Microstructure and properties of Cu-2Ag alloy sheet prepared by ‘Upward + Thermomechanical Treatment’

Li Ming-Mao1, Zhao-Xin Li1,*, Tang Ying-Ying1 and Zhu Ming-Biao2

1 Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou, 341000, People’s Republic of China
2 Jiangxi Advanced Copper Industry Research Institute, Yingtan, 335000, People’s Republic of China
* Author to whom any correspondence should be addressed.
E-mail: 2413991151@qq.com

Keywords: Cu-2Ag, upward continuous casting, solid solution, aging, performance

Abstract
In this paper, the Cu-2Ag sheet is prepared by the new process of upward method, and the alloy sheet was prepared by continuous cold rolling and thermomechanical treatment of solution aging. Through scanning electron microscopy, transmission electron microscopy, performance testing and other means, the effects of upward, rolling, solid solution, aging and other processes on the forming process of silver-copper alloy is systematically analyzed, so as their microstructure, mechanical properties and electrical properties. The results show that it is feasible to prepare the Cu-2Ag sheet by the upward method, which can meet the requirements of subsequent forming and use performance: Cu-2Ag has a dispersion precipitation effect, and a reasonable heat treatment process that can produce a large number of nano-level spherical silver-rich solid solutions uniformly dispersed in the copper matrix, thereby optimizing the properties of the alloy. After being treated by solution, it has the best performance under 450 °C × 48 h aging, with a hardness of 74.9 HV0.2 and conductivity of 92.7% IACS.

1. Introduction

Generally speaking, the effect of solid solution strengthening on the conductivity and strength of copper is contradictory [1]. However, silver is different from other elements that are solid-soluble in copper, when the content of silver is less, the electrical conductivity and thermal conductivity of copper will not decrease much, the impact on plasticity will be minimal, and the recrystallization temperature, creep strength and fatigue strength of copper will be significantly increased. Therefore, copper-silver alloys are widely used in the preparation of pulsed strong magnetic field coils, high-speed train wires, integrated circuit lead frames and other fields [2–4].

In recent years, scholars in this field have reported a series of research results on Cu–Ag alloys under cold deformation processing [5–8], however, such reports mostly focus on silver–copper alloys with high silver content of 6wt.%–24 wt.% or with lower silver content of 0.1 wt.% and below. J B Liu et al [7, 9] prepared Cu-12wt.%Ag and Cu-24 wt.%Ag alloys with dual-phase filament structure through cold drawing of large deformation and intermediate heat treatment. Although they have all shown an ultra-high tensile strength of about 1 GPa, their electrical conductivity is relatively poor (Cu-12 wt.%Ag alloy <85%IACS, Cu-24 wt.%Ag alloy<75%IACS). Xiaowei Zuo et al [10] prepared Cu-6wt.%Ag alloy by vacuum induction melting, and its hardness reached a peak value of 126 HV when it was aged at 450 °C, at this time, its conductivity was about 88% IACS. Cu-0.1 wt.%Ag alloy has high electrical conductivity, but its tensile strength is poor [8]. Therefore, the Cu–Ag alloy with a silver content of 0.1–4 wt.% is more likely to obtain a good match of strength and conductivity. Also, in comparison with the silver–copper alloy with higher silver content, it can lower costs greatly.
The traditional Cu–Ag alloy preparation process is mostly non-vacuum melting or vacuum melting and semi-continuous ingot or iron mold ingot production, followed by face milling and hot processing [11–14], and finally cold processing. Due to the great loss of materials in the milling surface, the large investment in hot rolling equipment and complex processes, the yield of Cu–Ag alloy is very low, which is very inappropriate for niche products such as Cu–2Ag. Upward continuous casting is a short-process and efficient production process. The copper alloy surface after upward can still remain bright and clean even without milling. And through direct cold processing, the process flow can be greatly shortened, the yield rate can be greatly increased, and the energy consumption can be reduced. From the equilibrium phase diagram, the Cu–2Ag alloy has the possibility of precipitation strengthening, the solid solution treatment is expected to increase the solid solubility of Ag in Cu, the aging treatment can make the Ag phase more dispersed, which is expected to achieve precipitation strengthening, refine grains and reduce segregation.

