



Optimization of processing Cu-Cr alloys via aluminothermic reduction

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Abstract

Copper-Chromium materials are widely used for medium voltage application as electrical contacts for a voltage range 1kV - 52kV and as vacuum interrupters. Chromium within Copper-matrix provides high security against welding during short circuits, low contact resistance and high arc erosion resistance. Due to the wide miscibility gap in the binary system production of Copper-Chromium requires extensive and cost-intensive processes. IME, RWTH Aachen University started to investigate an alternative process based on joint aluminothermic reduction of Chromium and Copper oxides with subsequent VAR remelting and successfully synthesized Copper-Chromium alloys with various Chromium contents via aluminothermic reduction.

The present work focusses on the optimization of the developed Aluminothermic process for Copper-Chromium metals. The used reductant agent Aluminium remains in the metal phase with a content of 1-4wt.-%. Different experiments were conducted to determining and reducing the final Al-content subjected to various Copper-Chromium compositions. Furthermore, investigations were performed to produce directly the electrode from aluminothermic reaction for remelting in VAR. The results were confirmed in up scaled experiments by using in-line aluminothermic reaction process.



1 Introduction

The combination of high thermal and electrical conductivity, high strength and long term stability insure Cu-Cr alloys a wide application in the area of medium voltage contacts. However, the production of this material requires extensive and complex processes due to the miscibility gap in the binary system of Cu-Cr. [1][2] The most frequently processing method consists of two steps: consolidation of electrode and vacuum arc remelting. The main target at the consolidation step is achieving a uniform distribution of the Cr-rich phase within the Cu-rich matrix. Different process methods are currently available e.g. hot isostatic pressing, vacuum sintering and vacuum induction melting. [3][4][5] The remelting step represents an essential process to receive the necessary homogeneity regarding microstructure and to control material and solidification defects. [6] The aluminothermy seems suitable to replace the consolidation step in order to produce the electrodes for the VAR process. After successfully synthesizing the bulk alloy of CuCr25 and CuCr40 the in-line process has to be developed for the present system. Furthermore it is of interest to determine the achievable minimal content of remaining Al.

2 Fundamentals

The aluminothermy defines the reaction between a metal compound and the reductant Aluminium that has a greater affinity to the compound than the target metal. The two most important characteristics of this reaction are the strong exothermic behavior and the high reaction rates. The input material mixture provided as powder is charged in a reactor that is lined with refractory material and will be ignited at the mixture surface. As soon as the ignition started at the top of the mixture the reaction front propagates through the entire mixture. For the present investigation the target metal materials are added as oxides and react as following reaction equations:



In order to ensure a self-propagating reaction front the energy density of the reaction should be adjusted very properly. Regarding an alloy composition with Chromium content in the range of 15-40-wt.% the heat of reaction eq.(2) is sufficient enough to provide an autotherm process with no need of external heat input. It is possible to add a flux as lime reducing the liquidus temperature of the alumina slag and furthermore providing an adjusting parameter for energy density of the input mixture. Preliminary trials targeting CuCr25 and CuCr40 showed the feasibility of synthesizing this alloy via aluminothermic reduction. Table 1 gives the composition of the metal product.



Table 1: metal composition of aluminothermic produced metal

	Cu in wt.-%	Cr in wt.-%	Al in wt.-%
CuCr25	73.2	22.5	4.3
CuCr40	62.1	32	2.9

It can be seen that the variation of Chromium content in metal product is high for Cr-rich alloys. However, the remaining Al-content in metal product of CuCr25 with 4,3 % is immensely high and has to be reduced. Therefore, the focus of the present investigation is to determine the Cr-content correlating to a minimal residual Al-content in the ATR product.

