

A high strength and high electrical conductivity Cu-Cr-Zr alloy fabricated by cryorolling and intermediate aging treatment

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ABSTRACT

Cu-1Cr-0.1Zr (wt%) alloy strips were fabricated by a two-stage cryorolling and an intermediate aging treatment. The microstructures, mechanical/electrical properties and precipitation behaviors of the alloy were investigated. The results show that a desired combination of the tensile strength (690.13 MPa) and electrical conductivity (67% IACS) were obtained after the primary 30% thickness reduction and intermediate aging at 450 °C for 2 h followed by a secondary 60% thickness reduction at the cryogenic temperature. The improved strength can be attributed to the interactions of twin boundaries strengthening, grain boundaries strengthening, precipitation strengthening and strain hardening. For the alloy manufactured by cryorolling and intermediate aging treatment, the twin/matrix lamellar thickness decreases 38% and 55% compared with the alloy manufactured by cryorolling and room temperature rolling, respectively. In particular, results from energy-dispersive spectroscopy (EDS) mapping show that a core-shell structure with the shell of Zr and the core of Cr appeared after the intermediately aging treatment.

1. Introduction

Copper and copper alloys have been widely used in electric, electronic, transportation and machinery manufacturing industries because of their excellent electrical and thermal conductivities [1]. However, for copper and its alloys, high strength and high electrical conductivity are mutually exclusive by nature. Copper alloys strengthened by simple or conventional approaches, such as solid solution alloying [2], strain hardening and grain refinement, cannot satisfy the growing industrial demands. Generally, solute atoms in the copper matrix inevitably deteriorate the electrical conductivity of alloys [3]. Therefore, precipitation strengthened copper alloys are developed to achieve an optimized combination of strength, electrical conductivity and wear resistance through aging treatment [4]. Specifically, the Cu-Cr-Zr alloys, as the typical precipitation strengthened copper alloys, have been used in variety of applications such as railway contact wire [5].

In recent years, severe plastic deformation (SPD) processes such as equal channel angular pressing (ECAP) [6,7], accumulative rolling bonding (ARB) [8], and high pressure torsion (HPT) [9] produce series

of ultrafine grained copper alloys with superior mechanical properties. High density of grain boundaries introduced by SPD process has significant effect on strengthening but little effect on the electrical conductivity [10]. Aging has also been implemented after SPD to promote precipitation hardening and improve conductivity in copper alloys [11,12]. Besides SPD processes, cryorolling, i.e., rolling at liquid nitrogen temperature (LNT) has been attempted on several metals and alloys to obtain ultrafine grained materials with high density of dislocations for improving mechanical properties [13–15]. Regarding high stacking fault energy (SFE) materials, cryorolling suppresses the dynamic recovery, thereby enhancing the efficiency of plastic deformation. The high density of dislocations in the cryorolled sample in turn provide more nucleation sites for precipitates during aging, and thereby improve the mechanical properties [16]. Regarding the materials with medium to low SFE, the dislocation motion is restricted to planar glide during cryorolling, which promotes the accumulation of stress for twinning, and thus deformation twins could be obtained easily [17]. Recent reports have pointed out that the addition of Cr and Zr could lower the SFE of copper matrix [18]. Hence, it is possible to form a high density of deformation twins in Cu-Cr-Zr alloys by cryorolling. Twin

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boundaries (TBs) can effectively block the dislocation motion; as a result, the strength of alloys can be improved further. In addition, the electrical resistivity of coherent TBs is about one order of the conventional grain boundaries (GBs) [19]. If it contains a high density of TBs, a metal is expected to be effectively strengthened without losing its high electrical conductivity. Meanwhile, aging treatment, which executes the precipitation of solute atoms, plays a critical role during the manufacture process of Cu-Cr-Zr alloys [20,21]. So cryorolling and aging treatment subsequently is a promising way to fabricate high strength and high electrical conductivity Cu-Cr-Zr alloys. Li et al. fabricated successfully a high strength and high electrical conductivity Cu-Zr alloy by cryorolling and subsequent aging treatment [22]. In comparison to SPD processes, cryorolling can achieve continuous producing, which has a great potential for large-scale industrial applications [23].

Thermo-mechanical treatment containing multiple cold deformation and aging process is one of the most sophisticated techniques applied in precipitation hardened alloys [24]. Yang et al. reported an enhancement of both tensile strength and electrical conductivity of Cu-Zr-B alloy through a double cold deformation and aging process [25]. So far, main studies report that the methods to fabricate high strength and high electrical conductivity Cu-Cr-Zr alloys are only focused on the one-step deformation and subsequent aging treatment [26,27]. In our study, the method of fabrication includes two-step deformation and an intermediate aging treatment. Meanwhile, it remains unclear that how the intermediate aging treatment in the interval of cryorolling influences the microstructures, mechanical and electrical conductivity properties of Cu-Cr-Zr alloys.

The main aim of this study is to develop a new method for fabricating high strength and high electrical conductivity Cu-Cr-Zr alloys. The effects of intermediate aging on the microstructures, mechanical and electrical conductivity properties of the cryorolled Cu-Cr-Zr alloys were investigated. What's more, the effects of precipitates on the deformation twins were discussed.

