Characterization of Cu-Ag-Y Alloy Synthesized by the Continuous Casting Technique

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Abstract: In order to develop a new type of electrical contact wires with high strength and high electrical conductivity, Cu-2Ag-0.5Y alloy was selected as materials. Cu-Ag-Y alloy was prepared by continuous casting, cold drawing and aging treatment. By means of the analysis of microhardness, electrical conductivity, scanning electron microscopy, and transmission electron microscopy, the aging properties and microstructures of the Cu-Ag-Y alloy were investigated at different aging temperatures and time after different cold deformation. The results show that the Cu-2Ag-0.5Y alloy has an excellent combination of microhardness and electrical conductivity aged at 500℃ for 4 h, the microhardness and the electrical conductivity reach 166 Hv and 82.2% IACS, respectively. The main strengthening mechanisms for the Cu-2Ag-0.5Y alloy are the work hardening and the second phase or interfaces strengthening. It was suggested that cold deformation prior to aging treatment can accelerate the precipitation of the second phase, and improve the comprehensive properties of the Cu-Ag-Y alloy.

Key words: metal materials; Cu-Ag-Y alloy; continuous casting; aging treatment; properties

CIF number: TG146.3　　**Document code:** A　　**Article ID:** 1004-0676(2014)S1-0084-06

连续铸造制备 Cu-Ag-Y 合金的特征

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摘　要：为研发一种具有高强度和高导电性的新型电接触导线，选择 Cu-2Ag-0.5Y 合金为实验材料。通过连续铸造、冷拉拔和时效处理工艺制得 Cu-Ag-Y 合金。采用显微硬度仪、导电率测试仪、扫描电镜和透射电镜，研究了不同时效温度和时间条件下预变形合金的显微组织与性能变化规律。结果表明，经 500℃/ 4 h 时效后，Cu-2Ag-0.5Y 合金获得了最佳的性能组合，其显微硬度和导电率分别为 166 Hv 和 82.2%IACS。Cu-2Ag-0.5Y 的主要强化机制为加工硬化、第二相强化或界面强化。时效处理之前的冷变形可以加速 Cu-Ag-Y 合金基体中第二相的析出，并提高合金的综合性能。

关键词：金属材料；Cu-Ag-Y 合金；连续铸造；时效处理；性能

In recent years, a great deal attention has been paid to develop the copper alloys with high strength and high electrical conductivity for applications such as the electrical resistance welding electrode, liner

Received: 2014-08-05
Foundation item: National Natural Science Foundation of China (51164015); Science and Technology Innovation Team of Kunming City (2012-01-01-A-R-07-0005); Scientific and Technological Cooperative Project (2012IB002); Key Basic Research Project of Yunnan Province (2011FA026)
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tube of continuous casting crystallizer, integrated circuit lead frame, electrical locomotive, high speed electric railways[1-3]. With the development of the electrical industry, there is a need to enhance the qualities of conventional electrical materials, including high strength, high electrical conductivity and good plasticity, so it is important to develop higher properties copper alloys[4-6]. The copper alloys include essentially two types: one is the alloy system of Cu with face-centered-cubic elements such as Ni, Ag, the other is the alloy system of Cu with body-centered-cubic elements such as Cr, Mo[7]. The microstructure and properties of the Cu-Ag alloy system have also been extensively investigated[8-12].

It has been proved experimentally that the microstructure and properties of Cu-Ag or Cu-Ag-M (M=Zr, Cr or Y) alloy were under influence of many factors such as the content of silver, alloy element addition, degree of deformation, solidification condition, thermo-mechanical processing etc[13-17]. For example, a newly developed Cu-Ag-Zr alloy based on Cu-Ag alloy has an excellent combination of mechanical strength and electrical conductivity. The high electrical conductivity of Cu-Ag-Zr alloy is due to the very low solubility of zirconium in copper, whereas the excellent strength is attributed to precipitation and particle dispersion strengthening mechanisms. It was reported that the microhardness and electrical conductivity of the Cu-Ag-Zr alloy can reach 134 HV and 84.6% IACS, respectively after aging treatment[18].

In order to understand further the effect of aging condition during the process on the microstructure and properties, and to develop a new Cu-Ag-Y alloy with high strength and high conductivity, the Cu-2Ag-0.5Y alloy (wt%) was selected as the object of present study. The electrical resistivity tester, microhardness measurement, scanning electron microscopy and transmission electron microscopy examination were performed to characterize the microstructures and properties of the alloy during the ageing process in the present paper.

