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

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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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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.

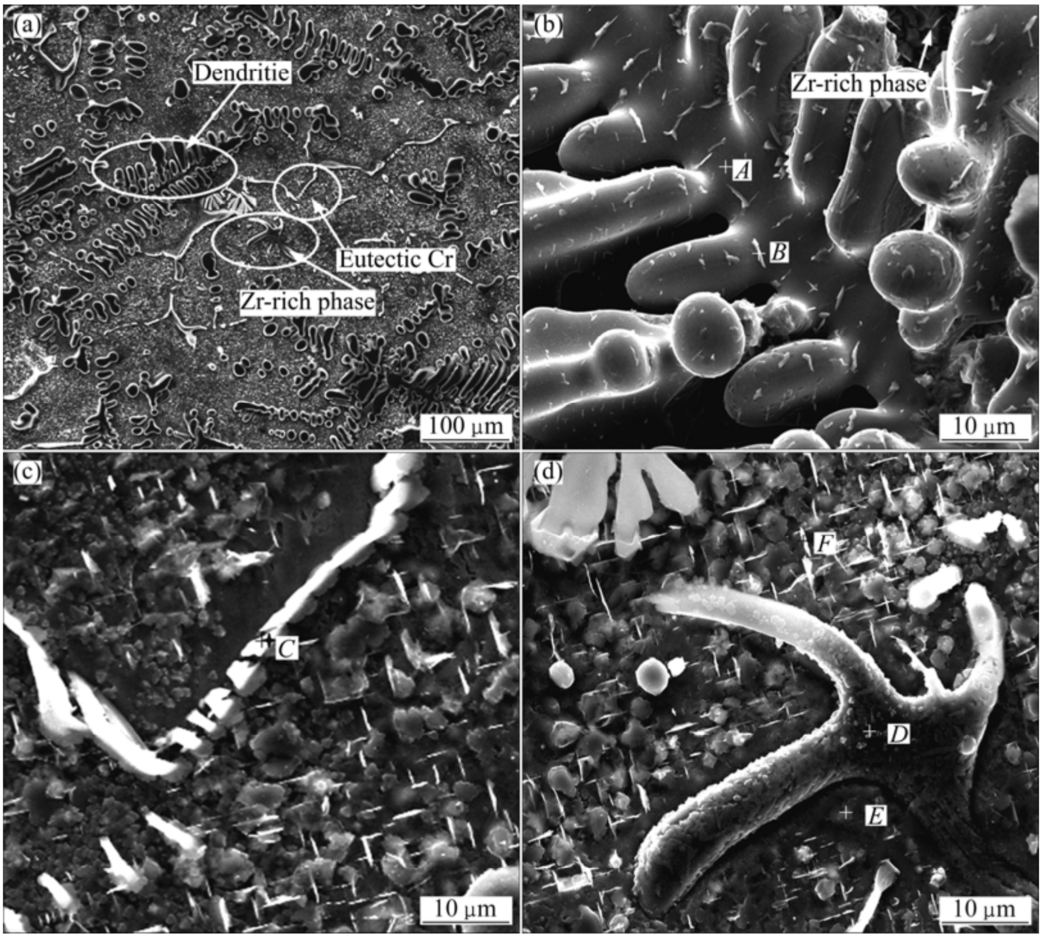

Fig. 1 SEM images of as-cast structure in Cu−15%Cr−0.24%Zr alloy: (a) Cr dendrites; (b) Zr-rich phase on Cr dendrite; (c) Eutectic Cr; (d) Zr-rich phase in matrix