Based on the above background, this paper takes Cu–Ag alloy with a silver content of 2 wt.% as the research object. This alloy is prepared by continuous upward under atmosphere protection, combined with cold rolling and solution aging processes. Then, the evolution of microstructure and properties of such alloy during the processing and preparation process is studied. By optimizing the alloy processing and preparation technology, a high-performance Cu–Ag alloy material is developed, in order to further improve the comprehensive properties of Cu–Ag alloys; it also provides important theoretical support and new experimental ideas for the design and preparation of new high-strength and high-conductivity copper alloys.

2. Experiment

The experiment uses high-purity cathode copper and pure silver ingots as raw materials to prepare alloy sheets through atmospheric melting-upward continuous casting. The thickness of the sheet is 11 mm and the width is 100 mm, the industrial production photos under upward state are shown in figure 1. The rough rolling mill is used to cold roll the sheet, and the thickness of the sheet after cold rolling is 5.5 mm, with the deformation of 50%. The cold-rolled sample was cut into 20 mm × 20 mm × 5.5 mm pieces, and then it was treated by solid solution at 900 °C × 2 h in a box-type resistance furnace. The cooling method was water quenching. Then the solid solution sample was aged in a box-type resistance furnace, with the aging temperature of 450 °C, and the aging time was 30 min, 2 h, 4 h, 8 h, 12 h, 24 h, 48 h, respectively.

Eddy current conductivity meter (Sigma2008B/C), Vickers hardness tester (FM-700, Japan Future-Tech) were used to measure the conductivity and Vickers hardness of the alloy under each state (test force is 1.961 N). Before the measurement, sandpaper is used to remove impurities and oxide scale on the surface of the material. The sandpaper with roughness of 60 mesh, 320 mesh, 800 mesh, 1200 mesh, 1500 mesh and 2000 mesh are used in sequence. The scratches on the surface of the material are required to be uniform and fine. Metallographic microscope (OM, Axioskop2, Zeiss, Germany), scanning electron microscope (SEM, MLA650F, FEI company in the United States, with energy spectrometer) were used to study the microscopic morphology and structure of the alloy, and energy spectrometer was used to analyze the second phase in the alloy. Transmission electron microscope (TEM, TecnaiG2–20, FEI Company, USA) was used to analyze the morphology and structure of the precipitated phase. The specimens observed by transmission electron microscope were sliced from loose materials and grounded into thin slices with a thickness of about 60 μm, and then punched into round foils with a diameter of 3 mm. The sample round foil is electrolyzed and double-sprayed by a double-spray electrolyzer at a voltage between 40–50 V, and the temperature of the double-spray liquid should be kept at about −40 °C. The double spray liquid is a mixture of nitric acid (concentration between 65% and 68%) and methanol (analytical grade) with a ratio of 1:4.

3. Results and discussion

3.1. Organizational analysis

Figure 2(a) is the finished product of the upward sheet, it can be seen that the outer surface of the upward sheet is smooth and the color is close to pure copper. The quality of the cast sheet is relatively good, for there are almost no large surface defects. The distribution of silver is also relatively uniform, for there is no obvious segregation, and the energy consumption per ton of the preparation process (generally within 400 KWH/ton) is low. In summary, it can be seen that the Cu–2Ag alloy sheet prepared by the upward continuous casting method is more feasible.

Figure 2(b) is a macrostructure diagram along the upward direction, it is a typical as–cast macrostructure consisting of a small amount of surface layer fine crystal regions and columnar crystal regions. The columnar crystals are relatively coarse, with a diameter of millimeters, it can be seen that some columnar crystals grow parallel to the upward direction, while others grow at a certain angle to the upward direction, its formation is
mainly related to the direction of heat dissipation and the anisotropy of crystal growth. Figure 2(c) is a cross-sectional metallographic diagram of the upward state, its central section is equiaxed, which shows that the columnar crystals in the upward state are close together, and the interface between the crystal grains is relatively straight, the shrinkage cavity tends to be small, and the organization is relatively dense.

The Cu-2Ag sheet prepared by the upward method has a regular shape, high density, a smooth surface without milling, and meets the needs of subsequent molding and use performance, compared with the traditional hot rolling method, it has significant advantages.