1 Experiment

The 99.95% Cu, 99.99% Ag and 99.99% Y in purity were used to prepare the Cu-2Ag-0.5Y alloy. The alloy ingots were prepared by continuous casting equipment of RT100 made by Rautomead Company. The ingots were solidified rapidly through pouring the alloy melt into a water-cooled copper mould. Subsequently, the alloy ingots of 15mm in diameter were cold forged and drawn to wires of 2mm in final diameter. The aging treatments were carried out using a tube electric resistance furnace under an atmosphere of nitrogen with the temperature accuracy of ±5℃. The samples with different aging temperatures and aging times during the aging process were taken to determine the microhardness and electrical conductivity and to analyze the microstructure.

The microhardness was determined using a micro Vickers hardness tester with a load of 1.961N, a holding time of 10s and each sample was measured five times to obtain the value. The electrical conductivity was determined by measuring the alloy samples using a FD101 metal conductivity tester with the accuracy of ±0.1% IACS, and every sample was tested for five times. The microstructure was observed using SEM of Hitachi S-3400N operated at 30 kV. The TEM examinations were carried out using a H800 transmission electron microscope operating at 200kV.

2 Results and discussion

2.1 Microstructures

The microstructure of the Cu-2Ag-0.5Y alloy at typical processing state is shown in Fig.1. The results show that the matrix of the alloy is substantially solid solution at solid solution state, but there are still some small particles that are not solid solved completely. At cold rolling sate, there are a large number of dislocations in the matrix, which are caused by cold working. After aging treatment, in addition to the retention of the sub-dislocation structure, there are some micrometer precipitates existing in the alloy matrix. Because the solid solubility of Y in Cu is less than 0.01% at room temperature in the matrix, the precipitates are Y or $Y_xAg_{(1-x)}$ particles which may have a coherent orientation relationship with Cu matrix.

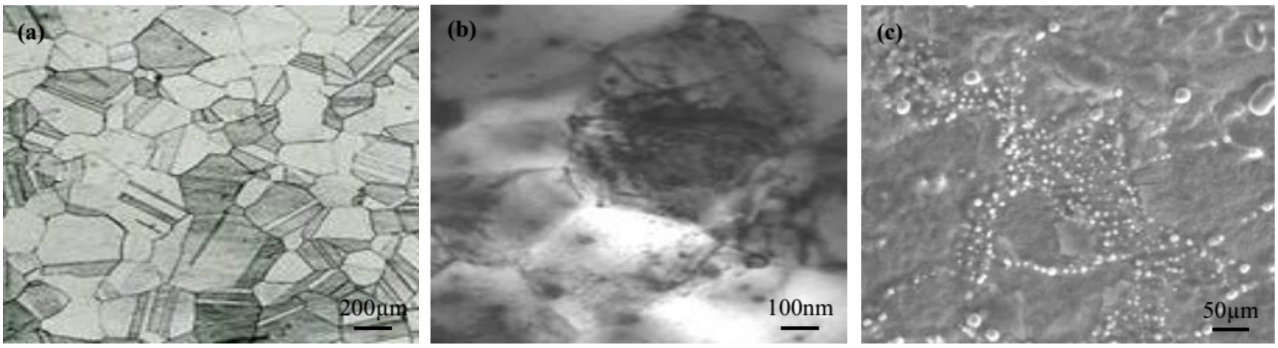

Fig.1 Microstructures of the Cu-2Ag-0.5Y alloy [(a). solution; (b). cold working; (c). aging]

图 1 Cu-2Ag-0.5Y 合金的显微组织 [(a). 固溶态；(b). 冷加工态；(c). 时效态]

2.2 Aging treatment

The effect of aging time between 1 h and 7 h for varying temperature on the microhardness is shown in Fig.2.