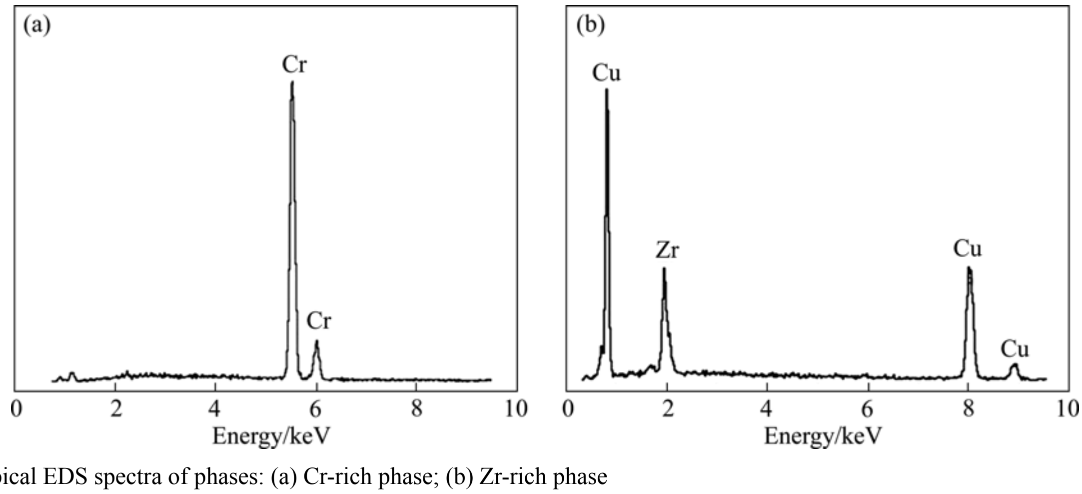

Fig. 2 Typical EDS spectra of phases: (a) Cr-rich phase; (b) Zr-rich phase

Table 1 EDS analysis of second phases in Fig. 1

Element	Point *A* or *C*		Point *B*		Point *D*		Point *E*		Point *F*	
	w/%	*x*/%	*w*/%	*x*/%	*w*/%	*x*/%	*w*/%	*x*/%	*w*/%	*x*/%
Cu			27.40	24.25	60.30	67.32	95.59	66.66	91.29	93.73
Cr	100	100	51.48	55.06			1.84	2.25		
Zr			18.03	10.99	36.64	28.49	1.59	10.09	8.71	6.27

3.2 TEM

In this study, both Cr and Zr contents are much higher than the maximum solid solubility of Cu at room temperature. Thus, the Cr and Zr precipitated phases occurred during alloy solidification. To determine the morphology and structure of precipitated phases, TEM and HRTEM were employed to analyze the microstructure of alloy.

Figure 3 shows the TEM image and selected area electron diffraction (SAED) pattern of as-cast structure of the Cu−15%Cr−0.24%Zr alloy. The bright field image shows that the short rod-like precipitate distributes in the matrix with a small size, in a sharp contrast to the structures of large size in SEM image of Fig. 1. Figure 3(c) shows the SAED close to precipitate phase and calibration results (Fig. 3(d)) indicate that the precipitate phase is Cr with body-centered cubic structure based on Cu matrix. There are two sets of diffraction spots of Cu-matrix in Fig. 3(d) because two Cu grains with different crystal orientations are selected to calculate the zone axis of Cu-matrix is $(\bar{1}12)$.

A lots of studies showed that there existed $CuZr_X$ intermetallic compounds in the as-cast structure of Cu−Cr−Zr alloys, such as Cu_3Zr [23], $Cu_{51}Zr_{14}$ [26] and Cu_5Zr [27]. Our study also found a similar phase in the grain boundaries of Cu matrix, as shown in Fig. 4.

Figure 4 shows the TEM image and selected area electron diffraction pattern of the alloy. The precipitate particles with large size about 240 nm can be observed on the grain boundaries. Figure 4(b) shows the dark field image of precipitate particles with large dimension. Figure 4(c) shows the SAED close to precipitate phase and calibration results confirm that the phase is Cu_5Zr intermetallic compound with face- centered cubic structure. The lattice parameters of the compound are $a=b=c=0.687$ nm.

To further determine the phase relation between the precipitate phase and matrix further, HRTEM was adopted to observe and analyze the atom arrangement at their interface. HRTEM image of Cu_5Zr/Cu interface is shown in Fig. 5. The diffraction spots in the upper right is the image of Fourier transformation (FT) of zone A, and calibration results show that the phase is Cu_5Zr, and the interplanar spacings are $(1\bar{3}\bar{1})$, (220) and $(3\bar{1}\bar{1})$. It is difficult to form coherent interface between the two phases since the lattice parameters of the Cu_5Zr compound are much larger than those of Cu-matrix phase ($a=b=c=0.3615$ nm), but the interface seems to be

