fcc-Cu and non-equilibrium Cu_9Zr_2 phases [3] can be formed. The high tensile strength (σ_f) and large plastic elongation (ε_p) of these alloys are attributed to their special non-equilibrium structure [7]. However, a novel conductive Cu-based alloy with higher σ_f and good electrical conductivity ratio (κ) is strongly required for the development of electrical connectors with lower height and finer pitch. By using this concept, we have successfully developed a new non-equilibrium Cu-based alloy with a σ_f of 1200 MPa, ε_p of 3.1% and κ of 30.7% IACS (defined as the resistivity ratio to the international annealed copper), respectively [8]. We found that the supersaturated Zr content in the fcc-Cu phase is decomposed by annealing, leading to the improvement of κ. In addition, the induced dislocations by cold rolling enhance σ_f. However, the annealing will weaken the effect of strengthening by cold rolling. It is therefore imperiously necessary to modify the process for production of novel Cu-based alloys with higher σ_f and better κ.

In this paper, we present our results on the microstructure, mechanical and electrical properties of Cu–Zr–Ag alloys produced by a modified precision die-casting (PDC) process [10], followed by annealing and cold rolling. In addition, we will discuss the possibility of using the newly developed Cu-based alloys as electrical contacting materials.

* Corresponding author. Tel.: +81 22 215 2840; fax: +81 22 215 2841.
E-mail address: rimcofmh@imr.tohoku.ac.jp (H. Miura).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.01.137

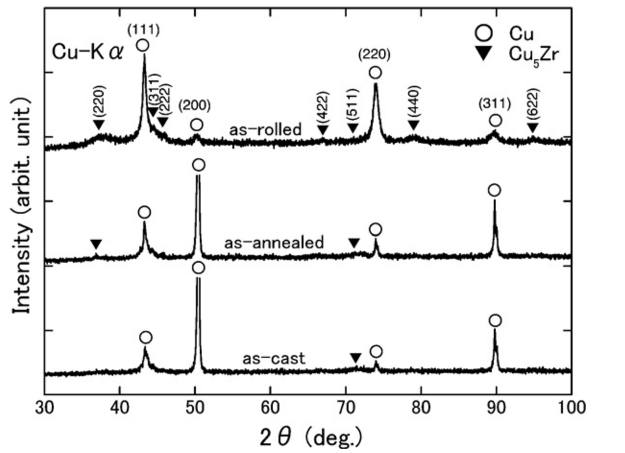

Fig. 1. XRD patterns of $Cu_{93.5}Zr_{5.5}Ag_1$ as-cast, annealed and cold-rolled alloy sheets.

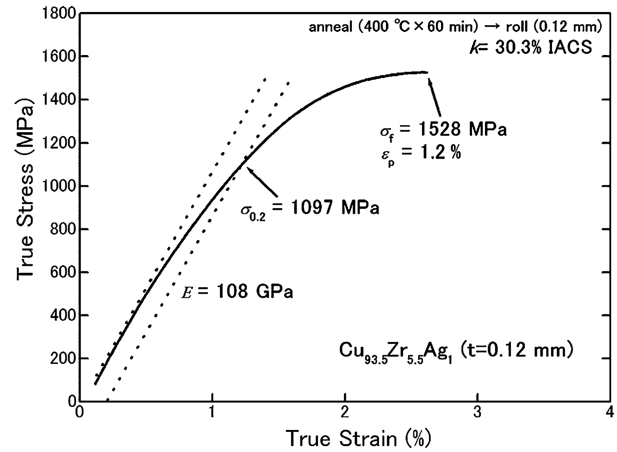

Fig. 3. True stress–true strain curves of the annealed and cold-rolled $Cu_{93.5}Zr_{5.5}Ag_1$ alloy sheets. The electrical conductivity measured by a DC four-probe method is also indicated.