3.1.1. Microstructure of Cu-2Ag alloy updraw sheet and cold-rolled sheet

Figure 3(a) is the SEM image of the upward state, which shows a certain number of spherical particles with a size of about 2–3.5 μm distributed on the copper dendrites, the results of energy spectrum analysis show that the spherical particles in figure 3(a) are all silver-rich solid solutions. The results of EDS point scanning analysis show that the silver content of silver-rich solid solutions is 55–72 wt.%, figure 3(d) is the EDS spectra of the silver-rich solid solution at point A in figure 3(a), the spacing between each spherical silver-rich solid solutions is more than tens of microns, and the silver content of the copper matrix is 0–1.3 wt.%, figure 3(e) is the EDS spectra of the copper matrix at point B in figure 3(a), indicating that there is still a large amount of silver not dissolved in the copper matrix. The silver content of the alloy is not high, and the eutectic structure formed is too small to present in the microscopic morphology. Figure 3(b) is the SEM image of the Cu-2Ag alloy after cold rolling, figure 3(c) is the morphology of the partial area in figure 3(b) been enlarged 20 times. It can be seen that the silver-rich solid solutions are elongated along the rolling direction, indicating that the silver-rich solid solutions participate in plastic deformation, which can hinder the movement of dislocations to a certain extent, thereby strengthening the alloy.

3.1.2. The micro morphology of Cu-2Ag alloy solid solution state and time precipitation

Figure 4(a) shows the microstructure of the alloy after solid solution at 900 °C for 2 h. It can be seen from the figure that it presents obvious annealing twins, the grains are connected to each other to form equiaxed crystals,
and the grain size is 105–210 μm, no obvious silver-rich solid solutions appeared in the matrix, indicating that after 900 °C × 2 h solid solution, the silver atoms were more completely dissolved.

Figures 4(b)–(i) are the precipitation morphology and diffraction spot analysis of Cu-2Ag alloy aged at 450 °C for different time. Figure 4(b) is the transmission brightfield image of the alloy aged at 450 °C for 30 min. It can be seen that after aging at 450 °C for 30 min, the spherical particles are distributed more uniformly on the matrix. The spherical particles are mainly 2–5 nm, and a certain number of spherical particles in 4–7.5 nm are still exist. By calibrating the electron diffraction patterns in the precipitation phase indicated by the arrow in figure 4(b), it is confirmed that they are face-centered cubic Ag. After aging, Ag precipitates from the copper matrix, nucleates and grows.

As shown in figure 4(d), it can be found that compared with 450 °C × 30 min aging, the number of precipitates after 450 °C for 4 h aging does not increase significantly. The size range of the spherical precipitated phase is between 4–7.5 nm, and the spherical precipitated phase with the original size range of 2–5 nm has grown.

After aging at 450 °C for 12 h, a small amount of rod-shaped precipitates appeared in the matrix, as shown in figure 4(f), the diameter of rod-shaped precipitates was between 2–3.5 nm.

After aging at 450 °C for 48 h, the rod-shaped precipitates in the matrix became coarser and the quantity also increased to a certain extent. As shown in figure 4(h), the diameter of the rod-shaped precipitates at this time was between 4.5–9.5 nm. Similarly, the electron diffraction patterns are calibrated in the precipitated phase within the selected areas indicated by arrows in figures 4(e), (g), (i) and confirm that they are all face-centered cubic Ag. The research of Gang Chen et al [13] showed that the rod-shaped nano silver-rich solid solutions should be transformed from spherical nano silver-rich solid solutions, the axis direction of the rod is ⟨110⟩, which should be the growth direction. This orientation relationship also promotes the formation of rod-shaped large particles.
and reduces the interface energy, and the spherical nano silver-rich solid solutions and rod-shaped nano silver-rich solid solutions have a coherent relationship with the copper matrix.

### 3.2. Performance analysis

Table 1 shows the microhardness and electrical conductivity values of the Cu-2wt.%Ag alloy in each state. From Table 1, it can be seen that the hardness and electrical conductivity of the upward alloy are lower, which is mainly due to the excessive coarse as-cast grains and certain casting stress. After cold rolling with a deformation of 50%, the hardness of the alloy has been greatly increased (more than doubled, about 68.5 HV0.2), and the electrical conductivity has dropped by 7.6% IACS. This is because, as the amount of deformation increases, the dislocation density increases, the dislocations are entangled, and the resistance to the movement of the dislocations increases. All of which result in work hardening, which greatly increases the hardness of the silver-copper alloy. From the perspective of hardness increase, under the same cold deformation, it is much higher than the work hardening level of pure copper and silver-copper alloys with low silver content, indicating that 2 wt.% Ag can significantly increase the work hardening rate of the alloy. At the same time, the cold-rolled alloy has more crystal defects, more serious matrix lattice distortion, and higher dislocation density, which hinder the movement of electrons. Therefore, the electrical conductivity decreases. Similarly, with respect to pure copper and silver-copper alloys with low silver content, cold deformation under the same amount of deformation reduces its electrical conductivity more significantly.