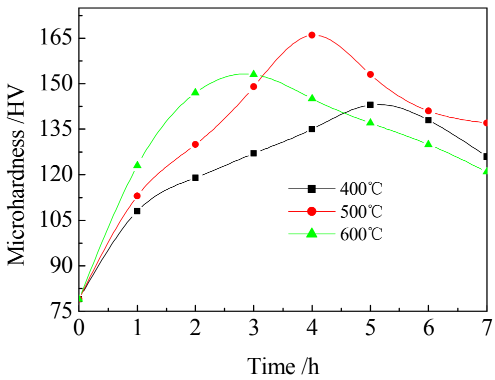

Fig.2 Curves of microhardness with aging time

图 2 显微硬度随时效时间的变化曲线

It can be seen that the microhardness of the Cu-2Ag-0.5Y alloy increases rapidly at the initial stage with the increase of aging time and then gradually increases till it reaches a peak, and then gradually decreases, because of the dispersion of the precipitation phase and coherence along with the matrix. From the aging curves in the interval from 400 ℃ to 600 ℃, it can be seen that the higher the aging temperature is, the lower the peak microhardness will be, and the aging time to the peak microhardness decreases, meanwhile, the shape of aging curve changes significantly with the aging temperature. The higher aging temperature is, the more rapidly the secondary phase precipitates. Therefore the larger amplitude of microhardness presents at the early stage of aging. A peak microhardness of 166 HV is observed after aging at 500 ℃ for 4 h, beyond which it decreases with the increase of the aging time. In addition, the higher aging temperature is, the greater growth inclination of the secondary phase is.

Fig.3 shows the effect of aging time between 1 h and 7 h at various temperatures on electrical conductivity of the Cu-2Ag-0.5Y alloy.

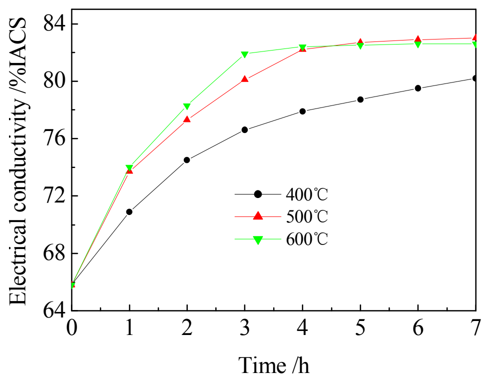

Fig.3 Curves of electrical conductivity with aging time

图 3 导电率随时效时间的变化曲线

It indicates that the electrical conductivity of

Cu-Ag-Y alloy increases with the increase of aging time and temperature. At the early stage of the aging process, the electrical conductivity of alloy increases rapidly, because the precipitation force of the secondary phase is great and precipitation speed is fast. and then tends to be stable, and the higher the aging temperature is, the quicker the increase of electrical conductivity at the early stage of the aging process will be. For instance, upon aging at 500℃ for 4 h, the value of electrical conductivity is 82.2 %IACS, but it is only 77.0 %IACS aging at 400℃. A solute in solid solution with copper has a much more powerful effect on decreasing the electrical conductivity than that it is present partly or wholly as a second phase. The increase in electrical conductivity of the Cu-Ag-Y alloy is attributed to removal of Ag and Y from the copper solid solution to form a second phase. The longer the aging time, the less the supersaturated vacancies and thus the slower the precipitation process will be. From the electrical conductivity curves in the interval from 400℃ to 500℃, it can be seen that the higher the aging temperature is, the more the electrical conductivity of alloy increases. As a result, Cu-2Ag-0.5Y alloy can attain a combination of microhardness and electrical conductivity with aging at 500℃ for 4 h, and the microhardness and electrical conductivity is about 166 HV and 82.2 %IACS.

2.3 Cold deformation before aging

The cold deformation before aging can greatly increase the number of defect, such as dislocation, vacancy, and so on, leading to aberration of lattice and improvement of free energy, which is beneficial to the nucleation and growth of the second phase[19-21].

The curves showing the electrical conductivity and microhardness of the alloy aging at 500℃, after 30% deformation respectively, with the time are presented in Fig.4. It can be seen that its tendency is almost as same as the one directly aging after solution. Due to the cold deformation before aging, the processes of precipitation are accelerated, making it possible that the amplitude of the electrical conductivity and microhardness are larger at the early stage of aging.

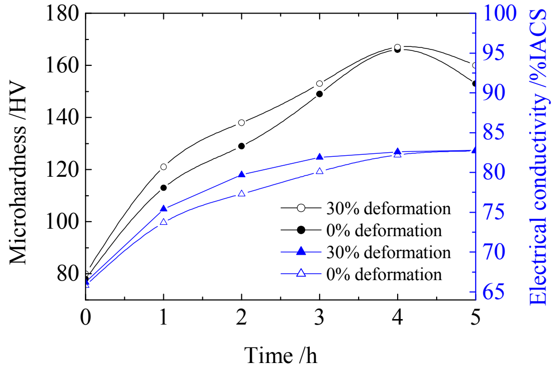

Fig.4 Microhardness and electrical conductivity of predeformed Cu-Ag-Y alloy with aging time at 500℃

图 4　预变形 Cu-Ag-Y 合金经 500℃时效后的导电率与显微硬度

The TEM image of the alloy aging at 500℃ for 20 min after 30% deformation is shown in Fig.5.

