Effect of trace La on microstructure and properties of Cu–Cr–In alloys

Haofeng Xie¹,²,⁴, Wenjing Zhang¹,², Shuhui Huang¹,², Huiming Chen¹, Hang Wang¹, Zhen Yang¹,², Lijun Peng¹,² and Bin Yang³

¹ State Key Laboratory of Nonferrous Metals and Processes, GRINM Group Co., Ltd, Beijing, 100088, People’s Republic of China
² GRIMAT Engineering Institute Co., Ltd, Beijing, 101407, People’s Republic of China
³ Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou, 341000, Jiangxi, People’s Republic of China
⁴ Author to whom any correspondence should be addressed.

E-mail: xie.haofeng@126.com

Keywords: Cu–Cr–In–La, tensile strength, intermetallic compound, rare earth

Abstract

The strength and conductivity of Cu–Cr–In alloys with trace La and different processing states were compared. Then, the influence of La on the structure and properties of the Cu–Cr–In alloy and the associated mechanisms were analyzed. The mechanical properties and microstructural evolution of the alloy were investigated via scanning electron microscopy, transmission electron microscopy, and tensile strength measurements. The results showed that the addition of 0.07wt% La to the Cu–Cr–In alloy had the effect of purifying the alloy melt and removing impurities, which improved the electrical conductivity of the alloy. However, the formation of rare earth intermetallic compounds reduced the tensile strength of the Cu–Cr–In–La alloy. After thermomechanical treatment, the Cu–Cr–In–La alloy reached a peak strength of 457 MPa and a conductivity of 85% IACS.

1. Introduction

The Cu–Cr alloy has high strength, excellent electrical and thermal conductivity, and good ductility; hence, it is widely used in applications such as high-speed rail contact wires [1], lead frames [2, 3], heat exchange materials [3, 4], and resistance welding electrodes [5]. As a typical age-hardening alloy, dispersed Cr particles precipitate from the matrix during the aging treatment and strengthen the alloy. Other elements are usually added to the Cu–Cr alloy to further improve its properties, such as Ag [6–8], Zr [9, 10], Mg [11], In [12, 13], and Sn [14]. Chen et al found that the addition of In to the Cu–Cr alloy resulted in a strong solid solution strengthening effect [13]. In addition, the Cu–Cr–In alloy displays good hot workability and has a high strength and high conductivity [13]. Chen et al [15] also found that In has a positive effect on improving the softening resistance of Cu–Cr–In alloys. Hence, the Cu–Cr–In alloy has good application prospects. Adding a small amount of rare earth elements can significantly improve the properties of the alloy, therefore, it is widely used in steel and copper alloys [16, 17]. Rdzowski et al [18] found that rare earth elements can refine the grains and improve the mechanical properties of the Cu–Ag alloy. Chen et al [17] also found that adding Ce to Cu–Cr–Ag can reduce the amounts of detrimental impurities in the alloy, such as O and S. After adding 0.089 wt% La to pure copper, the strength of the alloy significantly improved [19]. Furthermore, the addition of rare earth elements led to the formation of rare earth compounds in the Cu–Cr–Zr–Mg–Si alloy, which could pin dislocations and hinder their movement [20]. The addition of a small amount of rare earth elements could improve the structure, impurity content, and interface conditions of the alloy, resulting in alterations to the properties of the alloy. To further investigate the use of rare earth elements in Cu–Cr–In alloy, this paper studied the influence of the rare earth element La on the properties of the Cu–Cr–In alloy. Furthermore, the influence of La on the Cu–Cr–In alloy was explored via microstructural analysis. The results of this work can provide a theoretical reference for the application of rare earth elements in the Cu–Cr alloy system.
2. Experimental method

Pure copper (99.95 wt%), pure indium (99.99 wt%), Cu-8Cr (wt%) master alloys, and Cu-10La (wt%) master alloys were used in this work. Both the Cu–Cr–In and Cu–Cr–In–La alloys were melted using a medium-frequency induction furnace (ZP-45, Jiangyin Ruibang). The molten alloy was covered by charcoal to reduce oxidation. The alloys were cast in an iron mold and air cooled to room temperature. The composition of the alloy was measured via ICP (ICP, IRIS Intrepid II, Thermo Fisher Scientific), as shown in Table 1. After removing surface defects, a homogenization treatment at 920 °C for 2 h was carried out in a resistance furnace (SX2-18-13, Shanghai Shiyian).

