

Trans. Nonferrous Met. Soc. China 17(2007) s1049-s1054

Transactions of Nonferrous Metals Society of China

www.csu.edu.cn/ysxb/

# Effect of Y on structure and properties of copper and its alloy

CAI Wei(蔡 薇)<sup>1</sup>, LIU Rui-qing(柳瑞清)<sup>1</sup>, XIE Shui-sheng(谢水生)<sup>2</sup>, HUANG Guo-jie(黄国杰)<sup>2</sup>, ZHAO Jian(赵 健)<sup>1</sup>, ZHANG Zhen-feng(张珍锋)<sup>1</sup>

1. Faculty of Material and Chemistry Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China;

State Key Laboratory and Processing of Non-ferrous Metals,
Beijing General Research Institute for Non-ferrous Metals, Beijing 100088, China

Received 15 July 2007; accepted 10 September 2007

**Abstract:** The possibility of substituting 72.5Cu-22.7Zn-3.4Al brass for phosphorus bronze in some case that is now extensively used for elastic component, and purifying the scrap copper for recycling metal was investigated. By adding a little amount of rare earth Y into scrap copper and 72.5Cu-22.7Zn-3.4Al brass to research their structure and characteristics, especially the electric conductivity for scrap copper and HV for the brass were researched. The results show that the tensile strength, elongation and electric conductivity (IACS) of 0.38 mm strip of scrap copper with 0.04% Y, are 213.8 MPa, 23% and 98.5% that suit for the elastic components. The tensile strength, elongation and HV of 0.25mm strip of the brass with 0.03% Y are 665.1MPa, 2.86% and 226 that satisfy the usage requirement for the elastic components. Meanwhile, the cost is cheaper than phosphorous bronze because of implying 22.7% zinc in the brass, which has the actual application value.

Key words: Y; scrap copper; 72.5Cu-22.7Zn-3.4Al brass; electric conductivity; tensile strength

#### 1 Introduction

China is the largest consumer of copper in the world. It is impossible for us to support the consumption of 21% with 5% resources of the world anyway. Recycling scrap copper to save the natural resources and reducing the cost is a point that a lot of experts and managers of factories focus on [1–3].

For the elastic materials, on one hand, the tensile strength should be raised continuously, and the size of elastic components should be reduced. On the other hand, the alloy should have good features such as elasticity, magnetism and electrical conductivity. The bronze with beryllium, that has very good elastic and flexible function, is wildly used in different areas such as electronics industry, aviation and aerospace, instrument and household electrical appliances, but the dust of beryllium is poisonous and the toxicity of its compound is higher during smelting or forming, and the producing cost is high. Now scientists are looking for the Be-bronze to substitute this alloy in recent years, and have already

succeeded to manufacture some alloys that have quite good thermostability, high tensile strength at high temperature and no toxicity such as Ti-bronze, Al-Ni-brass and Cu-Ni-Sn alloy which have been used in elastic elements with high conductivity and they can partially replaces some Be-bronze alloy[4–7].

In this work, the main research involves the technology of smelting, casting and working, and the effect of Y on the structure and the characteristics of 72.5Cu-22.7Zn-3.4Al brass and scrap copper to improve the mechanical characteristics, especially the electric conductivity for scrap copper which could be used as electric material for recycling metal and the Vickers hardness (HV) and elongation of 72.5Cu-22.7Zn-3.4Al brass which could be used as elastic material with low cost.

## 2 Experimental

#### 2.1 Experimental of scrap copper

The scrap copper came from laboratory, the rare earth Y was added in form of Cu-10%Y master alloy.

The technique route of experiment are as follows:

Smelting and casting→Hot-rolling→Soften annealing→Cold-rolling→Finish annealing.

The iron-mould with dimensions of 20 mm× 80 mm×250 mm was heated to about 300 °C to avoid casting defects such as cracks and gas holes. Added Cu-Y alloy when the scrap copper was molten, then picked up the dregs and poured the molten metal into the mould. The thickness of ingots is 18 mm after both sides were milled.

Ingots were heated to 900 °C for 30 min to affirm that the copper would have good plasticity. The deformation was as high as 88.9% and the thickness of sheet hot-rolled was 2 mm.