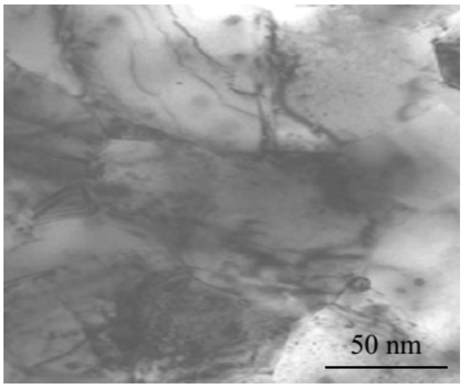

Fig.5 TEM image of Cu-Ag-Y alloy aging at 500℃ for 20 min after 30% deformation

图 5　30%预变形的 Cu-Ag-Y 合金经 500℃/20 min 时效后的 TEM 图片

It can be seen clearly that the high dislocation density is still remained in the alloy matrix and the secondary phase is dispersed, hardening the alloy to some degree. The microstructure essentially consists of dislocation network and fine dispersed precipitates. The dislocation is the thermodynamically unstable defect which has higher energy, and accelerates the nucleation and growth of the second phase. The dislocations act as the heterogeneous sites and the volume fraction of the second phase increases. As a result, the microhardness of the Cu-Ag-Y alloy with the cold deformation increases considerably and is higher than that directly aging after solution treatment. The electrical conductivity increases rapidly due to enhanced removal of Y from the copper matrix as well as increased volume fraction of the second phase.

Fig.6 shows the tensile fracture appearances of the Cu-Ag-Y alloy aging at 500℃ for 4 h which is the optimum conditions.

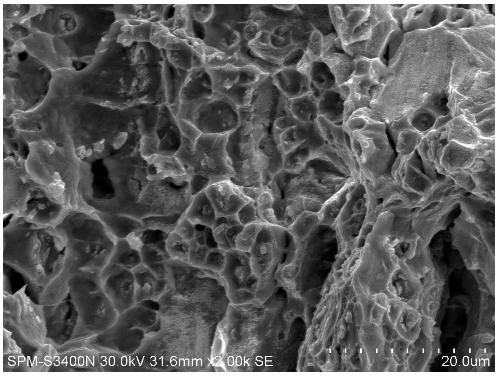

Fig.6 SEM image of Cu-Ag-Y alloy aging at 500℃ for 20 min after 30% deformation

图 6 30%预变形的 Cu-Ag-Y 合金经 500℃/20 min 时效后的 SEM 图片

The tensile fracture morphology shows a great number of large and deep dimples. It is illustrated that the severe plastic deformation occurs before breaking failure of the material. Plastic deformation takes place first at the crack tip and spreads across the solid as the applied load is increased beyond general yielding. It can be also seen from Fig.6 that the particles are occasionally separated and pulled out, and the tear ridges leave behind in the large and deep dimples. This demonstrates that the second phase particles combine firmly with the Cu matrix. The fracture mode of the material is the microporous polycondensation plastic fracture.

3 Conclusions

(1) Cu-2Ag-0.5Y alloy can obtain better comprehensive properties after aging at 500℃ for 4 h, the values of microhardness and electrical conductivity are 166HV and 82.2% IACS, respectively.

(2) Cold deformation prior to aging can improve the properties of the Cu-Ag-Y alloy. The precipitation of the secondary phase can also be accelerated with cold deformation before aging, so electrical conductivity and microhardness of the alloy are greatly improved.

(3) The precipitation of Ag and Y element from the supersaturated copper solid solution results in the increase of electrical conductivity and microhardness of the Cu-Ag-Y alloy, and the cold deformation can accelerate the precipitation of the Ag and Y from copper matrix.

References:

[1] Zhan Y, Xu Y, Yu Z, et al. Cu-Cr-Zr alloy matrix composite prepared by powder metallurgy method[J]. Powder Metall, 2006, 49(3): 253-256.

[2] Xie H F, Mi H J, Huang G J, et al. Effect of thermo-mechanical treatment on microstructure and properties of Cu-Cr-Zr-Ag alloy[J]. Rare Metal, 2011, 30(6): 650-656.

[3] Tian Y Z, Li J J, Zhang P, et al. Microstructures, strengthening mechanisms and fracture behavior of Cu-Ag alloys processed by high-pressure torsion[J]. Acta Materialia, 2012, 60(1): 269-281.

[4] Spassov T, Lyubenova L, Liu Y, et al. Mechanochemical synthesis, thermal stability and selective electrochemical dissolution of Cu-Ag solid solutions[J]. Journal of Alloys and Compounds, 2009, 478(1/2): 232-236.