The alloy was hot extruded using an extruder (XJ-500, Wuxi Yuanchang), with an extrusion ratio of 37.8, and then formed into an alloy rod with a diameter of 13 mm. The extruded alloy rod was then cooled to room temperature.

Extruded alloy rods were first cold drawn to a diameter of 7 mm followed by solution heat treatment at 950 °C for 60 min. Then, the solution-treated rods were cold drawn again to a diameter of 4.5 mm. Aging treatment was carried out at 450 °C for different durations (20, 30, 60, 120, 180, and 240 min).

According to American National Standard (NO. ASTME8/E8M-16a), tensile testing was performed using a universal testing machine (UTM5105X, Shenzhen SanSi). All of the tensile strength results are reported as the mean values of at least three measurements. According to Chinese National Standards (NO. GB/T 351-2019), the conductivity of each sample was tested three times and the average value was used.

The microstructures of the samples were characterized via optical microscopy (OM, BMM-90AE, Shanghai Bimu), scanning electron microscopy (SEM, MLA650F, FEI), and transmission electron microscopy (TEM, Tecnai-G2-F20, FEI). The specimens for TEM observation were sliced from the bulk materials, ground into thin foils with a thickness of ~50 μm, and punched into circular foils with a diameter of 3 mm. They were then electropolished using a twin-jet unit with a solution of 30 vol.% perchloric acid and 70 vol% methanol at ~30 °C with a voltage of ~25 V.

3. Results and discussion

3.1. Performance

In the present work, the structure of the Cu–Cr–In alloy was set as a reference for comparing the influence of rare earth La on the properties of the Cu–Cr–In alloy. The properties of the Cu0.54Cr0.17In and Cu–0.51Cr–0.19In–0.07La alloys after drawing and solution heat treatment are shown in Figure 1. The tensile strength of the extruded Cu–Cr–In–La alloy was 226.36 MPa, which was ~28 MPa lower than that of Cu–Cr–In. After cold drawing deformation, the strength of the Cu–Cr–In–La alloy increased to 339.03 MPa, which was ~81 MPa lower than the tensile strength of Cu–Cr–In. After forming a solid solution, the tensile strength of the Cu–Cr–In–La alloy decreased to 233.13 MPa. After the second cold drawing deformation, the tensile strength of the φ7 mm alloy rod increased, and the strength of Cu Cr in La alloy reached 408.25 MPa, which was ~12 MPa lower than that of Cu0.54Cr0.17In. Figure 1(a) shows that the addition of rare earth La results in the La-containing alloy exhibits a lower strength compared to Cu0.54Cr0.17In alloys after hot extrusion, cold drawing, solid solution treatment, and the second cold drawing.

Figure 1(b) shows the conductivity changes of the Cu0.54Cr0.17In and Cu–0.51Cr–0.19In–0.07La alloys after extrusion, cold drawing, solid solution treatment, and drawing. The conductivity of the Cu–Cr–In–La alloy after hot extrusion, drawing, solid solution treatment, and drawing was 59.32% IACS, 56.21% IACS, 51.52% IACS, and 52.07% IACS, respectively; these values were slightly higher than those of the corresponding Cu–Cr–In alloy.

The Cu0.54Cr0.17In and Cu0.51Cr0.19In0.07La alloys were subjected to 60% cold drawing deformation to φ4.5 mm and then subjected to a thermal aging treatment at 450 °C. Figure 2(a) shows the changes of the tensile strength and conductivity for the Cu0.54Cr0.17In, Cu0.51Cr0.19In0.07La alloy with increasing aging time. As the aging time increased, the Cu–Cr–In–La alloy reached its peak aging strength at 60 min and had an alloy

### Table 1. Composition of the experimental alloy (wt%).

| Alloy   | Cr  | In  | La  | Cu  |
|---------|-----|-----|-----|-----|
| 1#      | 0.54| 0.17| —   | Bal |
| 2#      | 0.51| 0.19| 0.07| Bal |

---

2. Experimental method

3. Results and discussion

3.1. Performance

Table 1. Composition of the experimental alloy (wt%).
tensile strength of 457 MPa, which was ~40 MPa lower than the Cu–Cr–In peak aging strength. After this, the strength of the alloy was generally stable with time. After over-aging for 6 h, the strength decreased to 429 MPa.

