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RESEARCH NOTE

Production of Cu-Cr-Zr Alloy Using Electroslag Remelting Technique

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ABSTRACT

This study focused on the effect of electroslag remelting process (ESR) on microstructure and composition of as-cast Cu-Cr-Zr alloy. The results revealed that applying ESR process resulted in a more uniform distribution of alloying elements. However, slight aggregation of large precipitates and inclusions existed in as-cast ingot. It was observed that impurities like P, S and Mg which had significant effect on electrical property were eliminated after ESR process. Moreover, further optimization of alloy composition which in turn would affect its mechanical and electrical properties was obtained through using ESR technique, successfully.

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1. INTRODUCTION

Owing to excellent electrical and thermal conductivity, copper and copper alloys are widely used as electric engineering materials [1-7]. Fabrication and processing technology of copper alloys with both high strength and high conductivity is widely demanded by the high technology sectors, such as current carrying parts of electrical switchgear, bus bars and short circuit bars, lead frame, bullet train, long-distance wire, heat sink material for International Thermonuclear Experimental Reactor (ITER) and different parts in electrical machines, etc [3]. Research and application experiences indicate that Cu-Cr-Zr alloys are promising to get the fine combination of mechanical properties like high softening temperature and excellent hot impact strength and electrical conductivity [4].

Traditional production processes often reach their limits when they come to manufacture Cu-Cr-Zr alloys in applications where components made of these materials are placed under high stresses. The material for such applications must be very pure and free of inclusions and undesired impurities [8]. As, elements like chromium and zirconium added to high copper alloys readily react with oxygen, they are, therefore, easily lost as oxides, if melting and casting techniques are not well controlled [6]. If the foundry practice is poor, these elements can either disappear in the dross that floats to the surface of the ladle or remain suspended in the liquid metal, transforming it to a semi-viscous sludge that can only be cast with difficulty [6]. Chemical analysis may confirm that a casting is within compositional specification, but the alloying elements may be present as compounds that will not dissolve when subjected to solution treatment. Moreover, chromium easily forms carbides and will, therefore, react with the graphite in crucibles or the charcoal commonly used to reduce the oxidation of the liquid copper [6].

Smelting and casting using controlled atmospheres like vacuum or a protective noble gas with high purity are common methods for producing these alloys [6]. Electroslag remelting (hereinafter this may be referred to as ESR process) is an especially attractive process which can be used in this field, too. It is an outstanding alternative to vacuum processes, characterized by relatively simple equipment, flexibility of technological parameters, high quality and low production cost. The ingots and materials manufactured using this process

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possess structures with uniform density and a high degree of homogeneity, no segregation or shrinkage cavities and no undesired impurities or oxide inclusions[7, 9-11]. However, less is known about the effect of this process on Cu-Cr-Zr alloys. It is reported that the chemical composition and especially processing technology of Cu-Cr-Zr alloys have been protected by patents or classified documents [4].

In this study, ESR was conducted on an ingot of Cu-Cr-Zr alloy prepared using an induction furnace and the effects of this process on microstructure, compositional amendments and losses of alloying elements of the alloy were studied and discussed. The aim of this research was to design ESR method to produce a homogeneous and defect-free ingot of Cu-Cr-Zr alloy with proposed chemical composition, in large scale.

2. EXPERIMENTAL PROCEDURES

Ternary alloy of Cu- (0.3-1.2%) Cr- (0.03 -0.3%) Zr was produced in an induction furnace using oxygen free high conductivity copper (OFHC) and Cu-4.8%Cr and Cu-32% Zr master alloys. Cu-4.8% Cr master alloy was produced in an induction furnace using oxygen free copper and electrolytic chromium parts. The surface of the melt was covered with coal and a small amount of magnesium (200 g) to lower the oxygen content of the alloy. Then, the melt was poured into a cast mold with graphite liner with 110mm in diameter and 750 mm heigh. Subsequently, an ingot weighting about 85 kg was cut and prepared to be refined through ESR machine consisting a water-cooling mold and a slag (40%CaF_2-30%NaF-20%Na_3AlF_6-6.7%ZrO_2-3.3%SiO_2) having a suitable specific resistance, melting point and viscosity in order to eliminate losses of alloying elements (Cr and Zr), casting defects and unwanted impurities like P, S and Mg. For optimizing chemical analysis of the alloy, suitable amounts of Cu, Cu-Cr and Cu-Zr master alloys were added to the alloy during remelting process. Diameter and height of the final ingot were 155 and 500 mm, respectively.