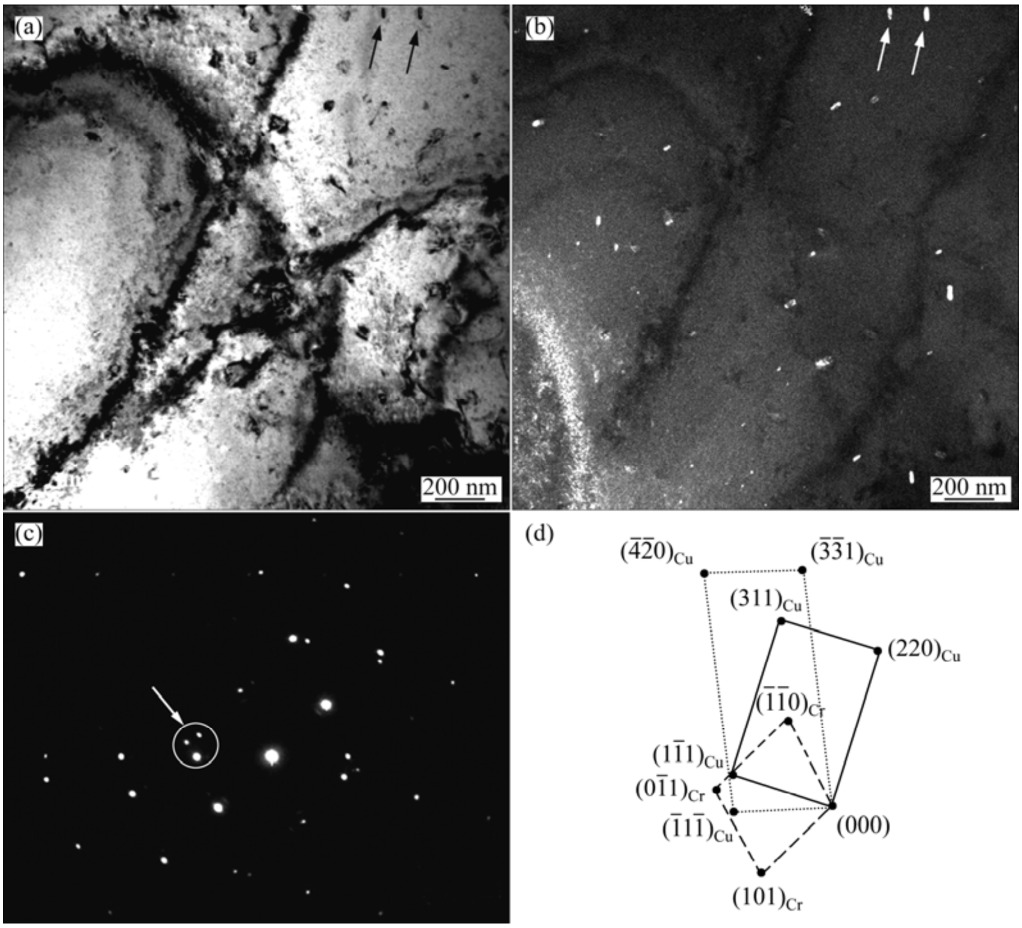

Fig. 3 TEM images of precipitated phases: (a) Bright field image; (b) Dark field image; (c) Selected electron diffraction pattern of precipitated phase; (d) Schematic drawing for (c)