[5] He X C, Wang Y M, Liu H S, et al. A study of the isothermal section of the Cu-Ag-Zr ternary system at 1023 K by diffusion triple technique[J]. Journal of Alloys and Compounds, 2007, 439(1/2): 176-180.

[6] He X C, Wang H, Liu H S, et al. Thermodynamic descri-ption of the Cu-Ag-Zr system[J]. Calphad, 2006, 30(4): 367-374.

[7] Jia S G, Ning X M, Liu P, et al. Age hardening chara-cteristics of Cu-Ag-Zr alloy[J]. Metals and Materials International, 2009, 15(4): 555-558.

[8] Xia C D, Wang M P, Zhang W, et al. Microstructure and properties of a hot rolled-quenched Cu-Cr-Zr-Mg-Si alloy [J]. Journal of Materials Engineering and Performance, 2012, 21(8): 1800-1805.

[9] Jayakumar P K, Balasubramanian K, Rabindranath T G, et al. Recrystallisation and bonding behaviour of ultra fine

grained copper and Cu-Cr-Zr alloy using ECAP[J]. Materials Science &Engineering A, 2012, 538: 7-13.

[10] Poblano-Salas C A. High temperature properties of Cu-Cr-Zr alloys processed by conventional inverse extrusion of atomised powders and comparison with conform consolidated powders[J]. Powder Metallurgy, 2009, 52(2): 124-134.

[11] Wang Z Q, Zhong Y B, Lei Z S, et al. Microstructure and electrical conductivity of Cu-Cr-Zr alloy aged with DC electric current[J]. Journal of Alloys and Compounds, 2009, 471(1/2): 172-175.

[12] Wei X, Wang J P, Yang Z M, et al. Liquid phase separation of Cu-Cr alloys during the vacuum breakdown [J]. Journal of Alloys and Compounds, 2011, 509(25): 7116-7120.

[13] Liu X J, Jiang Z P, Wang C P, et al. Experimental determination and thermodynamic calculation of the phase equilibria in the Cu-Cr-Nb and Cu-Cr-Co systems [J]. Journal of Alloys and Compounds, 2009, 478(1/2): 287-296.

[14] Yao D W, Meng L. Effects of solute, temperature and strain on the electrical resistivity of Cu-Ag filamentary composites[J]. Physica B, 2008, 403(19/20): 3384-3388.

[15] He J, Ji V, Meng L, et al. Effects of strain and annealing on the intensity and distribution of crystal texture in Cu-12 wt.%Ag[J]. Materials Science and Engineering A, 2008, 478(1/2): 305-313.

[16] Liu J B, Zhang L, Meng L, et al. Effects of rare-earth additions on the microstructure and strength of Cu-Ag composites[J]. Materials Science and Engineering A, 2008, 498(1/2): 392-396.

[17] Misjak F, Barna P B, Toth A L, et al. Structure and mechanical properties of Cu-Ag nanocomposite films[J]. Thin Solid Films, 2008, 516(12):3931-3934.

[18] Jia S G, Liu P, Song K X, et al. Aging property of Cu-Ag-Zr alloy[J]. Transactions of Materials and Heat Treatment, 2011, 31(9): 37-39.
贾淑果, 刘平, 宋克兴, 等. Cu-Ag-Zr 合金的时效性能[J]. 材料热处理学报, 2011, 31(9): 37-39.

[19] Ning Y T, Zhang X H, Qin G Y, et al. Structure and properties of the in situ filamentary composites based on the Cu-Ag alloy with different solidification conditions[J]. Precious Metals, 2005, 26(3): 39-49.
宁远涛, 张晓辉, 秦国义, 等. 不同凝固条件制备的 Cu-Ag 合金原位纤维复合材料的结构与性质[J]. 贵金属, 2005, 26(3): 39-49.

[20] Zhang X H, Li Y N, Ning Y T, et al. The advance of study on Cu-Ag alloy with high strength and high conductivity [J]. Precious Metal, 2001, 22(1): 47-52.
张晓辉, 李永年, 宁远涛, 等. 高强度、高导电性 Cu-Ag 合金的研究进展[J]. 贵金属, 2001, 22(1): 47-52.

[21] Morris D G, Benghalem A, Morris-Munoz M A. Influence of solidification condition, thermomechanical processing, and alloying additions on the structure and properties of in situ composite Cu-Ag alloys[J]. Scripta Material, 1999, 41(10): 1123-1126.