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Deoxidization of CuCr25 alloys prepared by vacuum induction melting ①

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[Abstract] The influence of crucible and vacuum on oxygen content of CuCr25 prepared by vacuum induction melting (VIM) has been investigated. The experimental results show that the selection of crucible is very important. Alkaline oxide MgO crucible can result in increment of oxygen content and segregation of Cr in the CuCr25 alloys prepared. Neutral oxide Al_2O_3 crucible has no contribution to oxygen in CuCr25. The results also indicate that some kinds of deoxidant, such as Al, are further beneficial to deoxidization of the alloys.

[Key words] CuCr25 alloys; crucible; vacuum; deoxidization

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1 INTRODUCTION

Low gas content is the basic requirement for CuCr25 contact material in vacuum interrupters. Because the released gas during current interruption could induce interrupting failure[1]. So the oxygen content must be lower than 0.05%, and nitrogen content must be lower than 0.005% according to the technical standard for CuCr contact materials. Usually, all CuCr contact materials prepared by powder metallurgy at home and abroad meet this criterion[2]. According to Simens report[3], the oxygen and nitrogen content of CuCr alloys through arc-smelting are lower than 0.035% and 0.005%, respectively.

Recently, a new technology was introduced, which could produce CuCr25 contact materials through Cu and Cr blocks melted by arc or plasma[4] or by vacuum induction melting[5]. The Cr powder was replaced by Cr blocks, so the cost of production decrease greatly. But the alloys contain rich oxygen, sometimes as high as 0.3%. Therefore, the applications of CuCr25 prepared by VIM in vacuum interrupter were restricted.

The reason why CuCr25 get such high oxygen during VIM should be investigated. In this paper, the CuCr25 alloys are prepared by VIM, with special attention to the deoxidization process for the alloy.

2 EXPERIMENTAL

Fragments of oxygen-free copper and pure chromium (≥99.9%) with a ratio of 75∶25 were put into a crucible which was fixed in a VIM furnace. As the furnace was evacuated to 1.5×10^{-1} Pa, the raw material began to be heated until melting. The melt was refined at 1 700 ℃ for a while. After melting, the melt was poured into a crystallizer cooled by circulating water. The CuCr25 alloys ingots, which weighs about 6 kg, were then obtained.

In the experiment, two kinds of crucible were chosen: alkaline oxide MgO and neutral oxide Al_2O_3 crucibles. Moreover, small amount of deoxidant Al was added for the purpose of deoxidization. The code name and composition of CuCr25 alloys and their crucible used are shown in Table 1.

Table 1 Code name and composition and crucible of experimental alloys

Composition/ %	Crucible	Code name
Cu75Cr25	MgO	A-CuCr25
Cu75 Cr25	Al_2O_3	N-CuCr25
Cu74.9Cr25Al0.1	Al_2O_3	N-CuCr25Al

The electric conductivity, relative density, dielectric strength and hardness of CuCr alloys were measured, respectively. Their microstructures were observed by Scanning Electron Microscopy (SEM), their composition distributions were analyzed by Energy Dispersive X-Ray Analysis (EDX).

The gas contents of raw materials and the as cast alloys were determined by a LECO analyzer.

3 RESULTS

Table 2 presents the main physical properties of experimental CuCr25 alloys. The properties of conven-

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Table 2 Physical properties of experimental alloys

Materials	Hardness HB	Relative density/ %	Breakdown field/ (10^8 V·m^{-1})	Electric conductivity/ (MS·m^{-1})	Oxygen content/ %	Nitrogen content/ %
A-CuCr25	90	98.8	1.79	13	0.2~ 0.35	5×10^{-4}
N-CuCr25	95	99.27	2.62	25	0.074	5×10^{-4}
N-CuCr25Al	93	99.1	2.59	23	< 0.05	7×10^{-4}
* CuCr50	-	> 99	2.57	> 15	< 0.05	$< 50\times10^{-4}$

* Conventional contact material prepared by powder metallurgy

tional CuCr50 alloy are also given in Table 2. The data shows that A-CuCr25 alloys contain high oxygen, which is harmful to their interrupting ability. Their breakdown field and electric conductivity are rather low, so they cannot be used for high voltage applications. The properties of N-CuCr25 alloys are improved greatly, their oxygen contents drop from $(2\sim4)\times10^{-3}$ to 0.07% or so. Their physical properties reach the level as for the conventional CuCr50. It could be concluded that the crucible has substantial influence on oxygen content and the physical properties of CuCr25 alloys. When the deoxidant Al was added into N-CuCr25, the oxygen content was further reduced to less than 0.05%, at the same time, however, a small amount of Al addition does not show any harmful effect on the physical properties of the alloys made.

4 DISCUSSION

4.1 Influence of crucible on microstructure and oxygen content

Fig. 1 shows the microstructure of A-CuCr25. The specimen is cut from the center of the ingot of A-CuCr25. Much inclusion is seen. They distribute in the form of segregation, which leads to the microsegregation of Cr, or spreads in the matrix. These inclusion and microsegregation would degrade the properties of CuCr25 alloys, such as electric conductivity and breakdown field[5~7]. By EDX analysis, these inclusions are mainly composed of metal element Mg whose oxide MgO constitutes crucible, in some of them, the Cr content is also high. Fig. 2 shows the microstructure of N-CuCr25. In the whole ingot, the microstructure is almost the same. Cr phase distributed in rich Cu matrix evenly. Apart from Cr and Cu, there are no other phases. It can also be confirmed that there are only two kinds of elements by EDX: Cu and Cr.

