In-Situ Observation of Melting and Solidification Process of CuCr Alloy by High Temperature Confocal Microscope

Jin-Ru Han, Zhi-He Dou, and Ting-An Zhang

Abstract In this paper, the melting process of CuCr alloy is observed in-situ by high temperature confocal microscope, followed by process solidification at a solidification rate of 1 °C/s. It is found that the melting process of CuCr alloy is mainly divided into two steps: the first step is the complete melting of Cu-rich phase matrix, and the second step is that Cr phase is gradually dissolved in molten Cu matrix. The solidification process of CuCr alloy can be divided into three stages: initial solidification stage, stable solidification stage, and final solidification stage. The temperature range of stable solidification stage is 1400 °C–1250 °C, at which time the solidification rate of the alloy is the fastest, and the solidification structure with uniform distribution of Cr-rich phase is obtained. Finally, the model of CuCr alloy is firstly established by Materials studio based on heterostructure theory.

Keywords CuCr alloy · High temperature confocal microscope · Melting and solidification · Heterostructure

Introduction

The process of liquid phase separation and the mechanism of second phase coarsening are some of the key points in the study of immiscible alloys. As an immiscible alloy, the process of two-phase separation of CuCr alloy can be summarized as three stages (as shown in Fig. 1): the first stage is the nucleation of a small amount of Cr phase. In the second stage, nuclei grow up by various means of material transport (diffusion, Ostwald maturation, Marangoni motion, convection) and coarsen by collision and aggregation between nuclei. In the third stage, when Cr particles reach a certain size, under the action of the density difference between Cu and Cr components and

J.-R. Han · Z.-H. Dou (✉) · T.-A. Zhang
Key Laboratory of Ecological Metallurgy of Multi-metal Intergrowth Ores of Ministry of Education, Northern University, Shenyang 110819, Liaoning, China
e-mail: douzh@smm.neu.edu.cn

School of Metallurgy, Northern University, Shenyang 110819, Liaoning, China

S. Wagstaff et al. (eds.), *Materials Processing Fundamentals 2024*, The Minerals, Metals & Materials Series, https://doi.org/10.1007/978-3-031-50184-5_11

Marangoni motion, the second phase droplets begin to deposit or float, and the smaller droplets are continuously captured during the motion, that is, gravity coagulation and Marangoni coagulation occur, which eventually leads to the stratification of the melt [1]. At the same stage, many coarsening mechanisms work at the same time, especially the Marangoni motion of the second phase droplets in microgravity [2]. Therefore, the segregation of the Cr phase depends on its kinetic processes such as growth, collision, coarsening, settling or uplift, whereas when there is a temperature gradient in the melt, the second phase droplets undergo a Marangoni motion from the cold end to the hot end, and thus if the cooling rate is sufficiently fast that the alloy solidifies through the immiscible zone very quickly without the second phase having enough time to undergo coarsening and deposition, the CuCr alloys with a diffuse distribution of the Cr phase can be obtained.

The preparation technology of homogeneous immiscible alloys has always been the research hotspot and difficulty of immiscible alloys. The industrial preparation methods of CuCr alloys include powder metallurgy, infiltration, and vacuum consumable melting [3–5], but powder metallurgy mostly adopts solid phase sintering and does not involve the solidification process of liquid phase, whereas the infiltration method firstly sintered the Cr powder to the skeleton, and therefore does not involve the process of solidification of the second phase either.

Zhang has put forward a new idea of preparing large-size homogeneous CuCr immiscible alloy based on aluminothermic reduction, that is, firstly, copper oxide and chromium oxide are used as raw materials, and the miscible high temperature CuCr melt is obtained by aluminothermic self-propagation, at which time the theoretical adiabatic temperature can reach 2848 K, and then refined under the high-frequency magnetic field and subsequent solidification [6–9], so it is a liquid solidification