It is important to take an annealing to eliminate the work hardening and to recover the ductility before cold-rolling. To obtain the reasonable annealing technique parameters, the experiment was taken at 500, 550 and 600  $^{\circ}\mathrm{C}$  for 0.5, 1 and 1.5 h. The best annealing conditions are 550  $^{\circ}\mathrm{C}$ , 1.5 h for scrap copper having good electric conductivity by following cold-rolling and finish annealing.

Carried on an annealing to all of the plates according to the best parameter obtained before. Cold-rolling was taken in a four-high mill, the thickness of strip was 0.38 mm with 81% deformation.

To obtain suit are characteristics, a finish annealing was taken at low temperature to improve the ductility and conductivity.

Annealing temperature was decided according to the relationship of mechanical characteristics with the annealing temperature considering the effects of impurities, elements and work hardening. In this work, the annealing was carried out at 380  $^{\circ}$ C for 4.5 h.

### 2.2 Experimental of aluminum brass

The experimental procedure is Smelting and casting→Hot-rolling→First annealing→Cold-rolling→Second annealing→Cold-rolling.

The raw materials are tough cathode, pure zinc, pure aluminum sheet and Cu-10%Y alloy.

The dimensions of iron-mold were the same size as mentioned above. Put aluminum, zinc into the crucible, then tough cathode, covered with graphite powder when the metal was smelted at 1 080–1 120  $^{\circ}$ C, cast at 980–1 020  $^{\circ}$ C after removing dregs out off the crucible. The thickness of ingots milled was 18 mm.

The ingots were heated at 830 °C for 45 min for the hot-rolling and the thickness of plate was 5.5 mm after cogging.

To achieve large deformation in the cold-rolling, the best parameters for softening annealing must be decided. Adopted 450, 500, 550 °C for 0.5, 1, and 1.5 h and went on cold-rolling and analyzing.

The thickness of strip was 0.5 mm after the first cold-rolling with 90.9% deformation. The second annealing went on at 550  $^{\circ}$ C for 2 h. The finish strip was 0.25 mm after second cold-rolling with 50% deformation.

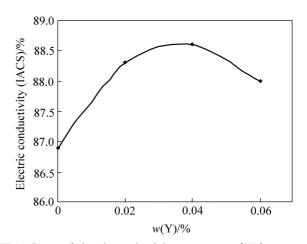
#### 3 Results and discussion

#### 3.1 Results and discussion about scrap copper

The curve of electric conductivity vs the content of rare earthy is shown in Fig.1. The microstructures of the ingots are shown in Fig.2.

Impurities such as O, S, P, Bi, Pb, Fe and Zn are usually in states of atom solution in scrap copper that distort crystal lattice, electrons will scatter during passing through, and in turn decrease the electric conductivity of scrap copper.

The active RE can form inclusion and compounds with those impurities. That will reduce the solution of impurities in copper. During smelting, those inclusions and compounds that have high melting point and low density easily float up into the molten dregs and is then moved away, the molten metal was purified, so electric conductivity increases by adding RE (Fig.1). Too much RE will not reinforce the refinement continuously, but increase the amount of residuals that act as impurities in scrap copper[8–9]. This is why the electric conductivity decreases when the content of RE is about to 0.06%. Electric conductivity is at its top value (88.5%) with 0.04% Y in scrap copper. Adding reasonable amount of RE can improve electric conductivity of scrap copper, Meanwhile, some residuals of RE compounds will be separated from the molten metal in second phases that act as cores for crystallization [10]. With the increase of Y content, the grains size reduce (Fig.2), correspondingly the flexibility of scrap copper becomes better.



**Fig.1** Curve of electric conductivity vs content of Y for as-cast ingots

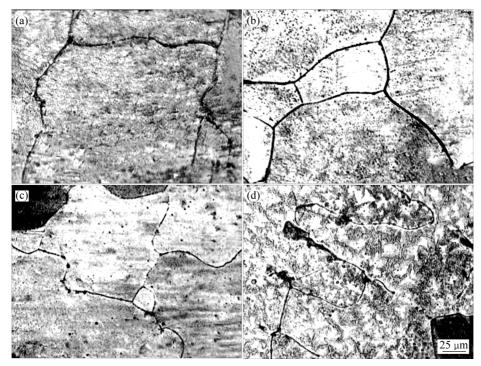
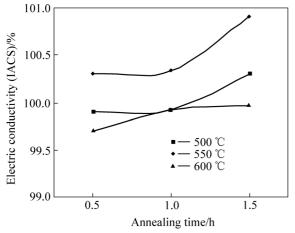