2. Experimental procedure

Ternary alloy ingots with the nominal composition of $Cu_{93.5}Zr_{5.5}Ag_1$ were prepared by arc melting a mixture of pure elements (above 99.9 mass% purity) under a purified Ar atmosphere. Rapidly solidified Cu–Zr–Ag alloy sheets with the length of 60 mm, width of 50 mm and thickness of 1.5 mm were prepared by the PDC method. The cooling rate of the PDC method is estimated to be several hundreds K/s [9]. Such a high cooling rate is attributed to high contact pressure between the mold and the molten alloy, leading to fine and disordered structure. The cast sheets were annealed at 673 K for 3.6 ks under ambient atmosphere, and then cold-rolled to prepare thin sheets with the length of about 200 mm, width of 52 mm and thickness of 0.12 mm, respectively. The phase identification for the as-cast, annealed and cold-rolled samples was carried out by X-ray diffractometry (XRD) and the structure of the samples was observed using optical and scanning electron microscopy (OM and SEM). The local disordered structure was examined by transmission electron microscopy (TEM). The mechanical properties such as σ_f, 0.2% proof stress ($\sigma_{0.2}$) and ε_p were examined under tensile stress at room temperature using an Instron testing machine. The annealed and cold-rolled sheets were punched out as dog-bone-shapes and tensile tests were carried out at a strain rate of $5.0 \times 10^{-4}\ s^{-1}$ with a gauge of 2 mm in width and 10 mm in length. The electrical resistance of each sample was measured by a DC four-probe method.

3. Results and discussion

Fig. 1 shows the XRD patterns of $Cu_{93.5}Zr_{5.5}Ag_1$ as-cast, annealed and cold-rolled alloy sheets. Only $(1\,0\,0)_{fcc}$-oriented phase with high diffraction intensity can be detected in the as-cast state. This result is similar to the one obtained for the rapidly solidified pure-Cu reported in Ref. [2], indicating that the major constituent phase is Zr supersaturated fcc-Cu. After annealing the presence of the Cu_5Zr compound is more evident, while the $(1\,0\,0)_{fcc}$-oriented structure still remains predominant. The $(1\,1\,1)_{fcc}$ peak is more pronounced upon rolling whereas the $(3\,1\,1)_{fcc}$ peak is broadened and weakened. The dislocations induced during cold rolling are most probably the cause for the appearance of the $(1\,1\,0)_{fcc}$ oriented texture [10]. Fig. 2 shows the cross sectional OM structures of the (a) as-cast, (b) annealed and (c) cold-rolled sheets, respectively. The horizontal direction represents the rolling direction. For the as-cast state (Fig. 2(a)), the structure exhibits a typical hypoeutectic feature, namely primary fcc-Cu dendrites with a secondary dendrite arm spacing (DAS) of about 2 μm and residual fine eutectic phases. Upon annealing (Fig. 2(b)), no significant changes are observed. The previous studies on similar alloy compositions have shown that the fine eutectic structure is composed of fcc-Cu and Cu_5Zr (cF24, a = 0.687 nm) compound [11]. Considering the XRD profile shown in Fig. 1, corroborated with Fig. 2(a) and (b) the structure of the as-cast and annealed $Cu_{93.5}Zr_{5.5}Ag_1$ alloys is composed of primary fcc-Cu dendrites (bright) and fcc-Cu + Cu_5Zr eutectic phases (dark gray). In addition, the EDX analysis reveals that the Zr content in the primary fcc-Cu dendrite phase and eutectic fcc-Cu phase is 1.8 ± 0.2 and 2.9 ± 0.2 at.%, respectively for the as-cast sample, After annealing, Zr content of both primary fcc-Cu dendrite phase and eutectic fcc-Cu phase is decreasing to 1.4 ± 0.3 and 2.7 ± 0.2 at.%. In fact, the Zr content in the Cu5Zr compound is increasing from 10.2 ± 0.4 to 11.7 ± 0.2 at.% by annealing. This decreasing in each Cu phase suggests that the supersaturated Zr is decomposed. However, no precipitates could be found in Fig. 2(b). The cast structure is extremely elongated along the rolling direction by heavy cold rolling with a thickness reduction ratio of 0.08 (Fig. 2(c)). Zr content of the primary fcc-Cu dendrite phase and eutectic fcc-Cu phase after cold rolling is further decreased to 1.2 ± 0.2 and 2.2 ± 0.3 at.%, respectively, indicating the mechanical deformation induced structural change [8]. Compared with the previous work [8], the high cooling rate was achieved by the PDC method, as evidenced by the smaller secondary DAS of fcc-Cu dendrites of about 2 μm and the lower Zr content in the Cu_5Zr phase of only 10.2 ± 1 at.%.