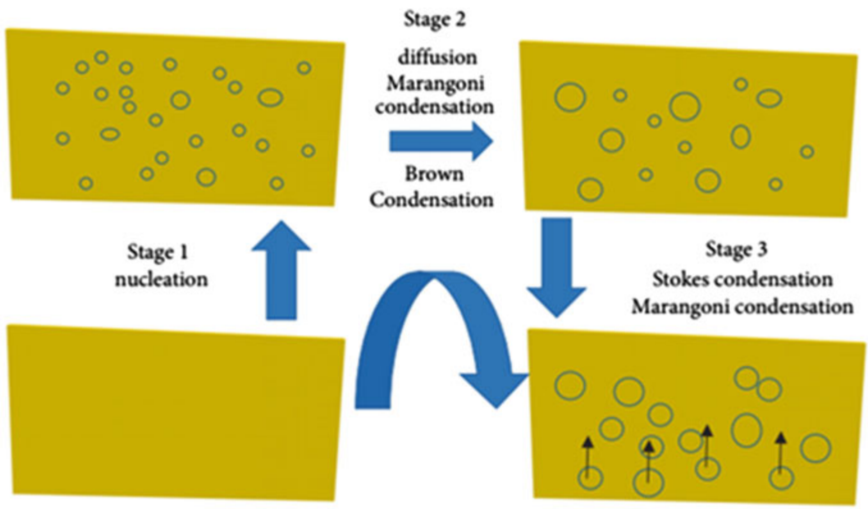

Fig. 1 Process of two-phase separation of CuCr alloy [1]

process, but the characterization of the actual solidification process of CuCr alloy is rarely mentioned at present. The heating furnace in the high temperature confocal microscope has good temperature control ability, with the heating rate ranging from 0 °C/s to 30 °C/s and the cooling rate ranging from 0 °C/s to 100 °C/s, which can accurately control the cooling rate of its samples [10, 11], which lays a foundation for the characterization of the solidification process of CuCr alloy. Therefore, the melting and solidification process of CuCr alloy is observed by high temperature confocal microscope, and the solidification curve is fitted to analyze the microstructure of CuCr alloy after solidification.

Experiment

The CuCr alloy used in this study is prepared by aluminothermic reduction-induction melting. Aluminothermic reduction is based on CuO, Cr_2O_3 as raw materials, Al as reducing agent, and add CaO as slagging agent, $KClO_3$ as heat generator, through the reduction reaction quickly obtained CuCr alloy melt, and the generation of by-products of Al_2O_3 leads to the solidification of the as-cast alloy internal holes and inclusions, so the induction refining is in order to strengthen the effect of slag-alloy separation, to solve the internal defects of the alloy, aluminothermic reduction and induction refining of the process flow is shown in Fig. 2. The chemical composition (mass fraction, %) of CuCr alloy is listed in Table 1. The sample is machined into a cylindrical shape (7 mm in diameter and 3 mm in height). Before in-situ observation, the sample is polished and placed in an alumina crucible, which is placed in the heating position of a metallurgical furnace with thermocouples. After evacuating the gas in the furnace with a vacuum pump, ultra-pure argon (99.99%) is continuously blown into the furnace to avoid oxidation of the sample surface.

The purpose of this study is to explore the melting and solidification process of CuCr alloy, so the phase diagram of CuCr alloy (as shown in Fig. 2) is analyzed. When the content of Cr in the CuCr alloy is 25.6%, CuCr25 alloy belongs to hyper-eutectic alloy, the melting point of the CuCr25 alloy is about 1600 °C, and there is no immiscible zone between two liquid phases in the solidification process. Thus the solidification process of the CuCr25 alloy starts with the transformation of $L \rightarrow \mathrm{Cr} + L_{\mathrm{Cu}}$, that is, the primary crystal Cr crystallizes from the Cr-rich liquid phase, and the liquid phase transforms to Cu-rich phase. If the solidification rate is slow, it will easily lead to alloy segregation phenomenon, so it is beneficial to obtain homogeneous CuCr alloy if the rapid solidification technology can be applied to the solidification process of CuCr alloy [12, 13]. Therefore, the CuCr25 sample is heated to 1640 °C within 672 s by high temperature confocal, kept at 1640 °C for 30 s, then cooled to about 1100 °C at a solidification rate of 1 °C/s, and the furnace power supply is turned off at 1100 °C to cool the sample to room temperature. The heating and solidification process curve is shown in Figs. 3 and 4.