For optical microscopy studies, selected samples of the as-cast alloy (alloy 1) and refined alloy with ESR process (alloy 2), were polished and etched in a solution of HCl, $FeCl_3$ and alcohol. For scanning electron microscopy (SEM) investigations, as well as energy dispersive X-ray spectroscopy (EDXS) studies a MIRA II TESCAN scanning electron microscope was used.

3. RESULTS

Chemical composition of alloy 1 and alloy 2 are shown in Tables 1 and 2, respectively. These results illustrate that impurities like P, Mg and S were eliminated within ESR process. As Cr is detrimental to electrical properties (resistivity increase of 4.9 μΩ.cm per 1 wt.% addition for this element has been reported) its amount was lowered, while the amount of other alloying elements was not appreciably changed [8].

Microstructural investigations of alloy 1 and alloy 2 using optical microscope in transverse section are shown in Figures 1a and b and 2a-c, respectively. Ultrasonic testing and visual observation of ingots revealed that macro and micro-voids in the casting part were deleted from the ingot structure and the refined alloy was dense and without any defect. Surface quality of alloy 2 was much better than alloy 1, meaning that there was no need for further machining treatment of the ingots after refining with ESR. It can be observed in Figure 1a that in alloy 1 microstructure mostly consisted of coarse equiaxed grains of α phase, but in alloy 2 (Figure 2a), these grains were columnar. It is evident from Figure 1b that round discontinuous coarse primary precipitates were formed in alloy 1 along dendritic boundaries. Large amounts of these precipitates were also distributed in the matrix within the grain.

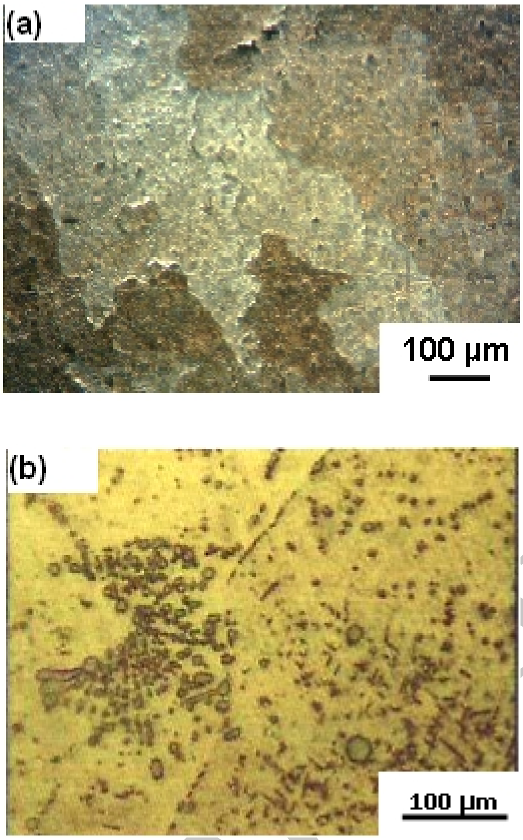
TABLE 1. Chemical composition of alloy 1

Cu	Zn	Pb	Sn	P
Base	0.004	0.0127	0.009	0.0129
Mn	Fe	Ni	Si	Mg
0.0111	0.035	0.015	0.047	0.105
Cr	As	Sb	Cd	Co
1.18	0.0019	0.0001	0.0021	0.001
Al	Nb	Bi	S	Be
0.007	0.021	0.002	0.009	<0.0001
Zr	B	Ti	Ag	C
0.139	0.00025	<0.0004	<0.25	0.003

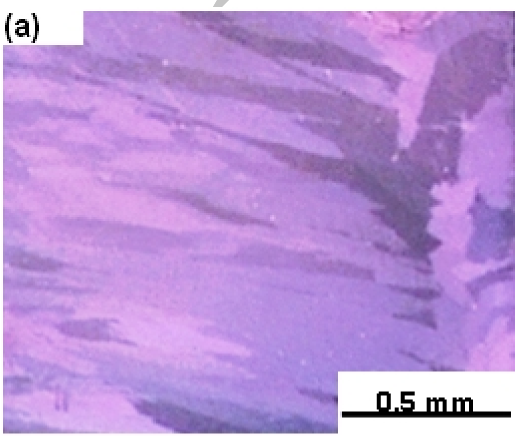
TABLE 2. Chemical composition of alloy 2

