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# Analysis of phase in Cu−15%Cr−0.24%Zr alloy

Li-ming BI[1], Ping LIU[2], Xiao-hong CHEN[2], Xin-kuan LIU[2], Wei LI[2], Feng-cang MA[2]

1. School of Energy and Power Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China;
2. School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China

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**Abstract:** The vacuum medium-frequency induction melting technology was employed to prepare the Cu−15%Cr−0.24%Zr alloy. The scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were used to analyze the phase composition, morphology and structure of the alloy. The results reveal that the as-cast structure of the alloy consists of Cu matrix, Cr dendrite, eutectic Cr and Zr-rich phase. A large number of Cr-precipitated phases occur in the Cu matrix, and $Cu_5Zr$ particles can be found in the grain boundary of Cu matrix. The HRTEM images prove that there is a semi-coherent relationship between $Cu_5Zr$ and Cu matrix.
**Key words:** Cu−Cr−Zr alloy; as-cast structure; in-situ composite; precipitated phase

## 1 Introduction

Deformation-processed in-situ Cu−Cr fiber-reinforced composites are potential electric materials with high strength (>1000 MPa) and high conductivity (70% IACS), as well as excellent comprehensive properties [1−3]. As compared with other deformation-processed in-situ fiber-reinforced composites of Cu−Ag or Cu−Nb alloy, Cu−Cr alloy has a lower price-performance ratio, and thus attracts more attention [4−8]. The comprehensive properties of such materials can be enhanced by the addition of the third element. To date, ternary alloying elements such as Ti, Zr, Ag, Co and rare earth have been applied to Cu−Cr alloy. It has been proven that with the addition of above-mentioned elements, the tensile strength of Cu−Cr alloy has been improved to different extents, with no obvious deterioration of conductivity [9−15]. Among them, Zr has a significant promotion effect on the tensile strength and thermal stability of deformation-processed Cu−Cr alloy in-situ composites [16,17]. It has been suggested that the material performance is optimized upon the addition of Zr element as the CuZr intermetallic compounds are formed during the solidification of alloy [18,19].

In recent years, researches regarding deformation-processed Cu−Cr in-situ composites have focused largely on their structure and performance after heavy deformation, with only a brief introduction to the as-cast structure. It is considered that the aforesaid as-cast structure of such alloys consists of Cu matrix, Cr dendrite and Cu−Cr eutectics [20−22]. Presently, there are a large number of reports on the phase composition of Cu−Cr−Zr ternary alloy. For example, ZENG and HAMALAINEN [23,24] studied the isothermal phase diagrams of Cu-rich corner of the Cu−Cr−Zr ternary system at 940 °C and 960 °C, respectively. It is found that there mainly are Cu, Cr, $Cr_2Zr$ and $Cu_3Zr$ phases [23,24]. In addition, KUZNETSOV et al [25] calculated the vertical cross-section diagram of the system with 0.4%Zr and 0.5%, 1.5% and 5%Cr, respectively. The results showed that the Cu, Cr, $Cu_3Zr$, $Cu_51Zr_{14}$, $Cu_8Zr_3$ and $Cu_{10}Zr_7$ phases were involved in this system. However, the previous researches contain relatively low Cr content (<1%), thus can be substantially different from those containing high Cr content (>10%) regarding the phase composition.

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**Corresponding author:** Ping LIU; Tel/Fax: +86-21-55271682; E-mail: liuping@usst.edu. cn
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The phase composition, morphology and structure in as-cast alloys impose direct impacts on the comprehensive properties of in-situ composites after heavy deformation. The high strength of Cu−Cr system in-situ composites is chiefly due to the Cr fibers, and the Cr fibers are developed by dendritic Cr of as-cast structure through heavy deformation. Although the eutectic Cr in as-cast structure also occupies a certain proportion, it cannot develop into Cr fibers. Instead, the presence of eutectic Cr will lead to a reduction of composite material in strength. Because the dislocations will pile up near the eutectic Cr when a external force is applied to the composite material, a serious local concentration of stress occurs, then cracks are induced. So, if one wants to improve the strength, minimal eutectic Cr will be more desirable in the as-cast structure. The research shows that the tensile strength and softening temperature of Cu−Cr in-situ composite containing 0.2%Zr can be improved at more than 100 MPa and 50 °C for the formation of CuZr intermetallic compound with high hardness and high melting point [19,20]. Thus it can be seen that the performance Cu−Cr in-situ composite could be increased by a proper content of CuZr intermetallic compound. Therefore, it is necessary to perform a detailed study on the as-cast structure of Cu−Cr−Zr alloy with high Cr content.