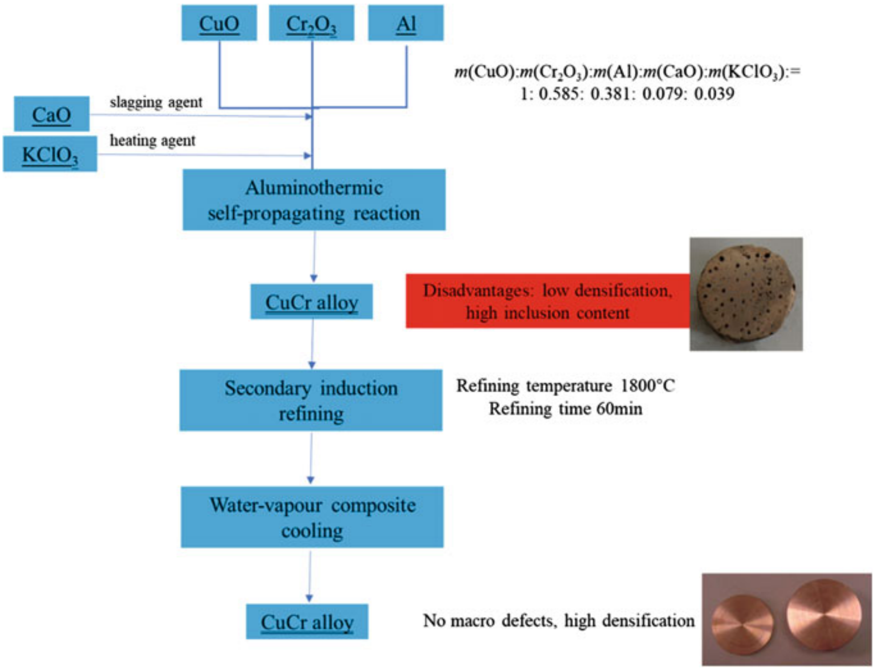

Fig. 2 The process flow of aluminothermic reduction-induction refining

Table 1 Composition of CuCr alloy prepared by aluminothermic reduction-induction refining

Sample	Cu%	Cr%	Al%
CuCr25	Bal	25.6	0.23

Results and Discussion

High Temperature Confocal In-Situ Observation of Melting Process of CuCr Alloy

Figure 5 shows the melting process of CuCr alloy observed in-situ by high temperature confocal microscope. When the temperature reaches 1177.1 °C, it is observed that the Cu matrix begins to melt, and when the temperature gradually rises to 1397.4 °C, it can be observed that the Cu-rich matrix melts completely, and the Cr phase exists in the initial state. With the temperature rising further, but not reaching the melting point of the alloy, the Cr phase has begun to dissolve in the Cu matrix gradually, with the proportion of Cr phases gradually decreases, and when the temperature rises to 1640.3 °C, it has completely appeared in the state of melt. Therefore, by observing the melting process of CuCr alloy in-situ, it is determined that the melting

