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# Microstructure evolution and enhanced properties of Cu-Cr-Zr alloys through synergistic effects of alloying, heat treatment and low energy cyclic-impact

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**Abstract:** In this paper, Cu-Cr-Zr alloys prepared by vacuum melting with adding La and Ni elements, were heat-treated and aged, followed by plastic deformation using low-energy-cyclic-impact tests, in order to simultaneously improve their mechanical and electrical properties. Results showed that grain size of the casted Cu-Cr-Zr alloys was significantly reduced after the solid solution aging and plastic deformation process. There were a lot of dispersed Cr and Cu<sub>5</sub>Zr precipitates formed in the alloys, and the numbers of dislocations were significantly increased. Accordingly, the hardness was increased from 78 HV to 232 HV, and the tensile strength was increased from 225 MPa to 691 MPa. Electrical conductivity has not been significantly affected after these processes. The enhancement of overall performance is mainly attributed to the combined effects of solid solution hardening, fine grain hardening, and precipitation/dislocation strengthening.

**Key words:** Cu-Cr-Zr alloy; properties; low-energy cyclic-impact; microstructure; micro-alloying; solution and aging

## 1. Introduction

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Cu-Cr-Zr alloy has good properties such as high strength, superior electrical and thermal conductivities, good fatigue and abrasion resistance. It is widely used in integrated circuit lead frames, high-speed train contact lines and casting crystallizer [1-4]. In recent years, there is a critical requirement to improve mechanical properties of the Cu-Cr-Zr alloy for various applications. For example, Lin et al [5-8] reported effect of solid solution aging on the properties of Cu-Cr-Zr alloy. They found that the Cr and Cu<sub>5</sub>Zr phases in the alloy pinned the dislocations and increased the strength of the alloy. Li et al [9] found that addition of lanthanum (La) and cerium (Ce) significantly improved the hardness and increased the softening temperature of Cu-Cr-Zr alloy. Dai et al [10] studied the effects of adding La and Ce elements into the Cu-Cr-Zr alloy, and found that La and Ce reacted with O<sub>2</sub> and H<sub>2</sub>, and thus enhanced the degassing and dust removal effects in the smelting process. Shuai et al [11] added 2.5 wt.% Fe and 0.03 wt.% P into the Cu-Cr-Zr alloy, and found that the hardness of the alloy reached 125 HV, which was 20 HV higher than that of Cu-Cr-Zr alloy when 0.22% Fe and 0.06% P were added. León et al [12] reported that the Cu-Cr-Zr alloy prepared using an equal channel angular pressing (ECAP) method showed extensive dislocations within the grain structures, and the strength of the alloy was significantly improved. However, this was accompanied with the decrease of its ductility. Vinogradov et al [13] studied the properties of Cu-Cr-Zr alloy after the ECAP process followed by aging process. They reported that an ultrafine grain size of 160 nm was achieved after the plastic deformation, and the fatigue life of the alloy was significantly improved. Takata et al [14-15] reported formation of fine particles of second phases in the Cu-Cr-Zr alloys prepared using an accumulative roll bonding (ARB) process, which improved the elongation and tensile strength of the alloys. They reported that the deformation process had little influence on the conductivity of

the alloy. Islamgaliev et al [16] reported that a high pressure torsion (HPT) process of the Cu-Cr alloy operated at 300°C under a high pressure of 6 GPa not only refined the grains of the alloy, but also achieved a tensile strength of 790-840 MPa and an electrical conductivity of 81-85% IACS (International Annealed Copper Standard). Shakhova et al [17] reported that ultrafine grains of the Cu-Cr-Zr alloy were obtained after a multi-direction forging treatment, which enhanced the overall properties of the alloy.

Generally increasing the strength of copper alloys will lead to a significant decrease in their electrical conductivity, thus it is a critical challenge to significantly increase the strength of copper alloys, and simultaneously maintain their good electrical conductivity. In this paper, Cu-Cr-Zr alloy with both high strength and good conductivity was successfully obtained by adding small amounts of alloying elements of Ni and La during solid solution process, followed by heat treatment and low energy cyclic-impact deformation process. Ni is a solid solution strengthening element. It can improve strength of the Cu alloys but have little effect on its conductivity [18-20]. The rare earth element of La can refine the grain size, and it has a good long-term enhancement and smelting stability in the process of vacuum arc melting [21]. Therefore, we chose to add Ni (2wt%) element and La (0.3wt%) element (Cu-La master alloy) in the Cu-Cr-Zr alloy, in order to obtain a copper alloy with both high strength and high conductivity. As far as we know, there is no previous report which has applied multiple strengthening methodologies for the Cu alloys.