The analysis results showed that the oxygen content in Cu blocks was 10^{-4}% before melting and 1.3×10^{-3}% after melting, so Cu almost had no devotion to the increment of oxygen content of CuCr25 alloys. Cr blocks contained 0.12% oxygen. Oxygen is absorbed on the surface of Cr blocks, mainly existing in the form of Cr_2O_3, which is very stable and difficult to be removed under the experimental conditions[8].

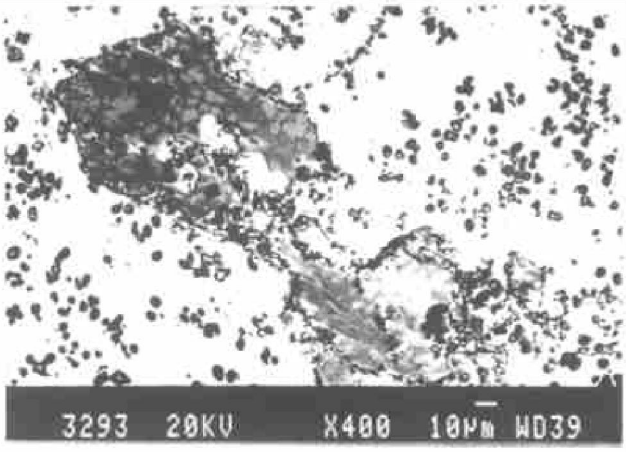

Fig. 1 Microstructure of A-CuCr25

Fig. 2 Microstructure of N-CuCr25

According to the principles of thermodynamics, Cr_2O_3 could take reaction to MgO, which made up crucible. The reactant can not be decomposed during melting. Because the melt was mixed by strong electro-magnetic force and the rate of solidification was great, the reactant couldn't float up completely and thereby was enclosed in the alloys during solidifying[9]. Meanwhile, MgO might be washed down from the crucible and enter the alloys. As a result, the oxygen content ascended and the properties and microstructure of CuCr25 were influenced negatively[10].

As for the Al_2O_3 crucible, it was rather stable and didn't react with the CuCr25 melt to an obvious extent. Thus, the increase of oxygen content was avoided. Therefore, the oxygen content dropped greatly, in comparison with A-CuCr25.

4.2 Influences of vacuum and deoxidant Al on oxygen in CuCr25

From 4.1, it was known that Cu had little contribution to the oxygen content of CuCr25 and Cr blocks contained 0.12% oxygen. The proportion of Cu and Cr was in a ratio of 75 to 25, the oxygen content of CuCr25 should be about 0.03%, if there were not other source of oxygen. For N-CuCr25, the Al_2O_3 crucible was adopted which limited the influence of crucible materials on oxygen content, so the vacuum had impacts on the rise of oxygen content in CuCr25.

A reaction of Cr and O_2 could be concluded from the following relationships[11]:

$$2Cr + (3/2)O_2 = Cr_2O_3 \qquad (1a)$$

$$\Delta G_T = -1159763 + 222.8T - RT\ln\left[\frac{1}{p(O_2)}\right]^{3/2} \qquad (1b)$$

where ΔG_T is Gibbs free energy for the reaction; R is the gas constant and $p(O_2)$ is oxygen partial pressure.

According to the principle of the thermodynamics, if reaction (1a) is fully suppressed, the following condition must be satisfied: $\Delta G_T > 0$.

The relationship between temperature at which the reaction couldn't take place and oxygen partial pressure that can be considered roughly as the lowest pressure can be calculated from (1a) and (1b). The results are given in Table 3. At 1 700 ℃, the reaction couldn't be suppressed provided that the oxygen partial pressure was lower than 1.94×10^{-13} Pa. Such low pressure is impossible to achieve technologically, so Cr could absorb O_2 from the vacuum during melting spontaneously, the oxygen content of CuCr25 grew.

Table 3 Relation between temperature and pressure

Temperature/ ℃	1 600	1 700	1 800
Pressure/ Pa	1.57×10^{-14}	1.94×10^{-13}	1.89×10^{-12}

In order to reduce oxygen in CuCr25, small amount of Al about 0.1% might be added as deoxidant. For deoxidization reaction[11]:

$$2Al + Cr_2O_3 = Al_2O_3 + 2Cr \qquad (2a)$$

$$\Delta G_T = -537937 - 15.69T\lg T + 163.05T \qquad (2b)$$

where ΔG_T is Gibbs energy for reaction (2a).

When the temperature is lower than 5 130.2 K, the reaction could take place spontaneously, which is easy to fulfill under the experimental conditions. Consequently, the oxygen content of the alloys could be reduced efficiently. Therefore, the harmful influence of the oxygen on the properties of CuCr25 is eliminated due to the addition of small amount of Al.

5 CONCLUSIONS

1) The crucibles have a great impact on the microstructure and properties of CuCr25 alloys fabricated by VIM. In reality, the MgO crucible can react with the CuCr25 melt. This lead to an increment of oxygen content in the alloys; while the Al_2O_3 crucibles possess high stability in high temperature and take no reactions with alloys, it is ideal crucible material to produce CuCr25 alloys.

2) During melting, the reaction $(4/3)Cr + O_2 = (2/3)Cr_2O_3$ could occur, which then lead to trap oxygen from the residual atmosphere in the vacuum chamber into CuCr25 alloys. However, Al can act as deoxidant for efficiently reducing the oxygen content of the alloys.

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