After a solid solution at 900 °C for 2 h, the microhardness of the alloy is again reduced to close to the as-cast level, while the electrical conductivity is greatly improved. That is because the alloy is completely recrystallized during the solid solution, and the strengthening effect of cold rolling on the alloy is completely eliminated. In
addition, cold rolling with three-dimensional compressive stress increases the density of the alloy and makes the structure more uniform after solid solution the silver atoms are solid-dissolved into the copper lattice, causing lattice distortion. On the one hand, the solute atoms in the matrix can effectively hinder the movement of

Figure 4. The micro morphology of Cu-2Ag alloy solid solution state and aging precipitation: (a) SEM image of solid solution at 900 °C for 2 h, TEM image (b), (d), (f), (h) and SAED image (c), (e), (g), (i) of Cu-2Ag alloy aged at 450 °C for 30 min, 4 h, 12 h and 48 h respectively.
dislocations and strengthen the alloy appropriately; on the other hand, the solid solution of silver could influence the conductivity of the copper matrix, but with an insignificant impact. It shows that the solid solution of silver does not greatly affect the electrical properties of copper.

Aging at 450 °C for different times, with the increased aging time, the hardness and electrical conductivity of the alloy have been improved, but the increment is not large. In terms of comprehensive performance, 450 °C × 48 h aging has the best performance, where the hardness is 74.9 HV0.2 and the conductivity is 92.7%IACS. Compared with the solid solution state, the hardness is increased by 11.6 HV0.2 and the conductivity is increased by 2.4%IACS. Combined with microstructure analysis, it can be known that the nano-level silver-rich solid solutions are dispersedly distributed in the copper matrix, which hinders the movement of dislocations to a certain extent, however, the Ag particles are relatively soft, so the hardness of the alloy increases not much after aging; on the other hand, due to the precipitation of the nano-level silver-rich solid solutions, the lattice distortion is reduced, and the scattering effect of electrons is reduced, so the conductivity is improved to a certain extent.

4. Conclusion

In this study, Cu-2Ag alloy sheets were prepared by continuous upward under atmosphere protection process, and then the alloy was cold rolled (deformation of 50%), followed by solution treatment at 900 °C for 2 h, as well as a different aging time at 450 °C. The evolution of the microstructure and properties of the Cu-2Ag alloy during the processing and preparation process is studied, and the conclusions are as follow:

(1) The Cu-2Ag sheet prepared by the upward method is feasible, the alloy plate has a regular shape, high density, smooth surface without milling, and meets the needs of subsequent forming and use performance. It has significant advantages in comparison with the traditional hot rolling method.

(2) The longitudinal section macrostructure of the Cu-2Ag alloy under upward state is composed of typical columnar crystals and surface fine-grained regions. A certain number of spherical silver-rich solid solutions with a size of about 2–3.5 μm are distributed on the copper dendrites. After cold rolling, the silver-rich solid solutions are elongated in the rolling direction.

(3) Cu-2Ag has a precipitation effect. After solid solution at 900 °C for 2 h, the silver atoms are completely dissolved. There is obvious annealing twin structure, and the crystal grains are connected to each other to form equiaxed crystals, the grain size is 105–210 μm, and there is no obvious silver-rich solid solutions appeared in the matrix. After aging at 450 °C for 30 min, the spherical silver-rich solid solutions are distributed more uniformly on the matrix, they are mainly 2–5 nm, and there are a certain number of spherical silver-rich solid solutions with a size of 4–7.5 nm. After aging at 450 °C for 4 h, the number of spherical silver-rich solid solutions did not increase significantly, and their sizes were basically between 4–7.5 nm. After aging at 450 °C for 12 h, a small amount of rod-shaped silver-rich solid solutions appeared in the matrix, the diameter of which was between 2–3.5 nm. After aging at 450 °C for 48 h, the rod-shaped

| Performance | Microhardness /HV0.2 | Conductivity/%IACS |
|-------------|----------------------|-------------------|
| upward      | 59.7                 | 75.2              |
| Cold rolled (30% deformation) | 128.2                | 67.6              |
| 900 °C × 2 h Solid solution | 63.3                 | 90.3              |
| 450 °C × 30 min aging | 68.3                 | 90.4              |
| 450 °C × 2 h aging | 71                   | 91                |
| 450 °C × 4 h aging | 70.5                 | 91.3              |
| 450 °C × 8 h aging | 76.3 | 91.2 |
| 450 °C × 12 h aging | 73.2 | 91.6 |
| 450 °C × 24 h aging | 73.7 | 91.8 |
| 450 °C × 48 h aging | 74.9 | 92.7 |

Table 1. The microhardness and electrical conductivity of Cu-2Ag alloy under each state.
silver-rich solid solutions becomes coarser and the number has also increased to a certain extent, at this time, the diameter of the rod-shaped silver-rich solid solutions is about 4.5–9.5 nm.