Fig.2 Structures of ingots with different contents of Y: (a) Without Y; (b) With 0.02% Y; (c) With 0.04% Y; (d) With 0.06% Y

Usually ingots have defects such as gas holes, imhomogeneity of content, low density, large size of grains, so the mechanical features and electric conductivity are not as high as we have expected. Grains break and recrystallize, the construct as-cast changed to forming structure during hot-rolling. Mechanical properties and electric conductivity are improved compared with as-cast.

The flexibility and conductivity of scrap copper were affected by softening annealing. It is important to study the effect of annealing temperature and holding time on the electric conductivity of scrap copper. Fig.3 shows the effects of annealing time on the electric conductivity at addition of 0.02%Y.



**Fig.3** Curves showing effect of annealing time on electric conductivity for scrap copper with 0.02%Y

It can be seen from Fig.3 that the curves change in the similar way. The extension of holding time is advantageous to improve the electric conductivity, eleminate the workhardening and to recover the flexibility, thus benefiting the recrystallization and growth of the grains. This means that the electric conductivity rises with the extension of holding time. The velocity of recrystallization and grains size increase with the increase of annealing temperature and holding time. The best conditions are annealing at 550 °C for 1.5 h.

The thickness of strip decreased to 0.38 mm with 81% deformation. With the deformation increasing, the work hardening of copper rises, so the tensile strength increases, the electric conductivity and elongation decrease.

During the cold rolling, the sum of dislocation increases, tangling and interaction of dislocations also increase, which turns to the decrease of the conductivity and elongation, and the increase of the tensile strength. To obtain the reasonable elongation and conductivity, the finish strip was annealed at low temperature for longer holding time (380 °C, 4.5 h). Fig.4 shows the curves of electric conductivity to the content of Y before and after annealing.

The 0.38 mm strip with 0.04% Y has good comprehensive properties, the tensile strength, elongation are 213.8 MPa and 23%, the electric conductivity (IACS) is 98.5%, which are enhanced separately by 2.7%, 9.5% and 2.2% compared with the scrap copper without Y. This satisfies the requirement for electric conductor.

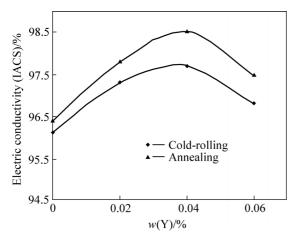


Fig.4 Curves of electric conductivity vs content of Y after annealing

# 3.2 Results and discussion about 72.5Cu-22.7Zn-3.4Al brass

Fig.5 shows that the effect of the content of RE on the microstructures of Cu-22.7Zn-3.4Al alloy. The grains size decreases with the increase of content of RE, which is advantageous to enhance the mechanical characteristics.

Fig.6 shows the effect of the content of RE on the hardness and elongation of ingots of brass. The hardness of alloy rises continuously with the increase of content of RE, because the element of RE can form compound with copper at high temperature. Those tiny particles with

high melting point often suspend in molten metal and act as cores in dispersion state during crystallization[11–12]. The grain size decreases with the increase of amount of grains, which turns to the improvement of mechanical properties of Cu-22.7Zn-3.4Al alloy.

Usually oxygen and sculpture in brass can form brittle compounds, which reduce the flexibility of alloy, which turn down the flexibility of alloy during cold-rolling. At the same time, the conductivity and features of anticorrosion and welding reduce. Rare earth elements have stronger affinity, rare earth oxides have good thermostability, and those compounds with low density will float up into the molten dregs and can be moved away easily, so the flexibility and elongation of alloy can be improved in this way[13-14]. Mechanical characteristics and flexibility can be improved by adding RE because the impurities content reduces and the grains refined. The HRB and elongation (72.5Cu-22.7Zn-3.4Al) brass as-cast with 0.03% Y are 57.3 and 18.8%, increased by 9.8% and 40.3% compared with the brass without Y.