As the aging progressed, the conductivity of the Cu–Cr–In and Cu–Cr–In–La alloys continued to increase and reached 84% IACS and 85% IACS, respectively, at the peak aging time of 60 min.

### 3.2. Microstructure

The as-cast structure of the Cu–0.51Cr–0.19In–0.07La alloy is shown in figure 3. The as-cast metallographic microstructure of the Cu–Cr–In–La alloy was a dendrite grain with black primary Cr phase particles between the dendrites, as shown in figure 3(a). As shown in the SEM morphology of the as-cast structure of the alloy in figure 3(b), a granular primary Cr phase was distributed at the grain boundary. In addition, there were 5-μm holes (P1) in the Cu matrix and small loose particles were present in the holes. Figure 3(c) shows that there was enrichment of the rare earth elements and a Cu–La intermetallic compound formed, as determined by EDS analysis of the small particles in the hole.

The microstructure of the as-cast Cu–Cr–In–La alloy after extrusion, drawing, solid solution treatment, and drawing is shown in figure 4. As shown in figures 4(a) and (b), the alloy after hot extrusion has a typical hot working structure, which was dominated by equiaxed grains. There was a small amount of twinning of the grains. Figure 4(c) shows that the alloy grains were extruded and broken during the drawing process, and the grains became smaller after 68% cold drawing deformation. In the drawing direction, the original equiaxed grains were broken and elongated and displayed an elongated grain structure, as shown in figure 4(d). In figures 4(e) and (f), the deformed grains recovered and recrystallized during the heat preservation process and formed a complete recrystallization structure. After the cold-deformed alloy was held at 950 °C for 60 min and then water-cooled for solution treatment, large equiaxed grains were observed and there was a large amount of twinning. A large number of small black particles were dispersed in the grains. After solution treatment, the Cu–Cr–In–La alloy was cold drawn to 60% deformation, the alloy grains were broken and elongated again.
resulting in fine equiaxed grains in the cross section and fine long strip grains in the longitudinal section, as shown in figures 4(g) and (h).

The SEM morphology of the solution-treated Cu–Cr–In–La alloy after cold drawing with 60% deformation is shown in figure 5. A large number of small second-phase particles were evenly distributed in the alloy matrix after cold deformation, as shown in figure 5(a). EDS composition analysis was carried out for the second-phase particles P2 and P3 shown in figure 5(a). The morphology of the P2 particles is shown in figure 5(b), and a particle size of ~0.6 μm was determined. EDS spectrum composition analysis showed that the P2 particles were the Cr-rich phase, and the observed holes were not corrosion pits formed around the particles during the corrosion process. The morphology of the P3 particles is shown in figure 5(c). The P3 particles were rich in the rare earth La phase with enrichment by S, O and other elements, as determined via EDS composition analysis. Table 2 shows the electronegativity difference between La and Cu, In, O, and S [21]. The electronegativity difference between La and O, S, Cu, and In decreased, while the electronegativity difference between La–O and La–S reached 2.34 and 1.48, respectively. The added La preferentially reacted with the impurities O and S in the alloy melt to form the corresponding intermetallic compound of rare earth, which purified the alloy. Thus, the resulting conductivity of the Cu–Cr–In–La alloy would be slightly higher than that of the Cu–Cr–In alloy, which is consistent with the experimental results.