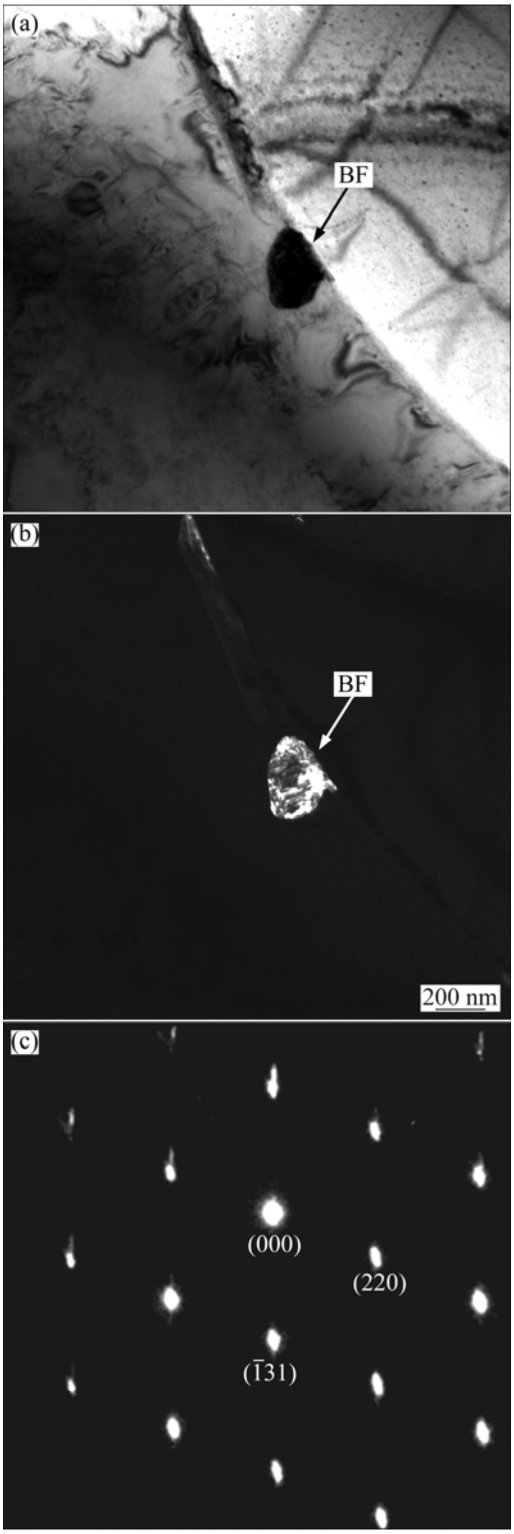

Fig. 4 TEM micrographs of Cu−15%Cr−0.24%Zr alloy: (a) Bright field image (Arrow shows precipitated phase); (b) Dark field image (Arrow shows precipitated phase); (c) Selected electron diffraction pattern of precipitated phase

planar and clean (Fig. 5(a)). In order to determine the interfacial orientation relationship, the image of IFFT is made in zone *B* in Fig. 5(a). Figure 5(b) clearly shows the position of misfit dislocations at the interface. So, it can be determined that there is a semi-coherent orientation relationship between the Cu_5Zr compound and Cu-matrix.

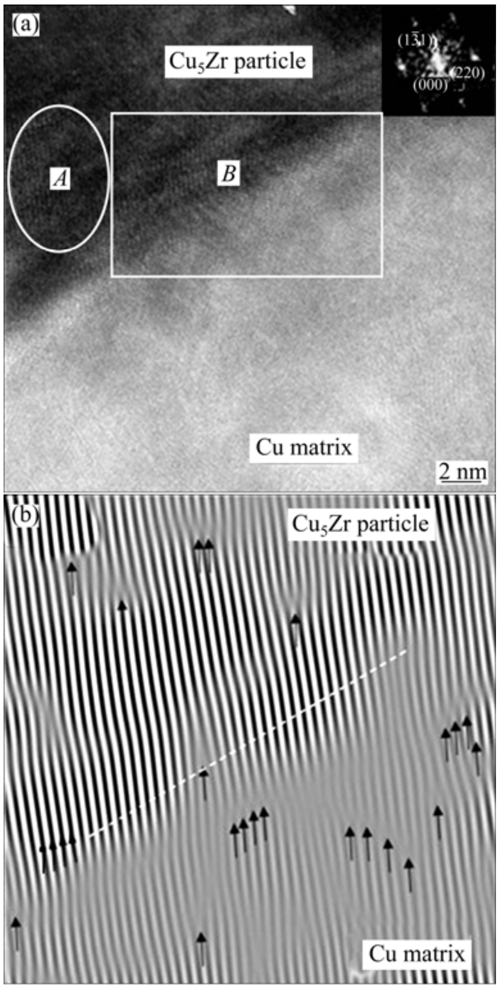

Fig. 5 HRTEM image of Cu_5Zr/Cu interface (a) and IFFT image (b) of zone *B* in Fig. 5(a)

4 Discussion

Based on the above experimental analysis, it can be concluded that the as-cast Cu−15%Cr−0.24%Zr alloy contains Cu matrix, Cr dendrite, eutectic Cr , Zr-rich phase, Cr precipitated phase and Cu_5Zr intermetallic compound. The Cu_5Zr intermetallic compound with large size investigated in this work is consistent with the results reported in Refs. [28,29], but there are not Cr precipitated phase mosaicism on coarse Cu_5Zr which is reported in Ref. [26].