To obtain strip with high elasticity, the large cold-rolling deformation must be taken. The thickness of plate hot-rolled is 5.5 mm with only 69.4% deformation. Ascast microstructure changes to working microstructure during the hot-rolling, at the same time the grains break and recrystallize, which leads to reduce the grain size and increase the defects in the crystal so that the hardness is enhanced with the increase of content of RE.

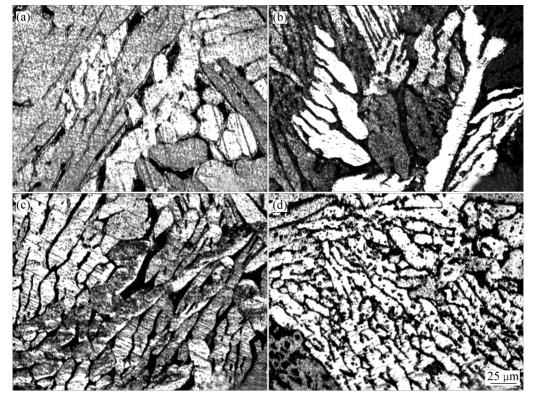
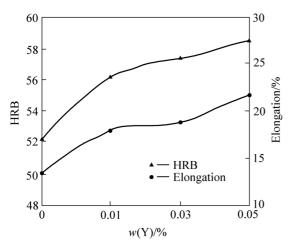


Fig.5 Microstructures of ingots showing effects of Y: (a) Without Y; (b) With 0.01% Y; (c) With 0.03%Y; (d) With 0.05%Y



**Fig.6** Curves of hardness and elongation of as-cast brass to content of Y

Because the cold-forming ability of brass is not as good as copper, to achieve large cold-deformation, it is important to study the relationship of hardness with annealing condition and to keep good flexibility for cold-rolling. Table 1 lists the annealing technology No. at different annealing temperatures. The results are show in Fig.7.

**Table 1** Annealing technology No. at different annealing temperatures

Annealing time/h	450 ℃	500 ℃	550 ℃
0.5	No.1	No.4	No.7
1	No.2	No.5	No.8
1.5	No.3	No.6	No.9

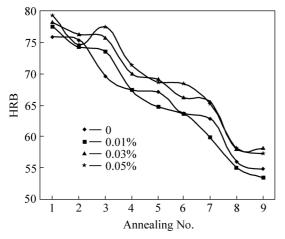
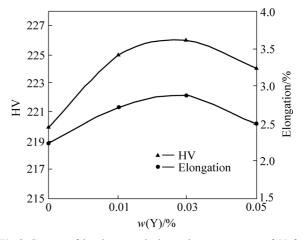


Fig. 7 Hardness curves of samples by different annealing technologies

Went on cold-rolling to confirm the cold-working ability. The result shows that the flexibility is not good enough for cold-rolling if annealed at low temperature and held for a short time. The flexibility was improved when the annealing temperature and holding time became longer. After annealing at 550 °C for 1 h or 1.5 h, the sheet was rolled to strip (0.5 mm thickness) with good appearance. At the end 550 °C for 1 h was adopted.

The thickness is from 5.5 mm to 0.5 mm with 90.9% deformation after cold-rolling, annealing again to recover the flexibility of alloy. Then went on finishing cold-rolling, the thickness decreased from 0.5 mm to 0.25 mm with 50% deformation. Fig.8 shows the curves of hardness and elongation of finish strip vs the content of Y.

It can be seen from Fig.8 that the 0.25 mm strip has high hardness, tensile strength and good elongation with 0.03% Y. Under this condition, the hardness (HV), tensile strength and elongation are 226, 665.1 MPa and 2.86% enhanced by 2.7%, 7.4% and 27.4% compared with the brass without Y. This satisfies the usage requirement for elasticity. The strip mechanical properties of 72.5Cu-22.7Zn-3.4Al brass with 0.03% Y are equal to those of QSn6.5-0.1 strip that the tensile strength is between 665 MPa and 805 MPa, and the elongation is between 2% and 14%[15].