## **2. Results and discussion**

Elemental analysis results of the casted Cu-Cr-Zr-2.0%Ni-0.3%La alloy obtained using the X-ray fluorescence (XRF) are shown in Fig. 1, which proves that the Ni and

La elements are successfully doped into the Cu-Cr-Zr alloy. Results also show that there is little loss of Ni and La elements during the smelting process.

Figures 2a to 2c show the microstructures of Cu-Cr-Zr-2.0Ni-0.3La alloy before and after solid solution and aging treatment, in which Figures 2a and 2b show the Cu-Cr-Zr alloy without and with adding elements. Comparing Figures 2b and 2c, after the solid solution aging process, the grains have been increased significantly and fine particles are precipitated in the matrix as can be seen from the yellow arrow in Figure 2c. This is because the alloying elements such as Cr, Zr, and Ni have very low solubility inside copper. Similar results were reported in Ref. [22] about this grain refinement effect. The energy dispersive X-ray spectrum (EDS) analysis of the position shown in the yellow arrow in Figure 2c proves that the precipitated particles contain three elements of Cu, Cr and Ni.

Figure 3 shows the microstructures of Cu-Cr-Zr-2.0Ni-0.3La alloy before and after the low-energy-cyclic-impact deformation up to 90%. It can be seen from the Figure 3a that the grains before deformation are approximately equiaxial. After the low-energy-cyclic-impact deformation, the grains are severely deformed as shown in Fig. 3b. It can be clearly seen the density of grain boundaries are significantly increased with more disordered distribution. As shown in Fig. 3c, the crystal grains are apparently deformed along the direction perpendicular to the applied force. Some crystal grains are severely deformed into strips, whereas a few of others still maintain their equiaxial grain shapes. This is simply because the crystal orientation of each grain is different, and their directions of slip planes/lines are different. When the direction of force is parallel to the crystal's slip direction, the grain will be significantly deformed.

Figure 3d is an inverse pole figure maps (IPF) of the alloy in the transversal direction (TD). It can be seen that the grains are mostly equiaxial, and the deformed grains are mostly along the (100) crystal plane (as shown in red color in Figure 3d). This is because the direction is perpendicular to the direction of the force, therefore, these fine particles may be broken into many small ones during the severe plastic deformation. Figure 4e shows a high resolution transmission electron microscope (HRTEM) image in the LD direction. It can be seen that the grains have been compressed and deformed to form fibrous bundles. The grain orientation has also been significantly changed as revealed from the different colors shown in Fig. 3e. This clearly indicates that in the process of strong plastic deformation, grains are not only refined, but also rotated. Previous studies [23-26] also reported the apparent refinement of copper grains after a severe plastic deformation. From this study, the Cu alloys clearly undergo a significant grain refinement after the low-energy-cyclic-impact deformation, and the fiber bundles have also formed, with a large numbers of dislocations and preferred crystal orientations generated in the alloys. Figure 3f shows the X-ray diffraction (XRD) spectra of Cu-Cr-Zr alloys after alloying and severe plastic deformation. There are four strong peaks of copper phases without the other peaks. This is because the Cu-Cr-Zr alloy has lower contents of Cr, Zr and alloying elements, which cannot be detected by XRD analysis. After alloying, the diffraction peaks are shifted to the left-side as indicated by the red dashed line shown in Figure 3f, which is mainly because the Ni elements have been solidly-dissolved into the copper matrix, thus resulting in an apparent lattice distortion. After plastic deformation, the crystal grains are refined and the diffraction peaks become broadened. The diffraction peak of (200) is significantly higher than that of the (111) plane, indicating that the orientations of the crystal planes in the grain have been changed after plastic

deformation, and the preferred orientation is now along the (200) direction. The XRD results are consistent with those obtained from the electron backscatter diffraction (EBSD).

According to references [27-30], the equation for calculating the dislocation density based on the XRD results is:

$$\rho = \frac{2\sqrt{3} \langle \varepsilon^2 \rangle^{1/2}}{d_{XRD} \times b} \quad (\text{Eq.1})$$

where  $\rho$  represents the dislocation density,  $\langle \varepsilon^2 \rangle^{1/2}$  is the microscopic strain,  $d_{XRD}$  is the grain size, and  $b$  is the Berber's vector. In a cubic system, the value of  $b$  is  $\sqrt{2}a/2$ , and  $a$  represents the lattice constant. The micro-strain can be obtained using the Jade software based on the diffraction peak of XRD. The dislocation density can be calculated based on the influence of the micro strain on the diffraction peaks, and the obtained results are listed in Table I. Results show that the dislocation density of the Cu-Cr-Zr alloy has been increased by about one order of magnitude after the cyclic plastic deformation of Cu-Cr-Zr alloy using the small energy repeated-impact test.