According to the energy spectrum analysis of point *E* in Fig. 1(d), there are traces of Cr and Zr in matrix Cu shown in Table 1. Firstly, Cr-rich phase and Zr-rich phase exist in the matrix. Secondly, a great amount of un-precipitated Cr and Zr exist in the matrix. Thirdly, the Cu−Cr eutectics and Cu−Zr eutectics distribute in the matrix.

In this experiment, the fine Zr-rich phase co-exists with Cr dendrite, like the burr growing out of Cr dendrite, as shown in Fig. 1(b). According to Fig. 1(b), it can be seen that they are formed in the alloy solidification process. Assuming that the coarse Cr dendrite is first solidified from the liquid state and the Zr-rich phase is solidified between the surface of Cr and liquid phase, thus the results in Fig. 1(b) can be obtained. Region *D* marked in Fig. 1(d) is the Zr-rich phase of large volume, and there are many other kinds of morphologies in addition to the starfish shape. It can be inferred in terms of the phase volume and morphology that the phase is formed through solidification with coarse Cr dendrite at the initial stage of alloy solidification.

5 Conclusions

1) SEM results show that there are five types of phases in the as-cast structure of Cu−15%Cr−0.24%Zr alloy, namely, Cu matrix, Cr dendrite, eutectic Cr, fine Zr-rich phase and coarse Zr-rich phase.

2) TEM results show that Cr precipitated phase distributes in Cu-matrix. Cu_5Zr intermetallic compounds are found in grain boundaries.

3) HRTEM results show that there is semi-coherent relationship between the Cu_5Zr and Cu matrix.

References

[1] DENG J Q, ZHANG X Q, SHANG S Z. Effect of Zr addition on the microstructure and properties of Cu−10Cr in situ composites [J]. Materials and Design, 2009, 30: 4444−4449..

[2] LIU Q, ZHANG X. Effect of processing and heat treatment on behavior of Cu−Cr−Zr alloys to rail way contact wire [J]. Metall Mater Trans A, 2006, 37: 3233−3238.

[3] RAABE D. MIYAKE K, TAKAHARA H. Processing, microstructure, and properties of ternary high-strength Cu−Cr−Ag in situ composites [J]. Mater Sci Eng A, 2000, 291: 186−197.

[4] HONG S I. Effect of Nb content on the strength of Cu−Nb filamentary microcomposites [J]. Jounal of Materials Research, 2000, 15(9): 1889−1893.

[5] ZHANG L, MENG L. Evolution of microstructure and electrical resistivity of Cu−12wt.%Ag filamentary microcomposites with drawing deformation [J]. Scripta Materialia, 2005, 52: 1187−1191.

[6] HAN K, VASQUEZ A A, XIN Y. Microstructure and tensile properties of nanostructured Cu−25Ag [J]. Acta Materialia, 2003, 51(3): 767−780.

[7] SPITZIG W A. Strengthening in heavily deformation processed processed Cu−20Nb composite [J]. Acta Metallurgica Materialia, 1991, 39: 1085−1090.

[8] BEVK J, HARBISON J P, BELL J L. Anomalous increase in strength of in situ formed Cu−Nb multifilamentary composites [J]. Journal of Applied Physics, 1978, 49(12): 6031−6038.

[9] SUN Z B, GUO J, SONG X P. Effects of Zr addition on the liquid phase separation and the microstructures of Cu−Cr ribbons with 18−22at.%Cr [J]. Journal of Alloys and Compounds, 2008, 455: 243−248.

[10] SONG J S, KIM H S, SONG S I. Deformation processing of Cu−Cr−X (X=Ag or Co) microcomposites [J]. J Mater Proc Technol, 2002, 130−131: 272−277.

[11] ZHANG D L, MIHARA K. TAKAKURA E. Effect of the amount of cold working and aging on the ductility of a Cu−15%Cr−Ti in-situ composite [J]. Mater Sci Eng A, 1999, 266: 99−108.

[12] SAKAI S, SUZUKI H G, MIHARA K. Effect of Sn addition on the mechanical and electrical properties of Cu−15%Cr in-situ composites [J]. Material Transactions, 2003, 44(2): 232−238.

[13] RAABE D, GE J. Experimental study on the thermal stability of Cr filaments in a Cu−Cr−Ag in situ composite [J]. Scripta Materialia, 2004, 51(9): 915−920.