**Fig.8** Curves of hardness and elongation vs content of Y for finish strip

#### 4 Conclusions

- 1) Rare earth Y can purify the molten metal, refine the as-cast grains, and improves the mechanical properties of scrap copper. 0.38 mm strip of scrap copper with 0.04%Y has good comprehensive properties. The tensile strength, elongation and electric conductivity (IACS) of strip are 213.8 MPa, 23% and 98.5%. That copper can be used as electric material for recycling metal.
- 2) The grains are refined and mechanical properties can be improved by adding Y into 72.5Cu-22.7Zn-3.4Al brass. Brass annealed at 550°C for 1 h has best

mechanical properties and flexibility for following cold-rolling.

3) The 0.25 mm strip of 72.5Cu-22.7Zn-3.4Al brass with 0.03% Y has good comprehensive properties that the hardness (HV), tensile strength and elongation are separately 226, 665.1MPa and 2.86%. This alloy can be used to produce elastic components with low cost.

#### References

- WANG Ji-wei. Brilliant prospects for recycling and utilization of copper in China[J]. China Resources Comprehensive Utilization, 2005, 1: 5-9. (in Chinese)
- [2] QIU Ding-fan, WANG Cheng-yan, WANG Chun. Recycling of scrap copper in China[J]. Nonferrous Metals, 2003, 55(4): 94–97. (in Chinese)
- [3] MA Zhuang, DI Li-li, ZHU Yu-jun. Effect of rare-earth element La and Ce on pure copper[J]. Foundry Technology, 2005, 26(3): 227–228. (in Chinese.)
- [4] SUN Jian-chun, LIU Xiao-wei, ZHOU An-ruo. Current study status and development tendency of elastic alloys [J]. Hot Working Technology, 2006, 35(18): 52–56. (in Chinese)
- [5] WANG Zhong-min, LIU Qun-shan, ZHANG Zhong-cheng. Study of aluminum-nickel-brass alloy as a substitute for beryllium bronze[J]. Hot Working Technology, 2003, 1: 49–50. (in Chinese)
- [6] YAN Yong, WANG Zhi-jun, DONG Chao-qun. Review and prospect of Chinese beryllium copper industry science and technology advance[J]. Chinese Journal of Rare Metals, 2003, 27(1): 66–68. (in Chinese)

- [7] LU De-ping, WANG Jun, ZENG Wei-jun. Study on high strength and high conductivity Cu-Fe-P alloys[J]. Mater Sci Eng A, 2006, 421(1): 254–257
- [8] ZHAO Yue-chao, ZHANG Lian-yong, MA Zhuang. Absorptive and effect of rare earth on casting copper[J]. Foundry, 2004, 53(9): 742–745. (in Chinese)
- [9] DANG Ping, ZHAO Lian-shan, LU Hua-yi. Effects of rare earth on microstructure and properties of pure copper[J]. Rare Metals, 1993, 12(4): 277-280.
- [10] ZHANG Zhen-feng; LIN Gao-yong; ZHANG Sheng-hua; BAO Yu-ping. Effects of Ce on structures and mechanical properties of pure copper[J]. Rare Metals, 2006, 27(5): 24–28, 79.
- [11] LI Zhen-do, ZHANG Lei, MENG Liang. Effect of rare earth elements on microstructure of Cu-6%Ag and Cu-24%Ag alloy[J]. Journal of Rare Earths, 2005, 23(3): 1007–1011.
- [12] XUE Song-bai, QIAN Yi-yu, DONG Jian. Equivalent activity coefficient phenomenon of cerium reacting with lead or bismuth in Ag, Cu and Zn alloy[J]. Journal of Rare Earths, 2002, 20(6): 626-629.
- [13] MAYun-qing, JIANG Cheng-bao, DENG Li-fen, XU Hui-bin. Effects of composition and thermal cycle on transformation behaviors, thermal stability and mechanical properties of CuAlAg alloy[J]. Journal of Rare Earths & Technology, 2003, 19(5): 431-434.
- [14] LIU Yong, LIU Ping, TIAN Bao-hong, LI Wei. Influence of RE on ageing precipitate characteristics and softening resistance of copper alloys contact wire[J]. Journal of Rare Metals, 2005, 23(4): 1006–1009.
- [15] HUANG De-bin. Nonferrous materials handbook[M].1st ed. Beijing: Chemical Industry Press, 2005. (in Chinese)

(Edited by LONG Huai-zhong)