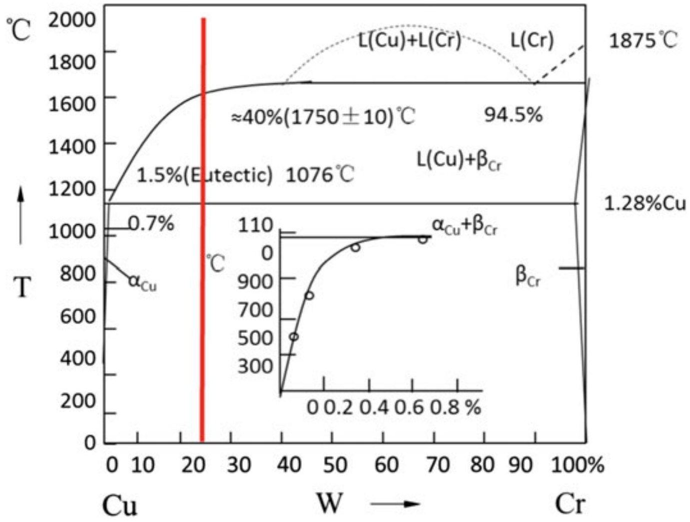

Fig. 3 Binary phase diagram of CuCr alloy

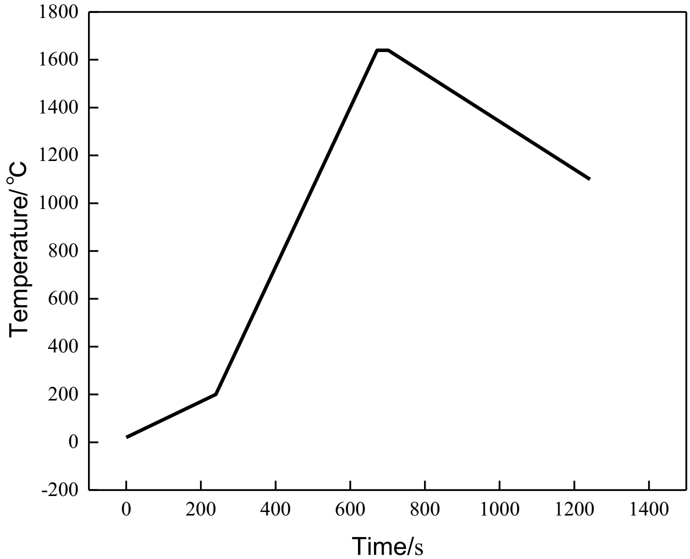

Fig. 4 Curve of heating and cooling process system of high temperature confocal microscope

process is mainly divided into two steps: The first step: Melting of Cu-rich matrix, when Cr phase exists alone; The second step: With the increase of temperature, Cr phase dissolves gradually in Cu matrix, and finally homogeneous alloy melt is obtained.

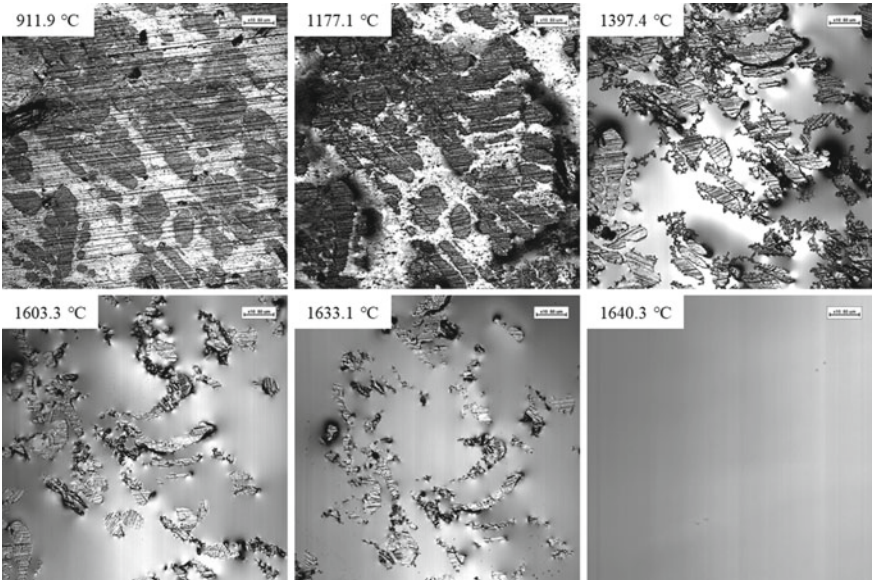

Fig. 5 In-situ observation of the melting process of CuCr alloy by high temperature confocal microscope

High Temperature Confocal In-Situ Observation of the Solidification Process of CuCr Alloy

Figure 6 shows the solidification process of CuCr25 alloy observed in-situ by high temperature confocal microscope, and the solidification rate of the alloy is 1 °C/s. It can be found from the figure that the initial solidification of CuCr25 alloy is found at 1550.2 °C. With the further decrease of temperature, the early solidified Cr phase nucleates and grows gradually. The growth of Cr-rich phase is completed at 1400.4 °C, because the Cr-rich phase is closer to a bright grain. In the subsequent solidification process, there are black areas wrapping bright Cr-rich phase. With the decrease of temperature, the liquid phase gradually decreases and the black solidification area increases, and the liquid phase in the alloy disappears completely at 1030 °C. At this time, after observing the solidified structure, it is inferred that the bright area is Cr-rich phase and the black area is Cu-rich phase. The microstructure of CuCr alloy after solidification is found to be 25.1~26.2% of the Cr phase area, combined with the liquid phase fraction in Fig. 6, it is found to verify this conjecture, which indicates that after the solidification of CuCr alloy, after the nucleation and growth of the Cr-rich phase, the Cr-rich phase edges of the Cu melt solidifies first, to achieve the wrapping of the Cr-rich phase. This is conducive to the inhibition of the growth and growth of the Cr-rich phase with the further reduction of the temperature until the Cu melt is completely solidified.