[14] XIA Cheng-dong, JIA Yan-lin, ZHANG Wan, ZHANG Ke, DONG Qi-yi, XU Gen-ying, WANG Ming-pu. Study of deformation and aging behaviors of a hot rolled–quenched Cu−Cr−Zr−Mg−Si alloy during thermomechanical treatments [J]. Materials and Design, 2012, 39: 404−409.

[15] XIA Cheng-dong, ZHANG Wan, KANG Zhan-yuan, JIA Yan-lin, WU Ying-feng, ZHANG Rui, XU Gen-ying, WANG Ming-pu. High strength and high electrical conductivity Cu−Cr system alloys manufactured by hot rolling-quenching process and thermomechanical treatments [J]. Materials Science and Engineering A, 2012, 538: 295−301.

[16] POPOVA E N, POPOV V V, RODIONOVA L A. Effect of annealing and doping with Zr on the structure and properties of in situ Cu−Nb composite wire [J]. Script Materialia, 2002, 46: 193−198.

[17] FUJII T, NAKAZAWA H, KATO M. Crystallography and morphology of nanosized Cr particles in a Cu−0.2% Cr alloy [J]. Acta Mater, 2000, 48: 1033−1045.

[18] WANG Z, GORY B, WANG Z G. Cyclic deformation behavior of Cu−30wt%Zn single crystals oriented for single slip—I. Cyclic deformation response and slip band behavior [J]. Acta Mater, 1999, 47: 307−315.

[19] CHEN Xiao-hong, LIU Ping, TIAN Bao-hong. Effects of micro-alloying on microstructure and mechanical properties of Cu−15Cr in-situ composites [J]. Transactions of Materials and Heat Treatment, 2009, 30: 44−48.

[20] CHEN Xiao-hong, LIU Ping, TIAN Bao-hong. Microstructure and properties of Cu−Cr in-situ composites [J]. Transactions of Materials and Heat Treatment, 2007, 28: 288−291.

[21] LEE K L, WHITEHOUSE A F. Elevated temperature tensile properties and failure of a copper-chromium in situ composite [J]. Journal of Materials Science, 2003, 38: 3437−3447.

[22] FUNKENBUSCH P D, COURTNEY H. Strengthening methods in crystals [J]. Acta Metallurgica, 1985, 33: 913−922.

[23] ZENG J K, HAMALAINEN M. A theoretical study of the phase equilibria in the Cu−Cr−Zr system [J]. J All Comp, 1995, 220: 53−61.

[24] ZENG J K, HAMALAINEN M. Phase relationships in Cu-rich corner of the Cu−Cr−Zr phase diagram [J]. Script Materialia, 1995, 12(32): 2009−2014.

[25] KUZNETSOV G M, FEDOROV V N, RODNYANSKAYA A L. Phase diagram of the Cu−Cr system [M]. Izv VUZ, Tsvetn Metall, 1977: 84−86.

[26] HUANG F X, MA J S, NING H L. Analysis of phases in a Cu−Cr−Zr alloy [J]. Scripta Materialia, 2003, 48: 97−102.

[27] CHEN Xiao-hong. Study on ultra high strength Cu−Cr in situ composites [D]. Xi'an: Xi'an University of Technology, 2009: 59−60. (in Chinese)

[28] BATRA I S, DEY G K, KULKARNI U D. Microstructure and properties of a Cu−Cr−Zr alloy [J]. Journal of Nuclear Materials, 2001, 299: 91−100.

[29] HOLZWARTH U, PISONI M, SCHOLZ R. On the recovery of the physical and mechanical properties of a CuCrZr alloy subjected to heat treatments simulating the thermal cycle of hot isostatic pressing [J]. Journal of Nuclear Materials, 2000, 279(1): 19−30.

Cu−15%Cr−0.24%Zr 合金的相分析

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摘 要：采用真空中频感应熔炼技术制备 Cu−15%Cr−0.24%Zr 合金，利用扫描电子显微镜(SEM)、能谱仪(EDS)及透射电子显微镜(TEM)对合金铸态组织的相组成、形态及结构进行研究。结果表明：Cu−15%Cr−0.24%Zr 合金的铸态组织由 Cu 基体、枝晶 Cr、共晶 Cr 和富 Zr 相组成；基体上存在许多 Cr 析出相，在基体的晶界上发现了 Cu_5Zr 析出相，析出相 Cu_5Zr 与 Cu 基体之间呈半共格方式排列。

关键词：Cu−Cr−Zr 合金；铸态组织；原位复合材料；析出相

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