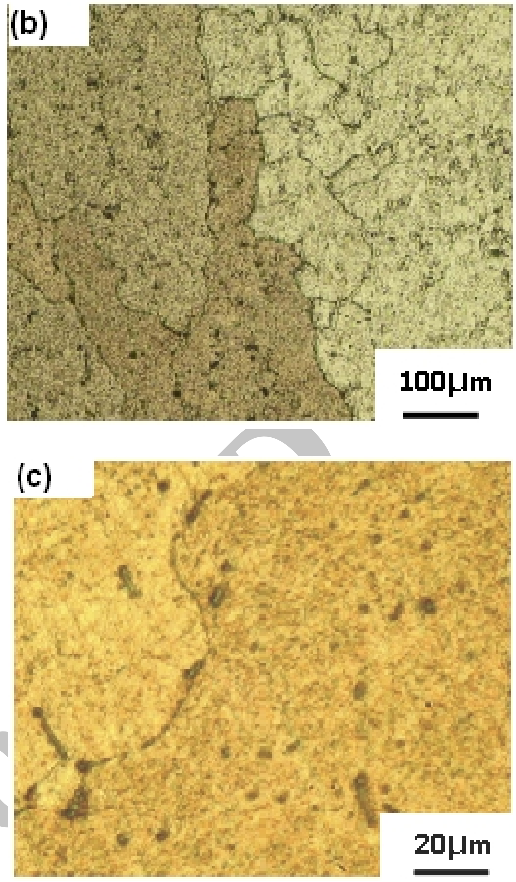
Cu	Zn	Pb	Sn	P
Base	0.0094	0.0057	0.0012	0.002
Mn	Fe	Ni	Si	Mg
0.0085	0.040	0.018	0.08	0.002
Cr	As	Sb	Cd	Co
0.65	0.002	0.0007	<0.0002	0.001
Al	Nb	Bi	S	Be
0.037	0.02	0.001	0.003	<0.0001
Zr	B	Ti	Ag	C
0.147	0.0019	0.0027	0.0003	0.002

In alloy 2, however, less precipitates were found in the matrix (Figure 2b). Higher magnification of the same sample (Figure 2c) reveals particles precipitated not only inside the grains, but also at the grain boundaries. While precipitates in alloy 1 were agglomerated in some areas, they were smaller in size in alloy 2 and can be seen rather uniformly throughout the matrix.



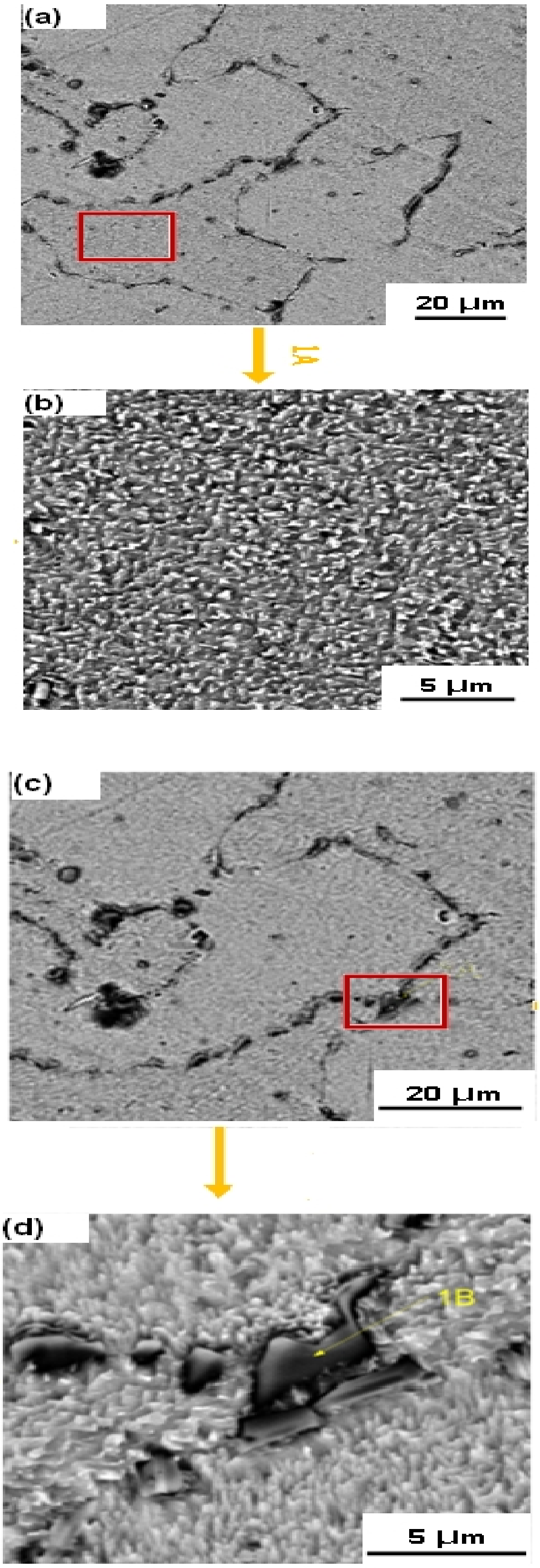
Figures 1.a and b. Microstructure of samples of alloy1 in different magnifications