Fig. 3 shows the true stress–true strain curves of annealed and cold-rolled $Cu_{93.5}Zr_{5.5}Ag_1$ alloy sheets. One can observe that $Cu_{93.5}Zr_{5.5}Ag_1$ sheets subjected to annealing exhibit the highest

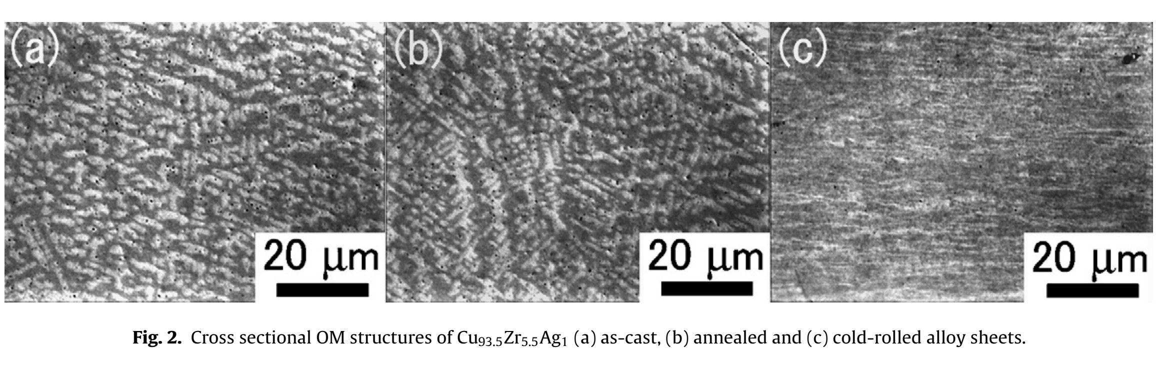

Fig. 2. Cross sectional OM structures of $Cu_{93.5}Zr_{5.5}Ag_1$ (a) as-cast, (b) annealed and (c) cold-rolled alloy sheets.

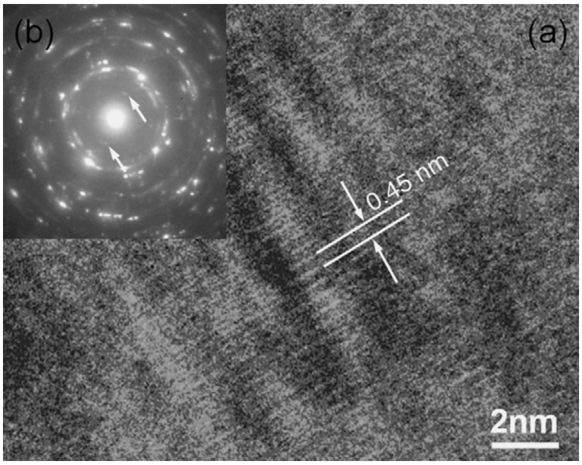

Fig. 4. (a) High resolution TEM image and (b) selected-area election diffraction pattern taken from. fcc-Cu phase in the annealed and cold-rolled $Cu_{93.5}Zr_{5.5}Ag_1$ alloy sheet.

σ_f of 1528 MPa. In addition, $\sigma_{0.2}$, Young's modulus (E) and ε_p are 1097 MPa, 108 GPa and 1.2%, respectively. The ε_p value obtained in the present study is lower than the one reported in our previous study [8]. However, the σ_f value exceeding 1500 MPa is much higher than that reported for Cu–Be alloy [12], indicating the successful preparation of low height electrical connector using thinner sheets. In addition, the effective decomposition of supersaturated Zr by annealing improves κ. On the contrary, no degradation in κ could be observed by following cold rolling. Consequently, relatively high κ of 30.3% IACS could be obtained.