2. Method

A test material with a nominal composition of Cu-1 wt%Cr-0.1 wt% Zr alloy was prepared by using electrolytic copper (purity of 99.99%), pure chrome (purity of 99.99%) and Cu-49.9%Zr master alloy in a vacuum induction furnace under argon atmosphere, and casted in a metal mould with a size of 40×50×150 mm³. The ingot was homogenized at 960 °C for 24 h and planed at both sides to remove the oxidation layer, followed by hot rolling at 850 °C from 29.95 to 21.50 mm with 28.21% reduction in thickness. The hot rolled samples were then solution treated at 960 °C for 1 h prior to water quenching. After removing the oxidation layer and surface defects, the specimens were subjected to rolling at room and cryogenic temperature with or without intermediate aging, respectively. The rolling-aging routes are summarized and labeled in Table 1. Cryorolling was performed by immersing the samples into liquid nitrogen for 15 min. Multiple passes were applied to deform the samples with 10% reduction in thickness for each pass, after which the plates were dipped in liquid nitrogen immediately and immersed for 10 min before further reduction.

Vickers micro-hardness (HV) was tested on the rolling plane employing a MH-50 type micro-hardness tester with 3 kg load and 15 s loading time. The samples with sizes of 20×20 mm² were used to

Table 1
Three kinds of rolling-aging routes.

Label	Rolling temperature	Rolling-aging route
RTR	20 °C	90% reduction, without intermediate aging
CR	LNT	90% reduction, without intermediate aging
CRA	LNT	30% reduction+450 °C aging for 2 h+60% reduction

measure Electrical conductivity employing a D60K digital electrical instrument, and each specimen was measured at least five times. Samples with a parallel length of 40 mm were tensile-tested on an Instron 5500 R universal tensile machine with an initial rate of 2 mm/min at 25 °C. Discs of 3 mm in diameter punched from a longitudinal section (Nominal direction-rolling direction plane) of the plates and were ground to 30 μm and then double jet thinned using a 25% nitric acid in methanol solution at -30 °C. Transmission electron microscopy (TEM) and scanning transmission electron microscopy-high angle annular dark field (STEM-HAADF) observations were both performed using a Talos F200x microscope operated at 300 kV.

3. Results and discussion

3.1. Deformation twins

Fig. 1 shows the typical cross-sectional bright field TEM images and the corresponding statistical distributions of the twin/matrix lamellar thickness of RTR, CR and CRA Cu-Cr-Zr samples. The microstructure of the RTR sample is characterized by lamellar structures (Fig. 1(a)), which is consistent with the typical feature of metals deformed at room temperature [28]. A high density of dislocation cells can be observed in the lamella parallel to rolling direction, and a small volume fraction of deformation twins also exists in the RTR sample. In the matrix of CR sample, a mixed microstructure is obtained consisting of many deformation twins, lamellar structures and dislocations (Fig. 1(c)). Fig. 1(e) shows that the microstructure of CRA sample is similar to that of the CR sample, which includes a large number of deformations twins in bundles and a small number of lamellar structures and dislocations. Meanwhile, Fig. 1(e) shows some spherical precipitates, after the 2 h aging treatment, distributed between the twin/matrix lamellae. The fine particles are expected to be Cr precipitates coherent with matrix as discussed elsewhere [29]. Statistical measurements from a large number of TEM images indicate that the average twin/matrix lamellar thickness of the RTR sample is 83 nm (Fig. 1(b)), 59 nm (Fig. 1(d)) and 37 nm (Fig. 1(f)), respectively. It can be known that the lamellar thickness of CRA sample decreases obviously compared with the CR and RTR samples, which decrease about 38% and 55%, respectively.

Generally, twin/matrix lamellar thickness, in addition to the volume fraction of twins, is a crucial structure parameter for the twinned materials, which plays a decisive role on the mechanical properties. Recent research indicates that an extremely high strength has been achieved in polycrystalline Cu with a high density of nanometer-thick twins [19]. In addition, formation of nano sized grains via fragmentation of nanoscale twins provides an alternative approach for grain refinement [30]. Formation of copious twins with nanoscale thickness becomes a necessary precursory process for this grain refinement mechanism. The formation of stable twins comprises the nucleation of twin embryos and their subsequent growth. The critical twin nucleus thickness, λ_c , can be described by the following equation [31]:

$$\lambda_c = \frac{5\pi\rho G\gamma_{TB}}{2\sigma^2} \quad (1)$$

where G is the shear modulus and ρ is the ratio of thickness to diameter of the twin embryo (a constant), γ_{TB} is the twin boundary energy (which is proportional to the SFE), and σ is the driving stress of twin nucleation. Due to the addition of Cr and Zr, the SFE for Cu-1Cr-0.1Zr alloy (0.037 ± 0.002 J/m²) was almost half of the SFE of oxygen-free high-conductivity copper (0.074 ± 0.004 J/m²) [18]. The lower SFE of Cu-Cr-Zr alloys leads to a smaller critical twin nucleus thickness (λ_c). Thus, it is easier to form deformation twins in the RTR Cu-Cr-Zr alloy compared with pure copper. It is known that the driving stress for twin nucleation (σ) increases with an increasing deformation strain rate and/or the decreasing deformation temperature for face centered cubic alloys [31]. According to Eq. (1), λ_c is inversely proportional to