Figure 4 shows the TEM images of Cu-Cr-Zr-2.0Ni-0.3La alloy after heat treatment (Figs. 4a-4c) and after small energy repeated-impact tests (Figs. 4d-4f). It can be seen from Figs. 4a and 4b that there are spherical precipitates. Based on the analysis from the electron diffraction patterns of these precipitates as shown in Fig. 4b, they are Cr, about 1  $\mu\text{m}$  in diameter. The high-resolution TEM image of the Cr particles is shown in Fig. 4c. The distance of Fast Fourier transform (FFT) spots were further measured, and the results show that the interplanar spacing of the Cr particles is 0.2347, which is consistent with the theoretical value ( $d_{\text{Cr}(200)}=0.23$  nm). The phase of  $\text{CuZr}_2$  can also be identified from the high-resolution TEM image.



Figure 4d shows the rod-shaped precipitates of the alloy after severe plastic deformation rate of 90%. TEM analysis shows that during the plastic deformation process, the second phase is hard and cannot be cut through by dislocation movements. The rod-shaped structures were identified as Cr from the diffraction patterns and there are also a small amount of CuZr intermetallic compounds, which are consistent with the results reported in Ref. [31]. A high-resolution TEM image of the precipitates is shown in Fig. 4d, and the Fast Fourier Transform (FFT) analysis showed that this is  $\text{Cu}_5\text{Zr}$  according to Ref. [32-33]. After the severely plastic deformation of the alloy, a large number of dislocations were generated inside the crystal structures. The arrows in Fig. 4f show a large number of dislocations and their entanglements, which are consistent with the calculated results of XRD analysis.

Figure 5 shows the engineering stress-strain curves of Cu-Cr-Zr alloy under different treatment conditions. Three stage deformation process can be identified, e.g., elastic deformation, plastic deformation and fracture failure. The Cu-Cr-Zr alloys at different process stages show significant changes of dimensions during the plastic deformation. When alloying elements are added to Cu-Cr-Zr alloy, the plasticity of the materials is significantly improved (compared with the brown and black curves), but the plasticity of the material is significantly reduced after the deformation treatment.

The strength of Cu-Cr-Zr alloy has been increased after adding Ni and La, which is mainly due to the solid solution strengthening and fine grain strengthening. However, the strength of the alloys has been increased sharply after the solution aging treatment, which is mainly attributed to the effect of precipitation strengthening. The strength of the alloy has been further increased after the low-energy-cyclic-impact tests, which is mainly due to the deformation strengthening.

From the stress-strain curve of the alloy shown in Figure 5, the specific performance parameters of the alloy in different states were obtained and are listed in Table II. The Cu-Cr-Zr-2.0Ni-0.3La alloy obtained by the deformation treatment after heat treatment shows the highest strength, and its tensile strength and yield strength are 691 MPa and 467 MPa, respectively. Compared with those of the as-cast Cu-Cr-Zr alloy and the as-cast Cu-Cr-Zr-2.0Ni-0.3La alloy, the yield strength and tensile strength of the alloys after the processes are improved by 28% and 24%, respectively. The improvement of yield strength and tensile strength indicates that Ni element and La element have the abilities to produce alloying strengthening effect. When the Ni and La elements were added to Cu-Cr-Zr alloy, the grain structure was refined. The La element has the functions of purifying the matrix and increasing the smelting stability in the process of vacuum arc melting. Compared with the as-cast Cu-Cr-Zr-2.0Ni-0.3La alloy, the yield strength and tensile strength of the Cu-Cr-Zr-2.0Ni-0.3La alloy after solution aging treatment were increased by 138.7% and 138.4%, respectively. The reason for the large increase in yield strength and tensile strength is that the Ni element is completely dissolved in the Cu grains of the matrix during the solution treatment. As a result, lattice distortion occurs, and the density of dislocations increases, which in turn causes dislocation accumulation and hinders the movement of dislocations. On the other hand, during the aging process, the original Cr and Zr elements are precipitated into dispersed second phases inside the matrix, which have a strong pinning effect within the grains and also at the grain boundary. The La element can prevent Cu grains from growing up during the heat treatment process, thus providing a fine grain strengthening effect. Under these three strengthening effects, the performance of the alloy after heat treatment has been greatly improved. However, after the low-energy cyclic deformation treatment, the

increased strength is not significant. The yield strength is only increased by 9%, and the tensile strength is only increased by 4%, whereas the ductility loss is about 30%. The possible reason is that although the low-energy deformation is performed, the final deformation rate is large, which will lead to significant increases in lattice distortion and crystal defects, which causes the decrease in the ductility. Ref. [14] previously reported that the tensile strength of Cu–Cr–Zr alloy specimens has been increased from 464 MPa to 573 MPa after 6-cycle accumulative roll-bonding (ARB) process, which is similar to our results.