To clarify the mechanical deformation induced structural changes and to understand the reason for ultrahigh strength, the local structure was examined by TEM. Fig. 4(a) and (b) shows the high resolution TEM image and selected-area electron diffraction (SAED) pattern for the subsequent cold-rolled annealed sheets. One can see clear fringes contrast with a period of about 0.45 nm (a) as well as extra diffraction spots (represented by white arrows) (b). These results suggest that some periodic local structure is formed during the mechanical deformation induced by cold-rolling. Assuming that a cold rolling is not a heating process, the formed periodic local structure seems to be purely structural rather than being a chemical one. Such a periodicity could be found for similar Cu–Zr binary alloy reported in [13]. However, the periodicity reported in [13] is composed of alternating small bands of fcc-Cu and Cu_5Zr-based superlattice structure with a periodicity of about 2 nm. By assuming the difference in periodicity and (1 1 1) spacing of Cu_5Zr structure, the present periodic local structure is possibly attributed to the newly precipitation of fine Cu_5Zr particle from the Zr-supersaturated fcc-Cu phase. In any case, high strength of exceeding 1500 MPa was obtained in the present Cu-based ternary alloy. In addition, the lower Zr content in fcc-Cu phase may be favorable to high κ and good bending ductility. It is thus concluded that these ultrahigh strength and better κ of the Cu–Zr–Ag annealed and cold-rolled sheets will enable us to design new electrical connectors with low height and fine pitch.

4. Conclusions

By a modified sequential process of PDC method, followed by annealing and cold rolling, non-equilibrium $Cu_{93.5}Zr_{5.5}Ag_1$ alloy sheets were prepared. Ultrahigh strength of 1500 MPa, plastic elongation of 1.2% and good κ of 30.3% IACS were obtained for the sheets with a thickness of 0.12 mm. Such excellent properties of the newly developed sheets are attributed to the local periodic structure, smaller secondary DAS and less Zr content in the Cu_5Zr compound. These results suggest that the newly developed $Cu_{93.5}Zr_{5.5}Ag_1$ alloy sheets with ultrahigh strength represent candidate material for miniaturized electrical connectors.

Acknowledgements

This study was supported by "New Energy and Industrial Technology Development Organization" (NEDO) under "Technological Development of Innovative Components Based on Enhanced Functionality Metallic Glass" project. The authors are grateful to Prof. Y. Hirotsu, and Prof. M. Ishimaru at Osaka University for TEM observations.

References

[1] Q.S. Zhang, W. Zhang, G.Q. Xie, A. Inoue, Mater. Trans. JIM 48 (2007) 1626–1630.
[2] H. Kimura, A. Inoue, K. Sasamori, H. Yoshida, O. Haruyama, Mater. Trans. JIM 46 (2005) 1733–1736.
[3] H. Kimura, A. Inoue, N. Muramatsu, K. Shin, T. Yamamoto, Mater. Trans. JIM 47 (2006) 1595–1598.
[4] A.R. Yavari, K. Ota, K. Georgarakis, A. LeMoulec, F. Charlot, G. Vaughan, A.L. Greer, A. Inoue, Acta Mater. 56 (2008) 1830–1839.
[5] A. Inoue, Mater. Trans. JIM 36 (1995) 866–875.
[6] A. Inoue, M. Matsushita, Y. Kawamura, K. Amiya, K. Hayashi, J. Koike, Mater. Trans. JIM 43 (2002) 580–584.
[7] A. Inoue, H.M. Kimura, K. Amiya, Mater. Trans. JIM 43 (2002) 2006–2016.
[8] H. Miura, N. Nishiyama, N. Togashi, M. Nishida, A. Inoue, Intermetallics 18 (2010) 1860–1863.
[9] M. Ishida, H. Takeda, D. Watanabe, K. Amiya, N. Nishiyama, K. Kita, Y. Saotome, A. Inoue, Mater. Trans. JIM 45 (2004) 1239–1244.
[10] W. Bose, J.K. Mackenzie, Prog. Metal. Phys. 2 (1950) 90.
[11] P. Villars, Pearson's Desk Edition, vols. 1–2, ASM International, Materials Park, OH, 1997.
[12] K.P. Jen, L.Q. Xu, S. Hylinski, N. Hylinski, Gildersleeve, JMEP 17 (2008) 714–724.
[13] K.H. Kim, J.P. Ahn, J.H. Lee, J.C. Lee, J. Mater. Res. 23 (2008) 1987–1994.