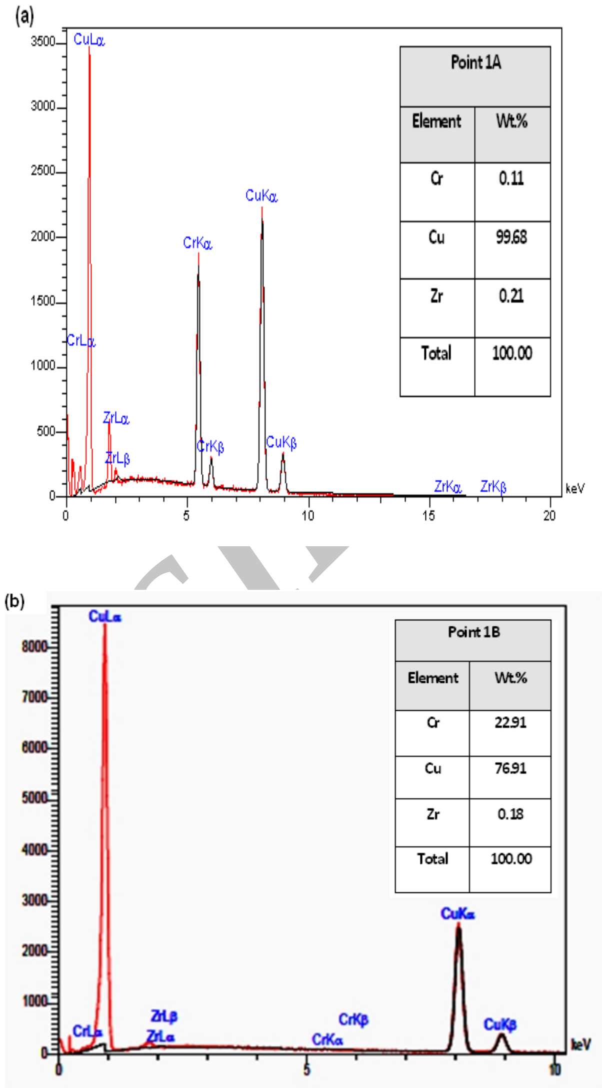


Figures 2a-c. Microstructure of samples of alloy2 in different magnifications

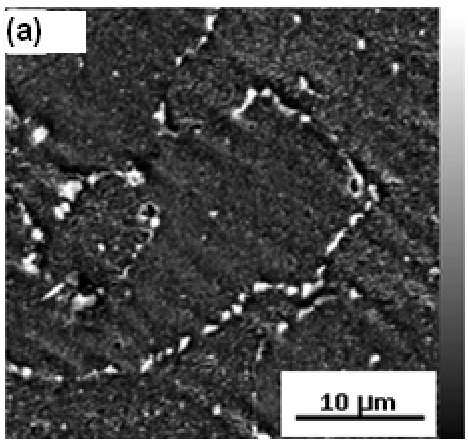
Smaller grain size in alloy 2 as compared with alloy 1 was a result of higher solidification rate in ESR technique (Figures 1a and 2a). SEM images presented in Figures 3a-d show detailed microstructures resulting from an ESR process on the alloy (alloy 2). According to these images, some precipitates were formed in grain boundaries. Quantitative EDXS analyses performed on these precipitates and on the matrix, as well, are presented in Figures 4a and b. Comparing EDXS analysis of points 1A and 1B reveals no significant change in Zr content of precipitates and matrix. Cr-enriched phases were formed and matrix was depleted from Cr. Figures 5a-d illustrate the x-ray maps of the microstructure. Atomic numbers of Cu, Cr and Zr are 29, 24 and 40, respectively which means that white precipitates should be Cr enriched and the darker matrix contains Zr. Evidently, Zr was scattered rather uniformly throughout the matrix while Cr was concentrated in special locations forming metallic precipitates.