After extrusion, primary drawing, solid-solution treatment, and secondary drawing, only a small amount of second-phase particles was present in the alloy structure, as shown in figure 5(a). Compared with the as-cast microstructure figures 3(a) and (b), the distribution of the second-phase particles was smaller and more uniform. The P3 particles shown in figure 5(c) had a size of ~1 μm. Compared with the P1 particles in figure 3(b), the size of rare earth compounds was markedly smaller. This indicated that the structure of the alloy was more uniform after solution treatment and cold drawing. After solution treatment, the primary Cr phase dissolved into the matrix in the form of Cr atoms, while the residual Cr phase and rare earth compound would redistribute with grain breaking during the extrusion and cold drawing deformation process. The brittle rare earth compound would also break into finer second phase particles, resulting in a finer and more uniform distribution of the second phase in the alloy.

3.3. TEM microstructure analysis
The Cu–0.51Cr–0.19In–0.07La alloy reached its peak-aging strength at 450 °C for 60 min with 60% cold drawing deformation. The microstructure of the Cu–Cr–In–La alloy for the peak aging state at 450 °C for 60 min is shown in figure 6. As shown in figure 6(a), a large rod-shaped particle and a spherical particle were found in the alloy matrix. During the heat preservation and cooling process of the solid solution, a large number of short rod-like Cr precipitates formed in the matrix of the Cu–Cr–La alloy and the average size was ~500 nm. The short rod-like Cr precipitates were also present in the Cu–Cr–In–La alloy after extrusion, cold drawing, and solid-solution treatment, as shown in figure 6(a). In addition, there were a large number of spherical particles with a size of ~200 nm in the matrix of figures 6(a) and (b). After hot extrusion and cold drawing deformation of the Cu–La compound shown in P1 in figure 3, the agglomerated compound was broken and dispersed into the Cu matrix; finally, fine spherical particles formed, as shown in figures 6(a) and (b). In addition, a large number of dislocation tangles were found around the small spherical precipitate, which indicated that the movement of dislocations during the deformation process was obstructed by hard particles, and dislocation tangles formed around the particles. These small rare earth compound particles had a strengthening effect in the alloy.
For the Cu–Cr alloy aging process, the solution Cr atoms nucleated and grew into nano Cr precipitates, which was also accompanied by the recovery and recrystallization of the deformed alloy structure. After deformation, the Cu–Cr–In–La alloy was aged at 450 °C and reaching a peak aging strength at 1 h, while its tensile strength decreased after 6 h of aging. The structure and morphology of the alloy precipitates after aging for 1 h and 6 h are shown in figure 7. The typical structure of the Cu–Cr–In–La alloy after aging at 450 °C for 1 h is shown in figure 7(a). There were a large number of small elongated grains in the matrix, and a large number of dislocations and dislocation tangles were distributed inside the grains. Many fine Cr precipitate were found in the matrix, and the precipitated phase size was ∼6 nm, as shown in figure 7(b). Because of precipitation strengthening and dislocation strengthening in the alloy, the tensile strength of the alloy increased and reached a peak strength after aging at 450 °C for 1 h.

The microstructure of the Cu–Cr–In–La alloy after holding at 450 °C for 6 h is shown in figures 7(c) and (d). Dislocations in the alloy matrix slipped during the aging process at 450 °C for 6 h, and a large number of

Figure 4. Metallographic microstructure of the Cu–Cr–In–La alloy under different conditions: (a), (b) extrusion; (c), (d) primary drawing; (e), (f) solution treatment; (g), (h) secondary drawing; (a), (c), (e), (g) the cross section of the alloy; (b), (d), (f), (h) the longitudinal section of the alloy.
dislocations tangled with each other and formed dislocation cells; the different dislocations merged and disappeared, and the dislocation density decreased. In addition, compared with the morphology of the peak aged precipitated phase, the Cr precipitates coarsening occurred in the alloy after aging for 6 h and the average size of Cr precipitates increased to ∼9 nm, as shown in figure 7(d). Because of the decreased dislocation density and the growth of the precipitated particles, the dislocation strengthening and precipitation strengthening effect were reduced and tensile strength of the alloy also decreased.