Figure 6a compares the hardness and electrical conductivity of Cu-Cr-Zr alloy after different processes. It can be seen that after alloying, the hardness of Cu-Cr-Zr alloy is slightly increased. The conductivity is decreased because the addition of elements increases the electron scattering effects. After the solution aging treatment, the hardness of the Cu-Cr-Zr-2.0Ni-0.3La alloy was significantly increased from 107 HV to 232 HV. Ref. [34] reported that the hardness peak values of Cu-Cr-Zr alloy after the ECAP is 227 HV<sub>0.5</sub>. It is similar to our results. The conductivity was improved from 40% IACS to 67% IACS, which was increased by 67.5%. This is because the aging process causes the dispersion and uniform distribution of the elements within the matrix. The subsequent low-energy-cyclic-impact deformation treatment increases the dislocation density of the alloy, thus resulting in an increase of hardness up to 242 HV and a decrease in conductivity to 62% IACS. The decrease of the conductivity is insignificant, which is the same as the results in the [35].

Figure 6b is a comparison of mechanical properties and electrical properties of Cu-Cr-Zr alloy. It can be seen that different treatment methods have shown significant influences on the properties of the copper alloys. For example, Ref. [32] reported that low temperature rolling and ageing processes have enhanced effects on the

performance. Most studies showed that the mechanical properties and electrical properties have opposite changes after the process, whereas our work clearly show an enhancement of both mechanical and electrical properties.

### 3. Conclusions

Following conclusions can be obtained from the experimental and analysis results:

(1) The alloying elements of Ni and La have been added into the Cu-Cr-Zr alloy after the vacuum arc melting processes, and the microstructures are uniformly distributed without apparent defects. The grain size of Cu-Cr-Zr-2Ni-0.3La alloy is reduced from 45  $\mu\text{m}$  to 23  $\mu\text{m}$ . The strength of Cu-Cr-Zr-2Ni-0.3La alloy is increased from 279 MPa to 665 MPa, and the conductivity is increased from 40% IACS to 67% IACS after solution hardened at 960°C and then aged at 450°C.

(2) After the treatment of Cu-Cr-Zr-2Ni-0.3La alloy with small energy repeated-impact up to 90%, fibrous morphology and grain refinement can be observed in the microstructure. The dislocation density has also been increased by an order of magnitude from  $1.83 \times 10^{14} \text{ m}^{-2}$  to  $1.462 \times 10^{15} \text{ m}^{-2}$ , the strength has been increased from 665 MPa to 691 MPa, and the electrical conductivity has been decreased from 67% IACS to 62% IACS.

(3) For vacuum arc melting Cu-Cr-Zr alloy after alloying process, heat treatment and low energy cyclic-impact, the strengthening mechanisms are identified as the combination of fine grain strengthening by rare earth La, solid solution strengthening by element Ni and precipitation strengthening by Cr and Zr particles.

### 4. Experimental

The process procedure is shown in Fig 7. The commercial Cu-Cr-Zr alloy (with its chemical composition listed in Table III) was obtained from Kunshan Yiyue Metal Company, China. The Cu-La intermediate alloy and the Ni were placed in the vacuum melting furnace up to 3Pa, then the chamber was filled with argon. This process was repeated for three times. When the vacuum of the sample chamber was below  $3.0 \times 10^{-3}\text{Pa}$ , the chamber was refilled with high purity argon gas. Its purpose was to

prevent copper alloys and La elements from being oxidized. The alloys were melted three to five times under an argon atmosphere, and then casted into 20×5×80 mm molds. The samples were quenched in water after heat treatment at 960°C for one hour, and then aged at 450°C for five hours. The as-prepared Cu-Cr-Zr-2.0Ni-0.3La alloy was mechanically deformed using a tensile tester with a low energy cyclic-impact process operated at the room temperature until the deformation strain reaches 90%. Low energy cyclic-impact was performed by continuously impacting the samples using a small amount of energy. During the process, the strains of the material were gradually accumulated, and the microstructure was gradually refined. The deformation mainly occurred on the surface of the alloy but with little changes in its core, thus there was little decrease in electrical properties. Finally, a large plastic deformation was generated. The method has the advantages of simple principle, easy operation, low manufacturing cost, and no special requirement for the size of the sample to be processed. The impact energy of the drop hammer was 4 J, and the cyclic rate was 5 times per minute. The deformation rate was 90%.