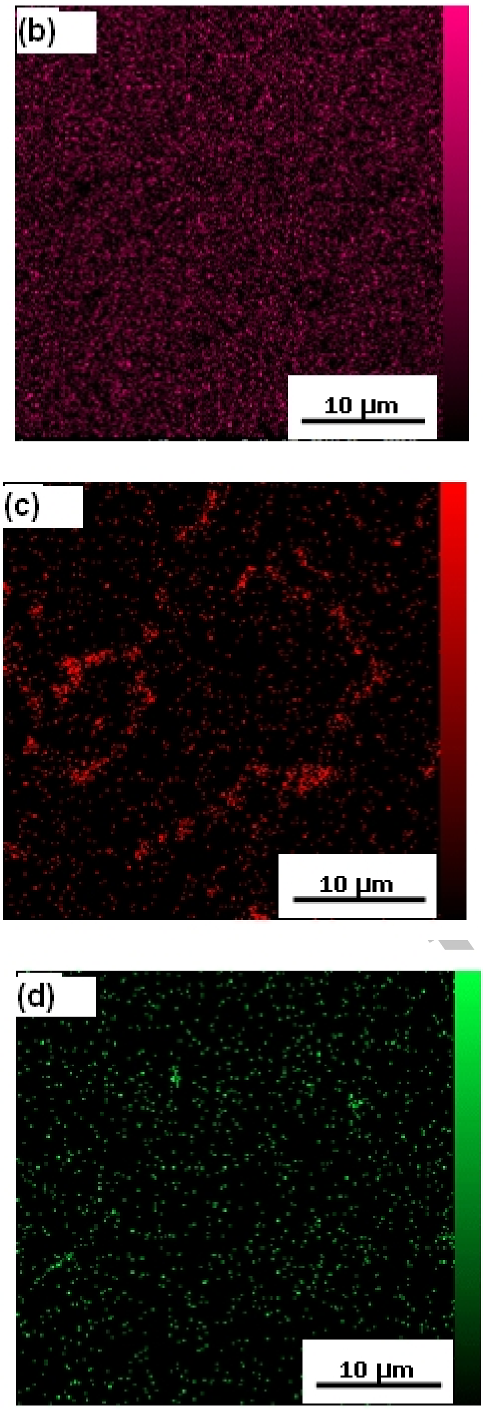


Figures 3a-d. SEM images (BSE) of the alloy after ESR process



Figures 4a and b. EDXS analyses of matrix and precipitates pointed in Figures 3a and d





Figures 5. X-ray map of the microstructure a) image of the alloy b) Cu map c) Cr map and d) Zr map

4. DISCUSSIONS

The results presented in this investigation reveal some important aspects of performing electroslag remelting process on microstructure and chemical composition of the Cu-Cr-Zr alloy. As this alloy is a precipitate hardenable one, as much as Cr is dissolved in the matrix, more and better distribution of precipitates will form and also the strength of the alloy will be higher. Zr, on the other hand, promotes hardening of the alloy by providing a good homogeneity of precipitates [5]. It is expected that samples of the refined alloy are generally harder and have higher strength than as cast one. Certainly, smaller grain size of refined alloy samples has an influence on hardness and strength according to Hall-Petch equation ($\sigma_{ys}=\sigma_0+kd^{-1/2}$). Increased interactions of precipitates with dislocations and distribution of alloying elements in the refined alloy (alloy 2) can be another reason for improved mechanical properties in this alloy according to Orowan strengthening mechanism [12]. In order to prove these claims, more investigations are needed in near future. Grain size and distribution of precipitates and alloying elements are attributed to the temperature and cooling conditions of the ESR process meaning that the temperature in the molten slag was higher than that in as-cast resulting in more Cr and Zr solution according to the Cu-Cr and Cu-Zr phase diagrams [13]. Subsequently, nucleation of precipitates would occur with decrease of temperature in the metal pool. The second contribution of ESR was to produce a homogeneous, sound and directionally solidified structure through maintaining the correct remelting rate and slag temperature. Indeed, this process provides a good condition for solidification with water cooling steel mold, where the cooling rate of the ingot in the ESR equipment was much faster than that in the steel mold used for casting alloy (alloy 1). It is true that undercooling increases with increment of cooling rate, resulting in increased nucleation rate [5]. Moreover, the growth of Cr precipitates either existing in high temperature melt or forming during cooling was inhibited. It is believed that Cr solidified after Cu and enriched melt from Zr solidified at the end stage of solidification [2]. Thus, relatively fast re-solidification resulted in a material with a relatively low level of segregation.