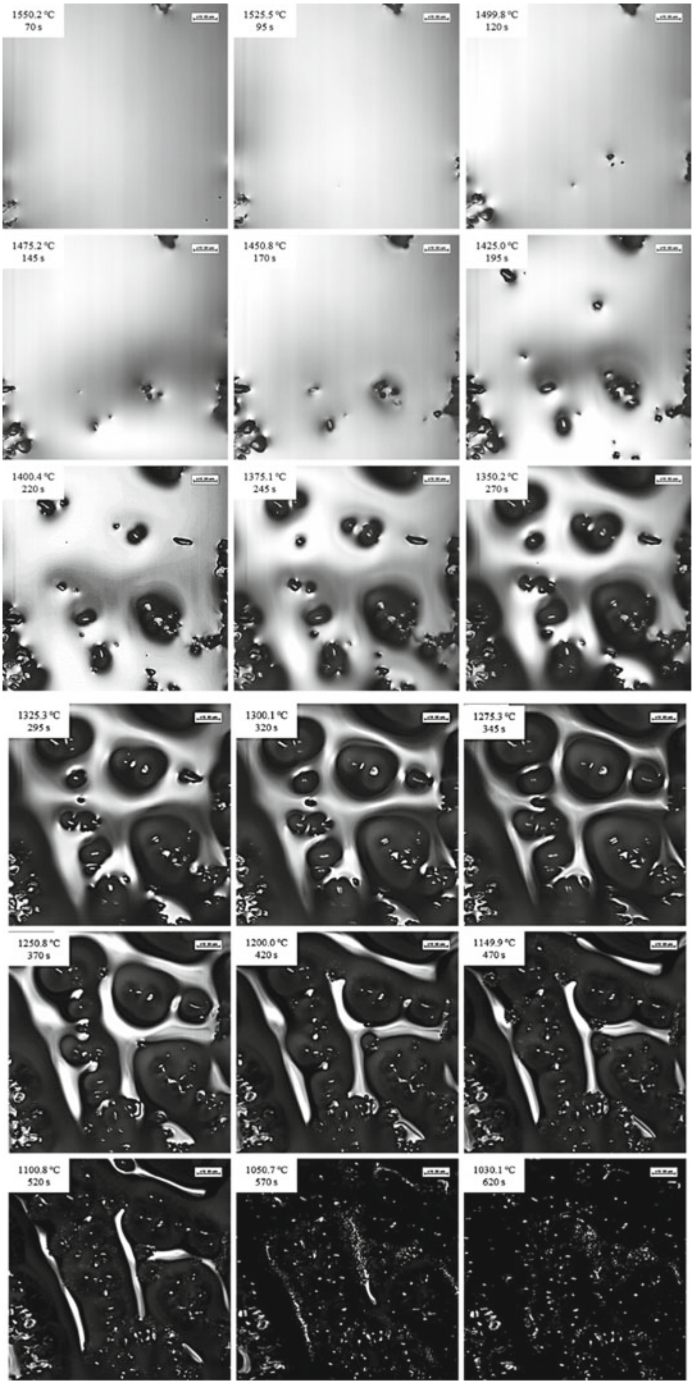

Fig. 6 In-situ observation of solidification process and solidification structure of CuCr alloy by high temperature confocal microscope