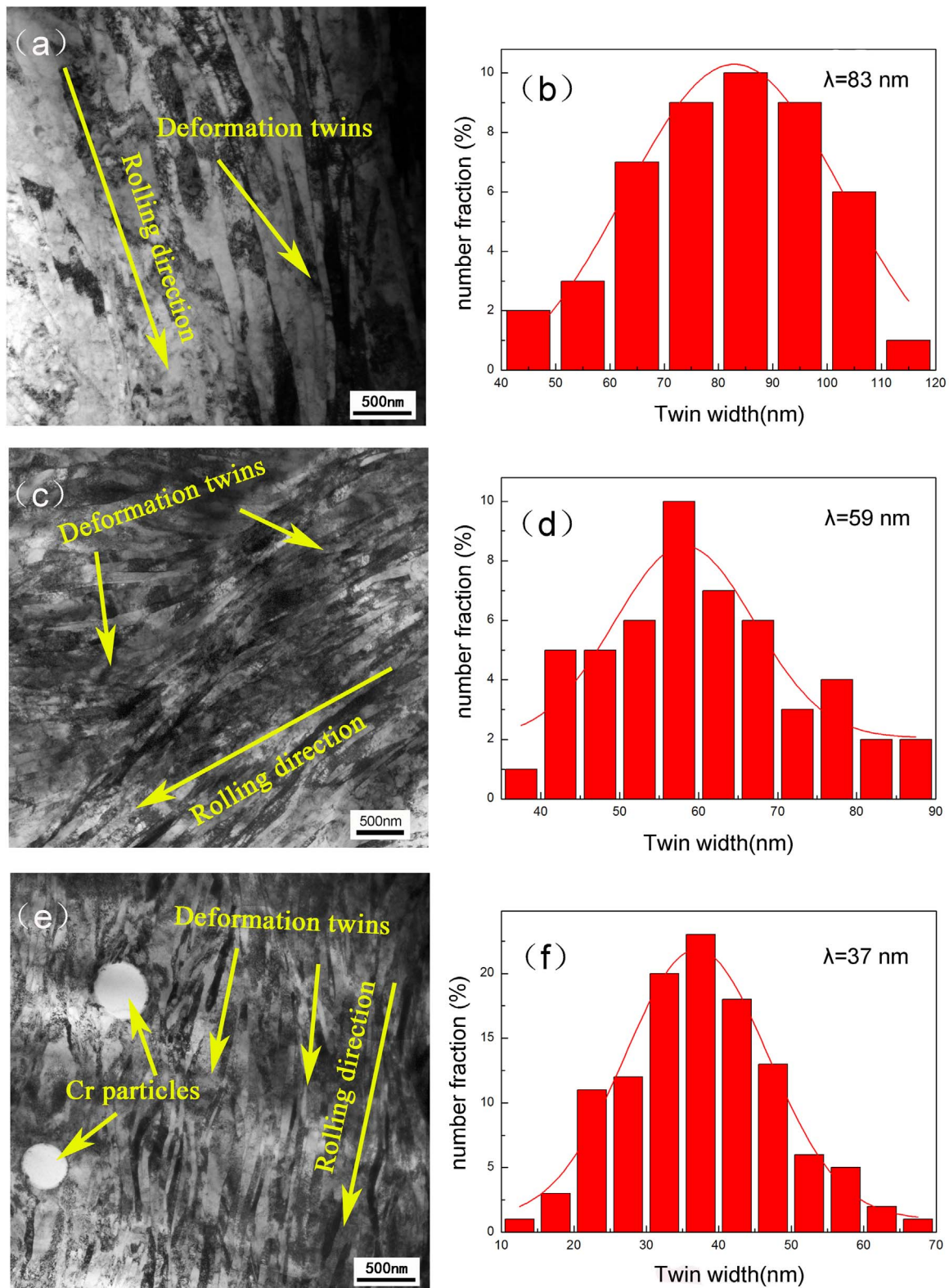


Fig. 1. A cross-sectional bright field TEM image of RTR sample (a), CR sample (c) and CRA sample (e); the statistical distribution of the twin/matrix lamellar thickness in RTR sample (b), CR sample (d) and CRA sample (f).

σ^2 , and thus cryorolling can effectively decrease the width of the twin/matrix lamellae of Cu-Cr-Zr alloys. It is obvious that the CR and CRA alloys have a larger volume fraction of deformation twins than RTR alloy. Rolling at low temperature increases the volume fraction of deformation twins and decreases the thickness of the twin/matrix lamellae at the same time. Apart from the deformation temperature

and strain rate, the globally applied stress τ also has an influence on the driving stress σ , and the relationship between the two can be describe by the following equation [32]:

$$\sigma = \frac{a\pi\tau^2}{Gb} \quad (2)$$

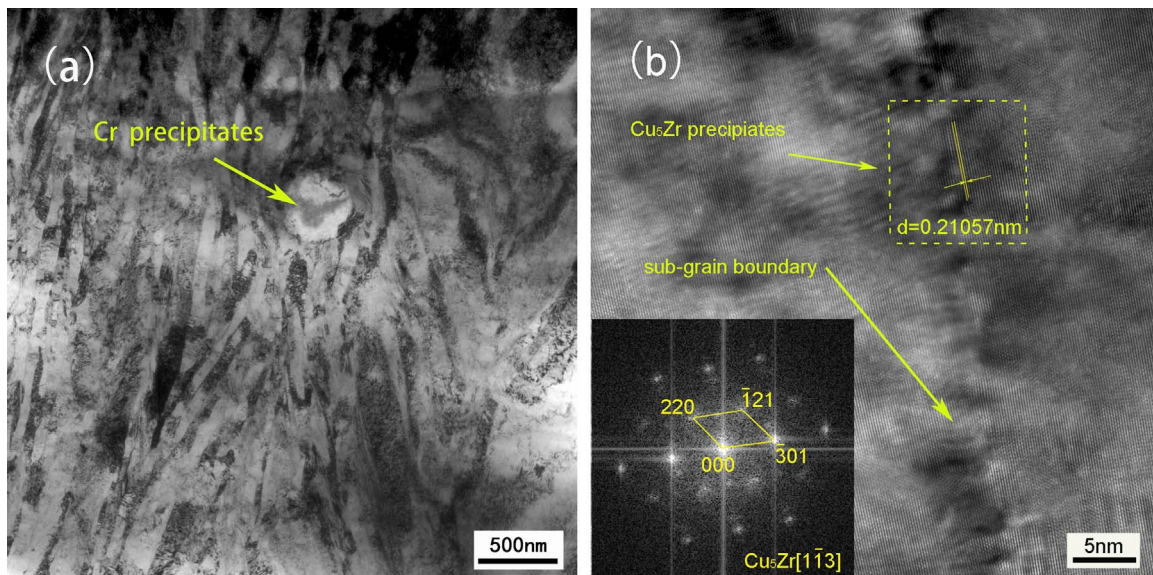


Fig. 2. (a) A bright field TEM image of Cr precipitates in CRA Cu-Cr-Zr alloy; (b) A HRTEM image of the precipitates in the matrix and the inset shows the FFT image along a $[1\bar{1}3]$ zone axis of Cu_5Zr .

where a is parameter that depends on the dislocation character, b is Burgers vector, l is the dislocation pile-up of length. During the intermediate aging treatment in the interval of cryorolling, fine spherical Cr precipitates (Fig. 1(e)) and Zr-enriched precipitates (Fig. 2) are distributed in the copper matrix. These precipitates can pin the motion of dislocations and induce local stress concentration, which leads to a bigger τ compared with the CR sample. Combining the Eqs. (1) and (2), it can be known that the λc is inversely proportional to τ^4 , and thus the increase of the applied stress τ has a significant effect on the width of twin/matrix lamellae. Therefore, the intermediate aging treatment in the interval of cryorolling can effectively decrease the thickness of the twin/matrix lamellae.

3.2. Precipitates

Fig. 2(a) describes a bright field TEM image of Cr precipitates in the CRA Cu-Cr-Zr alloy. It can be observed that Cr particles are surrounded by a high density of dislocations. Fig. 2(b) shows the typical coherent precipitates in the copper matrix (marked by a rectangle), which is confirmed by the fast Fourier transformation (FFT) image (the inset in Fig. 2(b)). The interplanar spacing of the precipitate is 0.21057 nm, which is consistent with the (311) plane of Cu_5Zr . This result agrees with the previous work, in which fine chromium and Cu_5Zr phase were observed [33]. Huang et al. also confirmed the existence of chromium and zirconium-rich phase in the Cu-Cr-Zr alloys [29].

As discussed above, the CRA process contains two stages cryorolling and an intermediate aging. In the first stage cryorolling, a large number of dislocations and vacancies were introduced into the matrix, which will provide sufficient nucleation sites for of the precipitation of Cr and Zr during the subsequent aging treatment [34]. After the formation of Cr and Cu_5Zr precipitates, the aged sample was then subjected to the second stage cryorolling. In this stage, the Cr and Cu_5Zr precipitates pin the motion of dislocations and stimulate much narrower twin/matrix lamellae (37 nm) compared with the cryorolled Cu-Cr-Zr alloy without precipitates. As a result, fine spherical Cr precipitates are surrounded by a large density of dislocations, and deformation twins in bundles bypassed the spherical Cr precipitates (Fig. 2(a)). What's more, the Cu_5Zr precipitates are distributed at twin boundaries, sub-grain boundaries, and within the twin/matrix lamellae (as seen in Fig. 2(b)). These precipitates strengthen both the twin/matrix lamellae and the intervals between twin bundles [22].

Fig. 3 describes the STEM-HAADF image and EDS mapping of the

CRA Cu-Cr-Zr alloy. The distribution of Cu, Cr and Zr element could be observed distinctly. The Cr-rich precipitates are almost spherical shape with an average diameter about 500 nm. The Zr element is widely distributed in the copper matrix and segregated at the edge of Cr-rich precipitates. More interestingly, it shows that the Cr-rich precipitate exists with a core-shell structure; the core is surrounded by a Zr-rich shell. Similar structure was discovered in the aged Cu-Cr-Zr-Si-Cr-Fe alloy [35] and Mg-Zn-Gd-Zr alloy [2].

The formation of the core-shell structure can be attributed to the fact that the formation of Cr-rich phases gradually consumes Cr from the solid solution, leading to a Cr-lean region in the vicinity of Cr-rich phase. It is the Cr-lean region that accelerates the diffusion or partitioning of Zr toward the Cr-rich phases, resulting in that the Zr atoms are concentrated around the Cr precipitates, and then forming the core-shell structure. The formation of the core-shell structure is proposed to reduce the strain between Cr-rich phases and Cu matrix, which can hinder the coarsening of Cr-rich phases and thereby increase its strengthening effect. Meanwhile, the structure causes a little decrease in electrical conductivity due to scattering conducting electrons by the dissolved solute atoms.

3.3. Mechanical properties and electrical conductivity

Fig. 4 shows the engineering stress-strain curves of the RTR, CR and CRA Cu-Cr-Zr alloys. The variations of the ultimate tensile strength (UTS) and electrical conductivity under different conditions are showed in Fig. 5. After the 90% rolling reduction in thickness, the UTS of the CR sample (559.27 MPa) is much larger than that of RTR sample (478.18 MPa). Meanwhile, the uniform elongation of CR sample (1.58%) is also improved compared with that of the RTR sample (1.12%). It should be noted that the UTS of the CRA Cu-Cr-Zr alloy is 690.13 MPa, which is increased by 23.4% and 44.3% compared with the CR sample and RTR sample. In addition, the hardness of the RTR, CR and CRA alloy approaches 151.33, 172.13 and 201.71 Hv, respectively. What's more, the electrical conductivity of the CRA sample (67% IACS) is increased prominently compared with the RTR (36.67% IACS) and CR (37.70% IACS) sample. It is obvious that the CRA process improves the tensile strength and electrical conductivity simultaneously.