Results obtained from this investigation demonstrate that ESR provide an alloy with high degree of cleanliness. P, S and Mg content of the as-cast alloy was lowered during ESR. The reason is that the ingot melts droplet-by-droplet in the ESR process and the alloy falls through the slag and re-solidifies at the base of the mold. The slag acts as a filter, absorbing these impurities by chemical reactions or physical flotation to the top of the molten pool. The remaining inclusions in ESR are very small in size and evenly distributed in the remelted ingot. The importance of eliminating these elements is that they affect electrical conductivity of the alloy, significantly. Limitations of oxygen (<0.002%) and of the total amount of impurities (<0.03%) are required for better resistance against embrittlement and better electrical conductivity. According to the results, inclusions like ZrO_2 and others which deteriorate the mechanical and also electrical behavior of the alloy resulting from fluxes and so forth was eliminated. In addition, the elimination of casting defects like porosities and cavities by ESR process is also important for the improvement of tensile properties. As mentioned before, controlling the Cr and Zr alloying elements is essential too, so the chemical analysis of the alloy was modified by adding controlled amounts of these elements to the alloy during ESR process.

The ESR ingot was made so as to produce a columnar-dendritic structure throughout, while the ingot made under other conditions like VAR process intended to provoke a solidification transition from columnar-dendritic to equaxial in the ingot center. Almost all of Cu-Cr-Zr alloys are cold worked and hardened through aging after being hot worked in processes like extrusion and so forth [14]. Since initial microstructure is a key factor in hot working from this point that as this structure is finer, less degree of hot work is needed to break it. However, more studies is required to confirm such a claim in an alloy refined by electroslag remelting.

5. CONCLUSIONS

- Electroslag remelting process with water cooling mould is a suitable method for producing high quality Cu-Cr-Zr ingot.
- During this process, due to presence of an active slag, impurities like P, Mg and S were removed but there was no change in chemical composition of the alloying elements (Cr and Zr).
- Minor composition adjustment should be done during ESR process.
- The macro and microstructure indicate that the properties of the Cu-Cr-Zr alloy prepared by this method should be in accordance with, and perhaps superior to the requirements and specifications of the standard alloy (CuCr1Zr in DIN 17666). The results of electrical and mechanical properties of produced ingot which verifies this claim would be published in near future.

6. ACKNOWLEDGEMENTS

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چکیده

در این تحقیق تأثیر فرایند ذوب مجدد با سرباره‌ی الکتریکی بر ریزساختار و ترکیب شیمیایی آلیاژ ریخته‌گری شده‌ی مس–کروم–زیرکونیم بررسی گردید. نتایج بررسی‌های انجام شده نشان داد که انجام این فرایند منجر به تولید ساختاری با توزیع یکنواخت عناصر آلیاژی گردیده است. در حالی که در آلیاژ ریخته‌گری شده تجمعاتی هرچند کوچک از رسوبات بزرگ و نیز آخال‌ها دیده شد. همچنین مشاهده شد که عناصری مانند فسفر، گوگرد و منیزیم که تأثیر قابل توجهی بر خواص الکتریکی دارند در این فرایند حذف شده‌اند. علاوه بر آن، بهینه سازی بیشتر ترکیب آلیاژ که به نوبه‌ی خود خواص مکانیکی و الکتریکی را تحت تأثیر قرار می‌دهد، به طور موفقیت‌آمیزی در این فرایند امکان پذیر است.

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