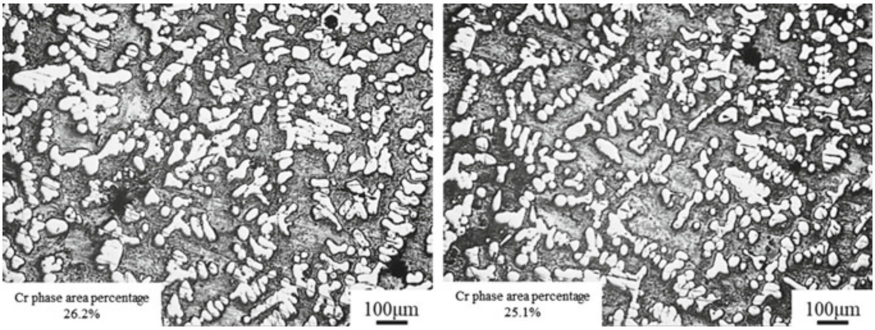

Fig. 6 (continued)

Figure 7 shows the relationship between liquid phase fraction and temperature during solidification of CuCr alloy. From the relationship between liquid fraction and solidification temperature, it is found that the solidification process can be divided into three stages: initial solidification stage, stable solidification stage, and final solidification stage. The temperature interval of the initial solidification stage is 1600 °C–1400°C, which is supposed to be the stage of Cr phase nucleation, and the temperature interval of the stable solidification stage is 1400–1250°C, which occurs the growth of the Cr phase and the solidification of the Cu matrix at the edge after the growth of the Cr phase, and at this time, the solidified Cu phase wraps around the Cr-rich phase, and the temperature interval of the final solidification stage is 1250–1030 °C, which should be all the solidification of the Cu substrate.

The fitted liquid fraction (f_L) as a function of temperature (T °C) [14]:

$$f_L = 1 - \frac{0.97}{1 + \exp(\frac{T - 1323.1}{50.1})} \quad (1)$$

Crystal Structure Characterization of CuCr Alloy

Zhou [15] clearly pointed out that monotectic alloys are heterostructures, so CuCr alloys are also typical heterostructures. According to the theory of heterostructure, the structure model of CuCr alloy was established for the first time by Materials studio, as shown in Fig. 8. The specific steps include the introduction of Cu and Cr crystal model, the tangent surface of (100) plane of Cu and Cr crystal, and the cell expansion according to the lattice constant, and finally the crystal layer is constructed.

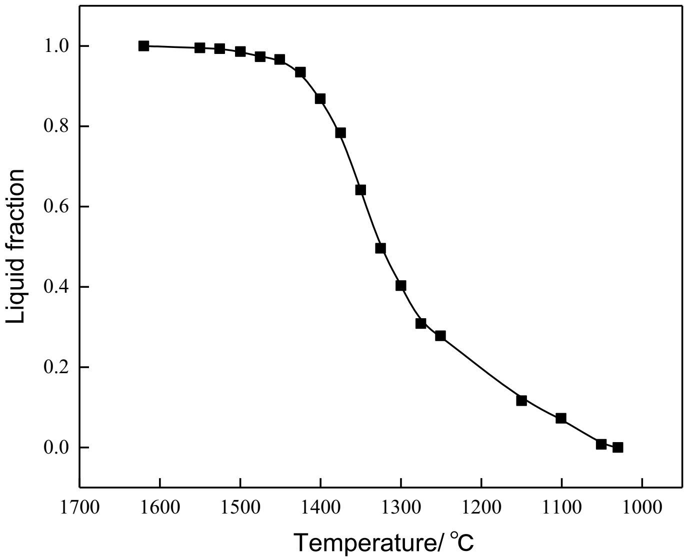

Fig. 7 Liquid phase fraction of solidification process of CuCr alloy

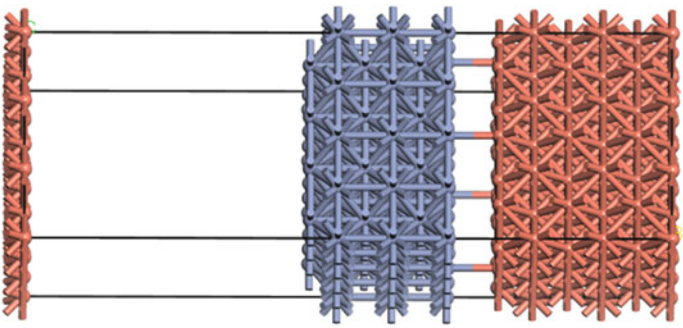

Fig. 8 Structural model of CuCr alloy established by materials studio

Conclusion

(1) The melting process of CuCr alloy is observed by high temperature confocal microscope. It is found that with the increase of temperature, the melting process of CuCr alloy was mainly divided into two steps. The first step is the melting of Cu-rich matrix, in which Cr phase existed alone; The second step is the gradual dissolution of Cr phase in Cu matrix with the increase of temperature, and finally the homogeneous alloy melt is obtained.