The prepared sample was ground and polished into a mirror form, and then was chemically etched using a mixed solution of 5 g FeCl<sub>3</sub>, 50 ml HCl and 100 ml H<sub>2</sub>O. Metallographic observation of the sample before and after impact process was performed using an Olympus GX71 optical microscope. The elemental composition analysis was investigated using a Bruker S8 Tiger XRF spectrometer. Microstructures of the samples were investigated using a scanning electron microscope (SEM, SU3500) equipped with an electron backscattering diffraction (EBSD). The changes of grain structures before and after deformation were analyzed using the EBSD. Chemical elements were analyzed using an EDS. Crystalline structures of the samples were analyzed using an XRD (XRD-7000S, Cu K-alpha radiation) with a two-theta scanning rate of 8° per minute. Mesophases and dislocations within the grain structures were studied using a transmission electron microscope (TEM, JEM-3010). Hardness was measured on polished sections of the samples using a Vickers micro-hardness tester (HV-120) under a load of 0.5 kg and a holding time of 15 s. The electrical conductivity of the samples was measured at room temperature using a D60K digital electrical instrument, and each specimen was measured at least three times to obtain an average reading. Tensile tests of the samples were carried out using an HT-2402 tensile testing machine on specimens with

a gauge length of 40 mm and a cross-section of 3mm×5mm at the extension rate of 1 mm/min.

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### **Compliance with ethical standards**

**Conflict of interest** The authors declare that they have no conflict of interest.

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## Tables:

Table I Micro-strain and dislocation density of sample after plastic deformation of Cu-Cr-Zr alloy

Sample	$\langle \epsilon^2 \rangle^{1/2}(\%)$	$\rho(10^{15})\text{m}^{-2}$
After aging treatment of Cu-Cr-Zr-2.0Ni-0.3La	0.007	0.183
After deformation of Cu-Cr-Zr-2.0Ni-0.3La	0.032	1.462

Table II Tensile strength, yield strength and elongation of Cu-Cr-Zr-x alloy under different treatment conditions

Sample	Elongation (%)	Yield strength (MPa)	Tensile Strength (MPa)
Cu-Cr-Zr	8.44	139	225
Cu-Cr-Zr-2.0Ni-0.3La	5.89	178	279
Heat treatment Cu-Cr-Zr-2.0Ni-0.3L	4.23	425	665
Deformation Cu-Cr-Zr-2.0Ni-0.3La	4.04	467	691

Table III Chemical composition of commercial Cu-Cr-Zr alloy

Element	Cu	Cr	Zr	Al	Mg	Fe	Si	P
Wt.%	Bal.	0.3-0.6	0.5	0.1-0.25	0.1-0.8	0.5	0.1	0.5

## Figure title:

Fig. 1. XRF analysis result of Cu-Cr-Zr-2.0Ni-0.3La alloy after vacuum melting

Fig. 2. Microstructure of Cu-Cr-Zr-X alloy

(a) Cu-Cr-Zr alloy as-cast condition; (b) As-cast Cu-Cr-Zr-2.0Ni-0.3La ;

(c) After solution aging of Cu-Cr-Zr-2.0Ni-0.3La;(d) the point scan of arrows in Fig.3g

Fig. 3. Microstructure of Cu-Cr-Zr-2.0Ni-0.3La alloy after 90% deformation with low-energy-cyclic-impact and XRD spectra of Cu-Cr-Zr alloy in different states

Fig. 4. TEM morphology of Cu-Cr-Zr-2.0Ni-0.3La alloy after heat treatment and deformation (a) local topography; (b) amplification of the precipitated phase and electron diffraction pattern; (c) figure (b) HRTEM around the precipitated phase; (d) local morphology in the TD direction after deformation; (e) figure (c) HRTEM; (f) dislocation after deformation

Fig. 5. Stress-strain curve of Cu-Cr-Zr-Ni-La alloy under different conditions

Fig. 6. Comparison of hardness and electrical conductivity of Cu-Cr-Zr alloy under different conditions and the Comparison of mechanical and electrical properties of Cu-Cr-Zr alloy

(a) Cu-Cr-Zr; (b) Cu-Cr-Zr-2.0Ni-0.3La; (c) heat treatment Cu-Cr-Zr-2.0Ni-0.3La; (d) deformation Cu-Cr-Zr-2.0Ni-0.3La

Fig. 7. Schematic illustration of preparation process of the Cu-Cr-Zr alloy