(4) The physical and mechanical properties of Cu-2Ag changed significantly under different processing conditions. The hardness and electrical conductivity of the upward state Cu-2Ag alloy are low. After cold rolling (50% deformation), the hardness of the alloy is greatly increased (increased by about 68.5 HV0.2), and the electrical conductivity is significantly reduced. After solid solution at 900 °C × 2 h, the hardness of the alloy dropped significantly to only 63.3 HV0.2, but it was slightly improved compared to the hardness of the upward state, after solid solution, the conductivity of the alloy reached 90.3%IACS. Under aging at 450 °C, with the increase of aging time, the hardness and electrical conductivity of the alloy have been improved, but the increase is not significant. The overall performance achieves best when aging at 450 °C × 48 h, for which the hardness is 74.9 HV0.2, and the conductivity is 92.7%IACS.

Acknowledgments

The authors greatly appreciate financial support from the key scientific and technological projects in Jiangxi Province (20181BCB19003), and Jiangxi University of Science and Technology.

ORCID iDs

Zhao-Xin Li https://orcid.org/0000-0003-4124-0281
Tang Ying-Ying https://orcid.org/0000-0001-9603-6232

References

[1] Liu J B, Zeng Y W and Meng L 2009 Crystal structure and morphology of a rare-earth compound in Cu–12wt.%Ag J. Alloys Compd. 468 0–76
[2] Hong S I and Hill M A 1998 Microstructural stability and mechanical response of Cu–Ag microcomposite wires Acta Mater. 46 4111–22
[3] Tian Y Z et al 2012 Microstructures, strengthening mechanisms and fracture behavior of Cu–Ag alloys processed by high-pressure torsion Acta Mater. 60 269–81
[4] Chang L L et al 2015 Strain softening during tension in cold drawn Cu–Ag alloys Mater. Charact. 108 145–51
[5] Sakai Y and Schneider–Muntau H J 1997 Ultra-high strength, high conductivity Cu–Ag ALLOY wires Acta Mater. 45 1017–23
[6] Zhang L and Meng L 2005 Evolution of microstructure and electrical resistivity of Cu–12 wt.%Ag filamentary microcomposite with drawing deformation Scr. Mater. 52 1187–91
[7] Liu J B, Meng L and Zeng Y W 2006 Microstructure evolution and properties of Cu–Ag microcomposites with different Ag content Mater. Sci. Eng.: A 435–436 237–44
[8] Coddet P et al 2015 Mechanical properties of Cu–0.1Ag Alloys deposited by cold spray with various powder feed rate and heat treatment J. Therm. Spray Technol. 24 119–23
[9] Liu J B and Meng L 2006 The characteristics of Cu–12 wt.% Ag filamentary microcomposite in different isothermal process Mater. Sci. Eng.: A 418 320–5
[10] Wang E et al 2016 Microstructure and properties of Cu–6wt% Ag composite thermomechanical-processed after directionally solidifying with magnetic field J. Alloys Compd. 676 46–53
[11] Ota H and Miyata H 2011 Precipitation kinetics and mechanism in Cu–7 wt.% Ag alloy Materials Sciences and Applications 92 889–910
[12] Korneva A et al 2019 Dissolution of Ag precipitates in the Cu–8wt.%Ag alloy deformed by high pressure torsion Materials 12 447
[13] Bittner F et al 2014 Dynamic recrystallisation and precipitation behaviour of high strength and highly conducting Cu–Ag–Zr–alloys Mater. Sci. Eng.: A 597 139–47
[14] Gao X et al 2016 Effect of cold rolling and heat treatment on properties and microstructure of Cu-24wt%Ag alloys Mater. Sci. Forum 850 755–61
[15] Chen G et al 2018 Effect of heat treatments on microstructures and tensile properties of Cu–3wt%Ag-0.5wt%Zr alloy Met. Mater. Int. 24 255–63