As mentioned above, cryorolling decreases the twin/matrix lamellar thickness and increases the volume fraction of deformation twins. These profuse nano-scale twins can effectively improve the tensile

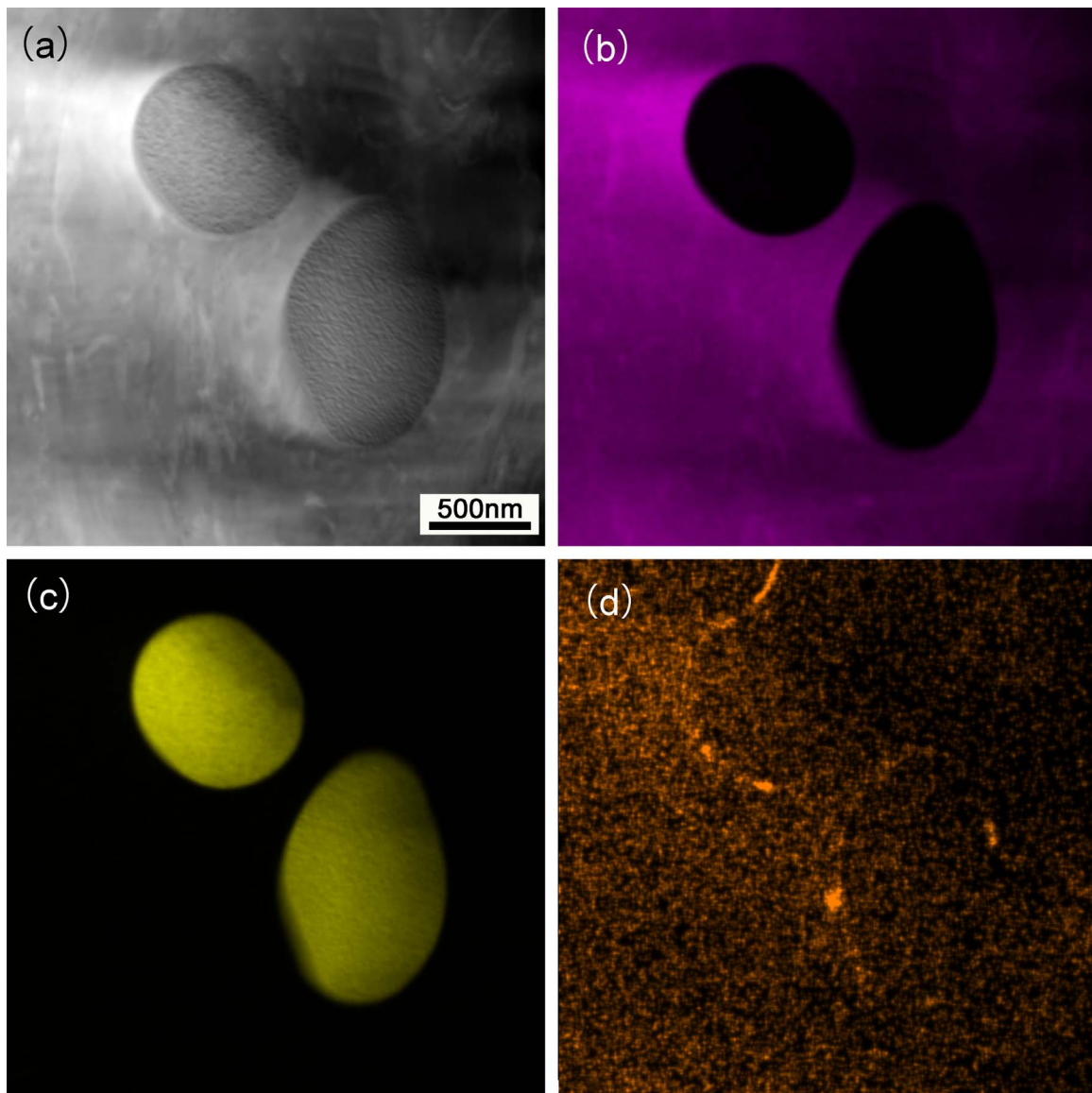


Fig. 3. (a) A enlarged STEM-HAADF image of precipitates in CRA Cu-Cr-Zr sample; (b) – (d) elemental mapping of Cu/Cr/Zr corresponding to (a).

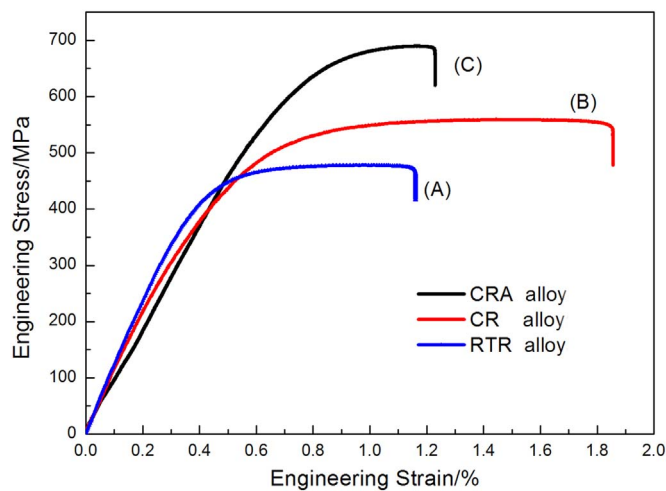


Fig. 4. Engineering Stress-strain curves of Cu-Cr-Zr alloys subjected to different processes. (A) RTR sample; (B) CR sample; (C) CRA sample.