Figures 1(a) and 2(a) show that the tensile strength of the Cu–Cr–In–La alloy in different states was lower than that of the corresponding Cu–Cr–In alloy. As shown in figure 8, SEM analysis was carried out to investigate the morphology after tensile strength testing of the Cu–Cr–In–La alloy at its peak strength after aging at 450 °C for 60 min. A large number of dimples can be seen on the fracture surface and can be ascribed to the typical plastic fracture morphology, as shown in figure 8(a). A small amount of particles (P4) can be seen in the dimple, and high-magnification images of the P4 particles were taken, as shown in figure 8(b). The particles were spherical and had a size of ∼1.5 μm. Based on EDS analysis, there was enrichment of La in the particle, which was in the form of the Cu–La compound, and the results are consistent with the small spherical particles seen in figure 5.

| Table 2. Electronegativity difference between La and Cu, In, O, and S. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Element | Electronegativity | Cu | In | O | S | La |
| Cu | 1.90 | 0 | 0.12 | 1.54 | 0.68 | 0.8 |
| In | 1.78 | 0.12 | 0 | 1.66 | 0.80 | 0.68 |
| O | 3.44 | 1.54 | 1.66 | 0 | 0.86 | 2.34 |
| S | 2.58 | 0.86 | 0.80 | 0.86 | 0 | 1.48 |
| La | 1.1 | 0.80 | 0.68 | 2.34 | 1.48 | 0 |

Figure 5. SEM morphology of the 60% cold deformed Cu–Cr–In–La alloy after solution treatment: (a) microstructure; (b) P2 particle morphology and EDS analysis; and (c) P3 particle morphology and EDS analysis.

Figure 6. The microstructure of the Cu–Cr–In–La alloy in the peak aged treatment at 450 °C.
Fine brittle particles of the Cu–La compound were present as second phase impurities in the Cu–Cr–In–La alloy matrix. During the alloy drawing process, cracks easily formed at Cu–La compound particles, which led to premature fracture of the alloy. This is the primary reason for the lower tensile strength of the Cu–Cr–In–La alloy compared with the Cu–Cr–In alloy.

4. Conclusion

(1) The peak aging treatment for the Cu–0.51Cr–0.19In–0.07La alloy was determined to be 450 °C for 60 min. A peak aging strength of 497.90 MPa and conductivity of 85.27% IACS were realized after peak-aging.
(2) On adding La to the Cu–Cr–In alloy, La reacted with O, S, and Cu to form corresponding rare earth compounds, which removed impurities and purified the alloy melt; hence, the conductivity of the alloy improved.

(3) Particles of the rare earth compound acted as impurities in the alloy matrix, which reduced the tensile strength of the alloy. Therefore, strict control of the added rare-earth elements is required during industrial production. Filtering measures should be taken after rare earth purification of the melt, which is of high significance for improving the strength and conductivity of the alloy.

Acknowledgments

This work was supported by the National Key R&D Program of China (No. 2016YFB0301400).

ORCID iDs

Haofeng Xie @ https://orcid.org/0000-0002-4832-6400
Shuhui Huang @ https://orcid.org/0000-0003-3734-5427
Hang Wang @ https://orcid.org/0000-0002-6930-7444