In this work, the detailed study was conducted on the composition, morphology and distribution of phases of as-cast structure of alloy with addition of 0.24% Zr into Cu−15% Cr alloy.

## 2 Experimental

### 2.1 Preparation of alloy

The Cu−15%Cr−0.24%Zr alloy was prepared by Cu (>99.95% purity) cathode electrolysis and with nominal compositions such as industrial-pure Cr and sponge Zr (>99.5% purity), which were smelted in a vacuum medium frequency induction furnace. The casting was performed using a cylindrical cast iron ingot mould (83 mm×180 mm). The ingot mould was preheated to approximately 100 ºC before casting. The inner surface of ingot mould was simultaneously fumigated with benzene to facilitate de-moulding and improve the ingot casting surface quality. The smelting process was conducted in a magnesia crucible at 1600−1650 °C.

### 2.2 Electron microscopy

The microstructure of the alloy was observed with a FEI QANTA450 field emission scanning electron microscope (FESEM), and associated phase composition was quantitatively analyzed with an energy dispersive spectrometer (EDS). The 63% $HNO_3$ solution was used as the corrosive liquid, and ethyl alcohol was applied to washing the alloy under ultrasonic wave post-corrosion.

The alloy was further examined by H−800 and JSM−2100 transmission electron microscope (TEM and HRTEM, respectively) with an accelerating voltage of 200 kV. The specimens were prepared by mechanically thinning dimpling and then ion milling at 3 kV with an incidence angle of 8°. After the micropore appeared, it was required to regulate the angle of electron gun to 4° and continue to perform thinning for 10 min.

## 3 Results and discussion

### 3.1 SEM and EDS analyses

Figure 1 shows the SEM images of the as-cast structure of Cu−15%Cr−0.24%Zr alloy. Figure 2 shows the EDS analysis of the classic phase Cr dendrite and Zr-rich phase of alloy. Results of EDS analysis for various phases shown in Fig. 1 are summarized in Table 1.

Figure 1(a) shows the macrostructure and Figs. 1(b), (c) and (d) are enlarged images of the local areas in Fig. 1(a). As shown in Fig. 1(a), there are dendrites Cr, eutectic Cr and Zr-rich phase in the Cu matrix. The EDS analyses for point *A* in Fig. 1(b), point *C* in Fig. 1(c) and points *D* and *E* in Fig. 1(d) prove the phase constitution.

As shown in Fig. 1(b), a large number of acicular structures are distributed on Cr dendrite. EDS analysis of point *B* in Fig. 1(b) indicates that the acicular phase consists of two elements, Cu and Zr (referred to as Zr-rich phase). There is a higher content of Cr element in point *B* in Table 1, so it is concluded that the phase is $CuZr_X$, and the Cr element comes from dendritic Cr. The major reasons focus on the following aspects: CuCrZr phase has not been found in the past research; the existence probability of $CrZr_X$ phase is very small; the EDS analysis of point *F* (*B* and *F* are the same phase) does not contain Cr elements.

As shown in Fig. 1(c), the type of morphology in Cu matrix is thin and short rods. EDS analysis of point *C* in Fig. 1(c) indicates that the short rod-like morphology is Cr, which is tens times smaller in size than Cr dendrite. Such a phase is considered whisker formed during a rapid solidification process.

As shown in Fig. 1(d), there are two types of morphologies in Cu matrix, including large starfish and thin needles. EDS analysis of large starfish-like structure (point *D*) and needle-like structure (the same as point *B*) shows that both structures are Zr-rich, with a similar composition. These results indicate that despite the similar composition, Zr-rich phases of the alloy occur in two forms, one with large dimension, non-uniform distribution and irregular shape and the other with small dimension, regular morphology and uniform distribution.