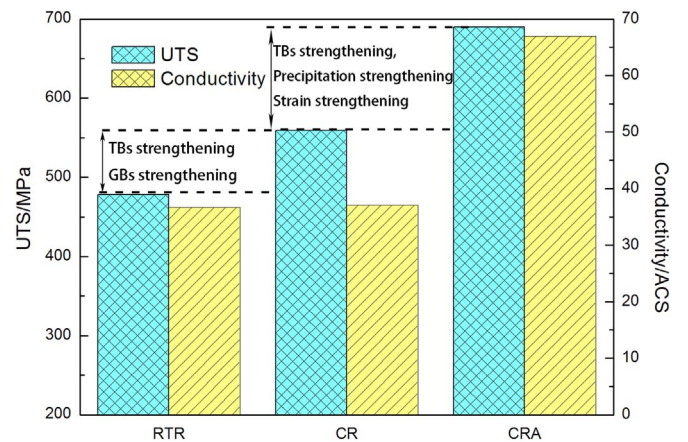


Fig. 5. The variations of the UTS and electrical conductivity under different conditions and the strengthening mechanisms of Cu-Cr-Zr alloys.

strength. Twin boundaries (TBs) have a strengthening effect similar to that of grain boundaries (GBs), and the increase in yield strength due to TBs $\Delta\sigma_{TB}$ can be described by a Hall-Petch-type relationship [36]:

$$\Delta\sigma_{TB} = K^{TB} \lambda_{TB}^{-\frac{1}{2}} \quad (3)$$

where K^{TB} is a constant, and λ_{TB} is the average twin thickness. According to Eq. (3), $\Delta\sigma_{TB}$ is inversely proportional to the average twin/matrix lamellae thickness λ_{TB} . As discussed above, the average twin/matrix lamellae thickness of the RTR, CR and CRA sample obeys the following relationship: $\lambda_{RTR} > \lambda_{CR} > \lambda_{CRA}$. Therefore, it can be inferred that $\Delta\sigma_{CRA} > \Delta\sigma_{CR} > \Delta\sigma_{RTR}$, which is consistent with the UTS of three kinds of samples. In addition, the fine crystallites derived from fragments of deformation twins play a role in improving the strength. Therefore, twinning and grain refinement strengthening are responsible for the improved strength of CR sample compared with RTR one. To improve strength further, an intermediate aging treatment was designed. After aging treatment, the Cr-rich precipitates and nano-scale Cu_5Zr precipitates are decomposed from the supersaturated solid solution, which is responsible for the improvement of UTS and electrical conductivity. In the following second stage cryorolling, the precipitates pin the motion of dislocations and deformation twins, and dislocations are piled up around the precipitates, resulting in introducing higher dislocation density. Therefore, besides TBs strengthening, precipitation strengthening and strain strengthening are responsible for the improved strength of the CRA samples compared with CR ones. Fig. 5 shows the strengthening mechanisms under different conditions of the Cu-Cr-Zr alloys intuitively.

As discussed above, the uniform elongation of the CR sample is higher than that of RTR sample. Cryorolling changes the plastic deformation mode and large numbers of deformation twins are developed in the CR sample. Dislocation slip plays a major role of the plastic deformation in the RTR sample while twinning bears the majority in the CR sample. Decreasing deformation temperature facilitates the formation of high density of twins and wide stacking fault ribbons generated by dissociated dislocations. The improved ductility is due to improved dislocation storage capacity and higher rate of strain hardening, which is caused by the formation of profuse twins and stacking faults [37,38]. What's more, the uniform elongation of CRA sample is lower than that of CR sample. It may cause by the interactions between precipitates and dislocations as discussed above.

It is known that the solute Cr and Zr atoms in the copper matrix act as impurity centers for the scattering of electron motions and thus deteriorate the electrical conductivity significantly. As a result, the electrical conductivity of the RTR and CR sample without aging treatment is only 36.67% IACS and 37.10% IACS, respectively. However, the electrical conductivity of the CRA sample rapidly increases to 67% IACS due to decomposition of the supersaturated Cu-Cr-Zr alloy and the formation of Cr-rich precipitates and nano-scale Cu_5Zr precipitates.

Therefore, the proper manufacturing route of the present Cu-Cr-Zr alloy strip is that: homogenization → hot rolling 30% → solution treatment → cryorolling 30% → aging at 450 °C → cryorolling to 90%. After the treatments of the route, the strength and electrical conductivity are simultaneously improved.

4. Conclusion

The microstructure, mechanical and electrical properties are studied in a Cu-1 wt%Cr-0.1 wt%Zr alloy. Based on the results obtained, the following conclusions can be drawn:

1. The intermediate aging treatment can decrease the thickness of the twin/matrix lamellae obviously. The average twin/matrix lamellar thickness of CRA sample is 37 nm, which decreases nearly 55% and 38% compared with that of the RTR and CR samples, respectively.
2. Cr-rich precipitate exists with a core-shell structure; the Cr-rich core is surrounded by a Zr-rich shell. This structure can prevent Cr particles from growing up resulting in a large increase in softening

resistance, and a little decrease in electrical conductivity due to scattering conducting electrons by the dissolved solute atoms.