(2) The solidification process of CuCr alloy can be divided into three stages: initial solidification stage, stable solidification stage, and final solidification stage. The temperature range of stable solidification stage is 1400–1250 °C, and the solidification rate of the alloy is the fastest. Finally, the solidification curve of CuCr alloy is fitted, and the heterostructure model of CuCr alloy is established.

References

1. Han JR, Dou ZH, Zhang TA, An W (2022) Progress in the preparation of large-size high-performance CuCr alloys. Adv Mater Sci Eng 2022. https://doi.org/10.1155/2022/1333985
2. Liu S, Jie J, Dong B (2018) Novel insight into evolution mechanism of second liquid-liquid phase separation in metastable immissible Cu-Fe alloy. Mater Des 156:71–81
3. Cao WC, Liang SH, Zhang X (2011) Effect of Fe on microstructures and vacuum arc characteristics of CuCr alloys. Int J Refract Met H 29(2):237–243
4. Cao WC, Liang SH, Zhang X (2011) Effect of Mo addition on microstructure and vacuum arc characteristics of CuCr50 alloy. Vacuum 85(10):943–948
5. Ma YQ, Lin HJ, Song DD (2014) Microstructure evolution and thermal physical properties of CuCr alloy after high pressure treatment. Rare Met 33(3):293–298
6. Han JR, Dou ZH, Zhang TA, An W (2023) Fe microalloying during the in-situ synthesis of homogeneous CuCrFe alloys by aluminothermic Self-propagating. J Mater Res Technol 25:95–106
7. An W, Dou ZH, Han JR, Zhang TA (2022) Microstructure uniformity control of CuCr alloy prepared in-situ by aluminothermic reduction coupled with permanent magnetic stirring. J Alloy Compd 96:170797
8. An W, Dou ZH, Han JR, Zhang TA (2022) Microstructure evolution and property strengthening of CuCr50 prepared by thermite reduction-electromagnetic casting during the heat treatment process. J Mater Res Technol 24:6533–6544
9. Han JR, Dou ZH, Zhang TA, An W (2022) Effect of reduction-slagging coupling of Cr_2O_3 during in-situ preparation of homogenic CuCr50 alloy by self-propagating high temperature synthesis metallurgy. J Mater Res Technol 19:3658–3669
10. Shen Y, Wang C (2019) In Situ observation of martensite lath growth behaviors in the coarse grained heat-affected zone of 12.5Cr-0.5Mo heat-resistant steel during simulated welding. Metall Mater Trans A 50(11):4955–4960
11. Zou X, Sun J, Matsuura H (2018) In Situ Observation of the nucleation and growth of ferrite laths in the heat-affected zone of EH36-Mg shipbuilding steel subjected to different heat inputs. Metall Mater Trans B 49(5):2168–2173
12. Xie M, Liu JL, Lu XY (2001) Investigation on the Cu-Cr-RE alloys by rapid solidification. Metall Mater Trans A 304–306:529–533
13. Wang YP, Zhang RL, You YM (2011) Review of the preparation of fine-grain and superfine-grain Cu-Cr alloys via rapid solidification. Gaoya Dianqi/High Voltage Apparatus 47(12):80–85
14. Miao ZJ, Shan AD, Wang W (2011) Solidification process of conventional superalloy by confocal scanning laser microscope. T Nonferr Metal Soc 21:236–242
15. Zhou SF, Xie M, Wu CY (2022) Selective laser melting of bulk immiscible alloy with enhanced strength: heterogeneous microstructure and deformation mechanisms. J Mater Sci Technol 14:81–87