References

[1] Liu Q, Zhang X, Ge Y, Wang J and Cui J Z 2006 Effect of processing and heat treatment on behavior of Cu–Cr–Zr alloys to railway contact wire Metall. Trans. A-Phys. Metall. Mater. Sci. 37A 3233–8
[2] Pang Y, Xia C D, Wang M P, Li Z, Xiao Z, Wei H G, Sheng X F, Jia Y L and Chen C 2014 Effects of Zr and (Ni, Si) additions on properties and microstructure of Cu–Cr alloy J. Alloys Comp. 582 786–92
[3] Hatakeyama M, Toyama T, Nagai Y, Hasegawa M, Eldrup M and Singh B N 2008 Nanostructural evolution of Cr-rich precipitates in a Cu–Cr–Zr alloy during heat treatment studied by 3 dimensional atom probe Mater. Trans. 49 518–21
[4] Morozova A, Mishnev R, Belyakov A and Kaibyshev R 2018 Microstructure and properties of fine grained Cu–Cr–Zr alloys after termo-mechanical treatments Rev. Adv. Mater. Sci. 54 56–92
[5] Wang Z Q, Zhong Y B, Cao G H, Wang C, Wang J, Ren W L, Lei Z S and Ren Z M 2009 Influence of dc electric current on the hardness of thermally aged Cu–Cr–Zr alloy J. Alloys Comp. 479 303–6
[6] Yuan D W, Wang J F, Chen H M, Xie W B, Wang H and Yang B 2018 Mechanical properties and microstructural evolution of a Cu–Cr–Ag alloy during thermomechanical treatment Mater. Sci. Tech-Lond. 34 1433–40
[7] Yuan D W, Yang B, Chen J S, Chen H M, Zhang J B and Wang H 2017 Upward continuous casting in the manufacture of Cu–Cr–Ag alloys: potential for enhancing strength whilst maintaining ductility Metall. Trans. A-Phys. Metall. Mater. Sci. 48A 6083–90
[8] Liu Y, Li Z, Jiang Y X, Zhang Y, Zhou Z Y and Lei Q 2017 The microstructure evolution and properties of a Cu–Cr–Ag alloy during thermal-mechanical treatment J. Mater. Res. 32 1324–32
[9] Chen J S, Wang J F, Xiao X P, Wang H, Chen H M and Yang B 2019 Contribution of Zr to strength and grain refinement in Cu–Cr–Zr alloy Mater. Sci. Eng. A 756 464–73
[10] Wang H, Gong L K, Liao J F, Chen H M, Xie W B and Yang B 2018 Retaining meta-stable fcc-Cr phase by restraining nucleation of equilibrium bcc-Cr phase in CuCrZrTi alloys during ageing J. Alloys Comp. 749 140–5
[11] Sun Y Q, Peng L J, Huang G I, Xie H F, Mi X J and Liu X H 2020 Effects of Mg addition on the microstructure and softening resistance of Cu–Cr alloys Mater. Sci. Eng. A 776 139009
[12] Chen H M, Gao P Z, Peng H C, Wei H G, Xie W B, Wang H and Yang B 2019 Study on the hot deformation behavior and microstructure evolution of Cu–Cr–In alloy J. Mater. Eng. Perform. 28 2128–36
[13] Chen H M, Yuan D W, Xie W B, Zhang J B, Wang H and Yang B 2019 A novel route for strengthening copper rods: non-solution heat treatment combined with pre-aging J. Mater. Process. Technol. 274 116290
[14] Luo Z Y, Luo F H, Xie W B, Chen H M, Wang H and Yang B 2018 A study on annealing-induced softening in cold drawn Cu–Cr–Sn alloy Materialwiss. Werkst. 49 1325–34
[15] Zhu Y Q, Tang L S, Xie W B, Chen H M, Wang H and Yang B 2020 Study on the softening behavior of Cu–Cr–In alloy during annealing Crystals. 10 312
[16] Chen R C, Wang Z G, Zhu F S, Zhao H J, Qin J and Zhong L Q 2020 Effects of rare-earth micro-alloying on microstructures, carbides, and internal friction of 51CrV4 steels J. Alloys Comp. 824 153849
[17] Chen H M, Yuan D W, Wu S J, Wang H, Xie W B and Yang B 2017 Relationship between microstructure and properties of Cu–Cr–Ag–(Ce) alloy using microscopic investigation Scanning 2017 1–8
[18] Rządziński Z, Głuchoński W, Sobśrawa J and Sobota J 2014 Effect of rare-earth metals addition on microstructure and properties of selected copper alloys Arch. Metall. Mater. 59 641–8
[19] Chen Y, Cheng M, Song H W, Zhang S H, Liu J S and Zhu Y 2014 Effects of lanthanum addition on microstructure and mechanical properties of as-cast pure copper J. Rare Earth 32 1056–63
[20] Yu FX, Cheng J Y and Ao X W 2011 Aging characteristics of Cu–0.6Cr–0.15Zr–0.03Mg–0.02S alloy containing trace rare earth yttrium Rare Met. 30 539–43
[21] James H 1983 Inorganic Chemistry: Principles of Structure and Reactivity. (London: Harper & Row)