3. The strength and electric conductivity of the Cu-Cr-Zr alloy are simultaneously improved by cryorolling and an intermediate aging treatment. Specifically, a desired combination of tensile strength (690.13 MPa) and electrical conductivity (67% IACS), can be obtained for the alloy after primary 30% cryorolling and aging at 450 °C for 2 h followed by secondary 60% cryorolling.
4. The improved strength of the Cu-Cr-Zr alloy is attributed to the interactions of TBs strengthening, GBs strengthening, precipitation strengthening and strain hardening during deformation and aging treatment.

Author contributions

S. Zhang, H. Kang and T. Wang conceived the idea and designed the experiment. S. Zhang, R. Li, Z. Chen performed the experiments. R. Li, H. Kang, W. Wang, C. Zou and T. Li contributed to the results analysis and discussion. S. Zhang wrote the paper.

Competing financial interests

The authors declare no competing financial interests.

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References

- [1] R. Mishnev, I. Shakhova, A. Belyakov, R. Kaibyshev, Deformation microstructures, strengthening mechanisms, and electrical conductivity in a Cu-Cr-Zr alloy, *Mater. Sci. Eng. A* 629 (2015) 29–40.
- [2] W. Zhai, W.L. Wang, D.L. Geng, B. Wei, A DSC analysis of thermodynamic properties and solidification characteristics for binary Cu-Sn alloys, *Acta Mater.* 60 (2012) 6518–6527.
- [3] L.X. Sun, N.R. Tao, K. Lu, A high strength and high electrical conductivity bulk CuCrZr alloy with nanotwins, *Scr. Mater.* 99 (2015) 73–76.
- [4] G. Pureck, H. Yanar, O. Saray, I. Karaman, H.J. Maier, Effect of precipitation on mechanical and wear properties of ultrafine-grained Cu-Cr-Zr alloy, *Wear* 311 (2014) 149–158.
- [5] Q. Liu, X. Zhang, Y. Ge, J. Wang, J.Z. Cui, Effect of processing and heat treatment on behavior of Cu-Cr-Zr alloys to railway contact wire, *Metall. Mater. Trans. A* 37 (2006) 3233–3238.
- [6] A. Vinogradov, V. Patlan, Y. Suzuki, K. Kitagawa, V.I. Kopylov, Structure and properties of ultra-fine grain Cu-Cr-Zr alloy produced by equal-channel angular pressing, *Acta Mater.* 50 (2002) 1639–1651.
- [7] A. Habibi, M. Ketabchi, M. Eskandarzadeh, Nano-grained pure copper with high-strength and high-conductivity produced by equal channel angular rolling process, *J. Mater. Process. Technol.* 211 (2011) 1085–1090.
- [8] Y. Takagawa, Y. Tsujiuchi, C. Watanabe, R. Monzen, N. Tsuji, Improvement in mechanical properties of a Cu-2.0 mass%Ni-0.5 mass%Si-0.1 mass%Zr alloy by combining both accumulative roll-bonding and cryo-rolling with aging, *Mater. Trans.* 54 (2013) 1–8.
- [9] R.K. Islamgaliev, W. Buchgraber, Y.R. Kolobov, N.M. Amirkhanov, A.V. Sergueeva, K.V. Ivanov, G.P. Grabovetskaya, Deformation behavior of Cu-based nanocomposite processed by severe plastic deformation, *Mater. Sci. Eng. A* 319–321 (2001) 872–876.
- [10] N. Takata, S.H. Lee, N. Tsuji, Ultrafine grained copper alloy sheets having both high strength and high electric conductivity, *Mater. Lett.* 63 (2009) 1757–1760.
- [11] N. Takata, Y. Ohtake, K. Kita, K. Kitagawa, N. Tsuji, Increasing the ductility of ultrafine-grained copper alloy by introducing fine precipitates, *Scr. Mater.* 60 (2009) 590–593.
- [12] R. Monzen, Y. Takagawa, C. Watanabe, D. Terada, N. Tsuji, Mechanical properties of precipitation strengthening Cu-base alloys highly deformed by ARB process, *Procedia Eng.* 10 (2011) 2417–2422.
- [13] Y.B. Lee, D.H. Shin, K.T. Park, W.J. Nam, Effect of annealing temperature on microstructures and mechanical properties of a 5083 Al alloy deformed at cryogenic temperature, *Scr. Mater.* 51 (2004) 355–359.
- [14] D. Singh, P.N. Rao, R. Jayaganthan, Effect of deformation temperature on

- mechanical properties of ultrafine grained Al–Mg alloys processed by rolling, *Mater. Des.* 50 (2013) 646–655.
- [15] T. Konkova, S. Mironov, A. Korznikov, S.L. Semiatin, Microstructural response of pure copper to cryogenic rolling, *Acta Mater.* 58 (2010) 5262–5273.
- [16] S. Nagarjuna, U. Chinta Babu, P. Ghosal, Effect of cryo-rolling on age hardening of Cu–1.5Ti alloy, *Mater. Sci. Eng. A* 491 (2008) 331–337.
- [17] H. Bahmanpour, A. Kauffmann, M.S. Khoshkhou, K.M. Youssef, S. Mula, J. Freudenberger, J. Eckert, R.O. Scattergood, C.C. Koch, Effect of stacking fault energy on deformation behavior of cryo-rolled copper and copper alloys, *Mater. Sci. Eng. A* 529 (2011) 230–236.
- [18] K. Kapoor, D. Lahiri, I.S. Batra, S.V.R. Rao, T. Sanyal, X-ray diffraction line profile analysis for defect study in Cu-1 wt% Cr-0.1 wt% Zr alloy, *Mater. Charact.* 54 (2005) 131–140.
- [19] L. Lu, Y. Shen, X. Chen, L. Qian, K. Lu, Ultrahigh strength and high electrical conductivity in copper, *Science* 304 (2004) 422–426.
- [20] W.X. Qi, J.P. Tu, F. Liu, Y.Z. Yang, N.Y. Wang, H.M. Lu, X.B. Zhang, S.Y. Guo, M.S. Liu, Microstructure and tribological behavior of a peak aged Cu–Cr–Zr alloy, *Mater. Sci. Eng. A* 343 (2003) 89–96.
- [21] Z.Q. Wang, Y.B. Zhong, X.J. Rao, C. Wang, J. Wang, Z.G. Zhang, W.L. Ren, Z.M. Ren, Electrical and mechanical properties of Cu–Cr–Zr alloy aged under imposed direct continuous current, *Trans. Nonferrous Met. Soc. China* 22 (2012) 1106–1111.
- [22] R. Li, H. Kang, Z. Chen, G. Fan, C. Zou, W. Wang, S. Zhang, Y. Lu, J. Jie, Z. Cao, T. Li, T. Wang, A promising structure for fabricating high strength and high electrical conductivity copper alloys, *Sci. Rep.* 6 (2016) 20799.
- [23] H.T. Liu, H.L. Li, H. Wang, Y. Liu, F. Gao, L.Z. An, S.Q. Zhao, Z.Y. Liu, G.D. Wang, Effects of initial microstructure and texture on microstructure, texture evolution and magnetic properties of non-oriented electrical steel, *J. Magn. Magn. Mater.* 406 (2016) 149–158.
- [24] W.Z. Chen, W.C. Zhang, H.Y. Chao, L.X. Zhang, E.D. Wang, Influence of large cold strain on the microstructural evolution for a magnesium alloy subjected to multi-pass cold drawing, *Mater. Sci. Eng. A* 623 (2015) 92–96.
- [25] Y. Ye, X. Yang, J. Wang, X. Zhang, Z. Zhang, T. Sakai, Enhanced strength and electrical conductivity of Cu–Zr–B alloy by double deformation–aging process, *J. Alloy. Compd.* 615 (2014) 249–254.
- [26] K.V. León, M.A. Muñoz-Morris, D.G. Morris, Optimisation of strength and ductility of Cu–Cr–Zr by combining severe plastic deformation and precipitation, *Mater. Sci. Eng. A* 536 (2012) 181–189.
- [27] M. Kermajani, S. Raygan, K. Hanayi, H. Ghaffari, Influence of thermomechanical treatment on microstructure and properties of electrosag remelted Cu–Cr–Zr alloy, *Mater. Des.* 51 (2013) 688–694.
- [28] Q. Liu, N. Hansen, Geometrically necessary boundaries and incidental dislocation boundaries formed during cold deformation, *Scr. Metall.* 32 (1995) 1289–1295.
- [29] H. Fuxiang, M. Jusheng, N. Honglong, G. Zhiting, L. Chao, G. Shumei, Y. Xuetao, W. Tao, L. Hong, L. Huafen, Analysis of phases in a Cu–Cr–Zr alloy, *Scr. Mater.* 48 (2003) 97–102.
- [30] Y. Zhang, N.R. Tao, K. Lu, Mechanical properties and rolling behaviors of nano-grained copper with embedded nano-twin bundles, *Acta Mater.* 56 (2008) 2429–2440.
- [31] Y. Zhang, N.R. Tao, K. Lu, Effect of stacking-fault energy on deformation twin thickness in Cu–Al alloys, *Scr. Mater.* 60 (2009) 211–213.
- [32] M.A. Meyers, O. Vöhringer, V.A. Lubarda, The onset of twinning in metals: a constitutive description, *Acta Mater.* 49 (2001) 4025–4039.
- [33] U. Holzwarth, H. Stamm, The precipitation behaviour of ITER-grade Cu–Cr–Zr alloy after simulating the thermal cycle of hot isostatic pressing, *J. Nucl. Mater.* 279 (2000) 31–45.
- [34] D.L. Zhang, K. Mihara, S. Tsubokawa, H.G. Suzuki, Precipitation characteristics of Cu–15Cr–0.15Zr in situ composite, *Mater. Sci. Tech.* 16 (2013) 357–363.
- [35] M. Hatakeyama, T. Toyama, J. Yang, Y. Nagai, M. Hasegawa, T. Ohkubo, M. Eldrup, B.N. Singh, 3D-AP and positron annihilation study of precipitation behavior in Cu–Cr–Zr alloy, *J. Nucl. Mater.* 386–388 (2009) 852–855.
- [36] H. Wen, T.D. Topping, D. Isheim, D.N. Seidman, E.J. Lavernia, Strengthening mechanisms in a high-strength bulk nanostructured Cu–Zn–Al alloy processed via cryomilling and spark plasma sintering, *Acta Mater.* 61 (2013) 2769–2782.
- [37] Y.L. Gong, C.E. Wen, Y.C. Li, X.X. Wu, L.P. Cheng, X.C. Han, X.K. Zhu, Simultaneously enhanced strength and ductility of Cu–xGe alloys through manipulating the stacking fault energy (SFE), *Mater. Sci. Eng. A* 569 (2013) 144–149.
- [38] Y.H. Zhao, Y.T. Zhu, X.Z. Liao, Z. Horita, T.G. Langdon, Tailoring stacking fault energy for high ductility and high strength in ultrafine grained Cu and its alloy, *Appl. Phys. Lett.* 89 (2006) 121906.