The subsequent process of vacuum arc remelting is also part of the present investigation. The VAR process presents a refining process with consumable electrode in a water cooled copper mould. The main objectives are the reduction of nonmetallic inclusions, formation of a controlled solidification structure and removal of dissolved gas and elements with high vapour pressure. The energy input is inserted by direct current electric arc in high vacuum atmosphere between electrode and base plate, during stationary remelting phase between electrode and melt pool. Figure 1 shows the schematic procedure of the vacuum arc remelting process. [6]

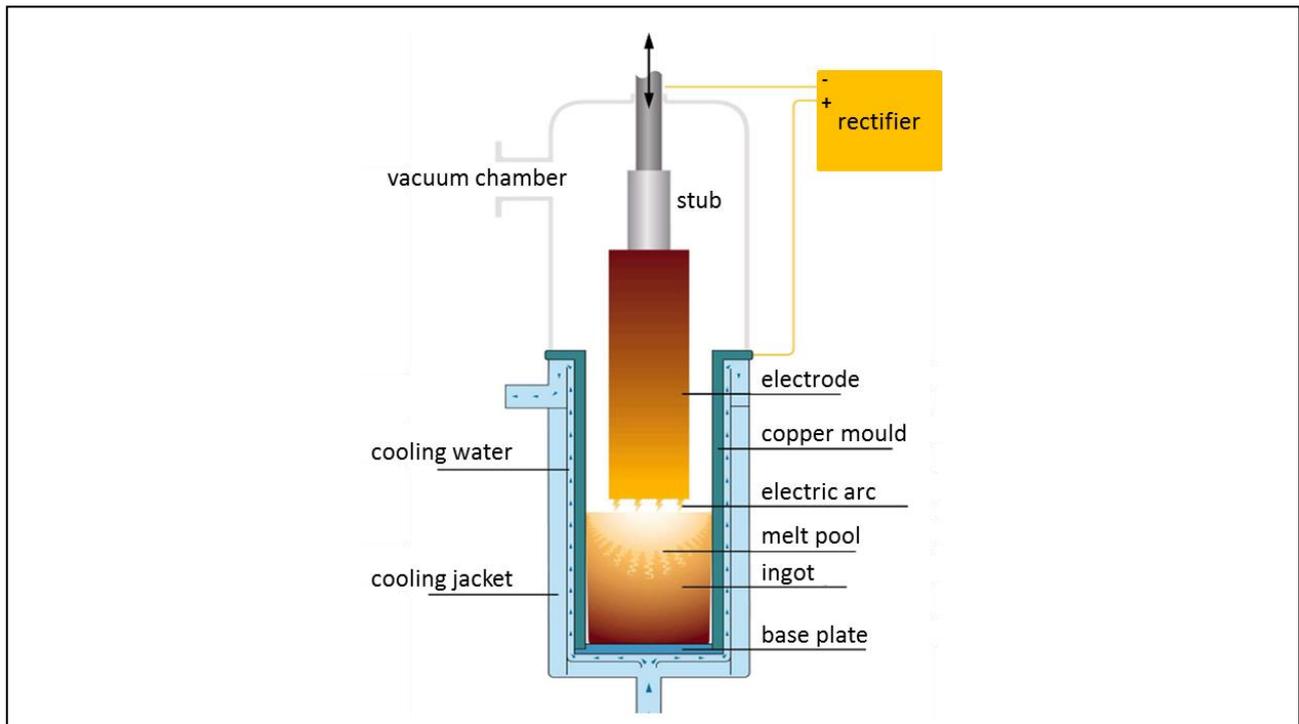


Figure 1: Schematic procedure of vacuum arc remelting [6]

In order to investigate the subsequent process of VAR the product of the aluminothermic process has to be chargeable for the VAR process. Therefore, the produced metal phase via ATR has to be casted directly into an electrode. It is of interest how the change in the process procedure effects the quality of the metal product regarding target composition and micro structure.



4 Experimental Procedure

Preliminary trials are performed to determine the mixture with the lowest residual content of Al. Therefore the Cr-content in target alloy is varied between 40 and 15 wt.-%. Furthermore different mixtures were tried regarding the charge of Cr_2O_3 . According to eq. (1) stoichiometric and over stoichiometric addition of Cr_2O_3 were investigated to ensure complete consumption of the reductant Aluminium. The preliminary trials are performed in an Al_2O_3 lined steel vessel with a filling volume of 25 liters. The charging material is 20 kg. In all conducted experiments an adequate phase separation between metal and slag is observed.

In order to produce the electrode directly from the ATR process the produced metal phase has to be inserted to a mould giving the required round rod shape. The major challenge is the high reaction rate. However an adequate separation between metal and slag phase is unavoidable so the metal phase has to settle down inside the vessel. This results in a very short time slot that is available for casting and it has to be defined very properly. Figure 2 shows the construction of reactor and jointed casting mould.

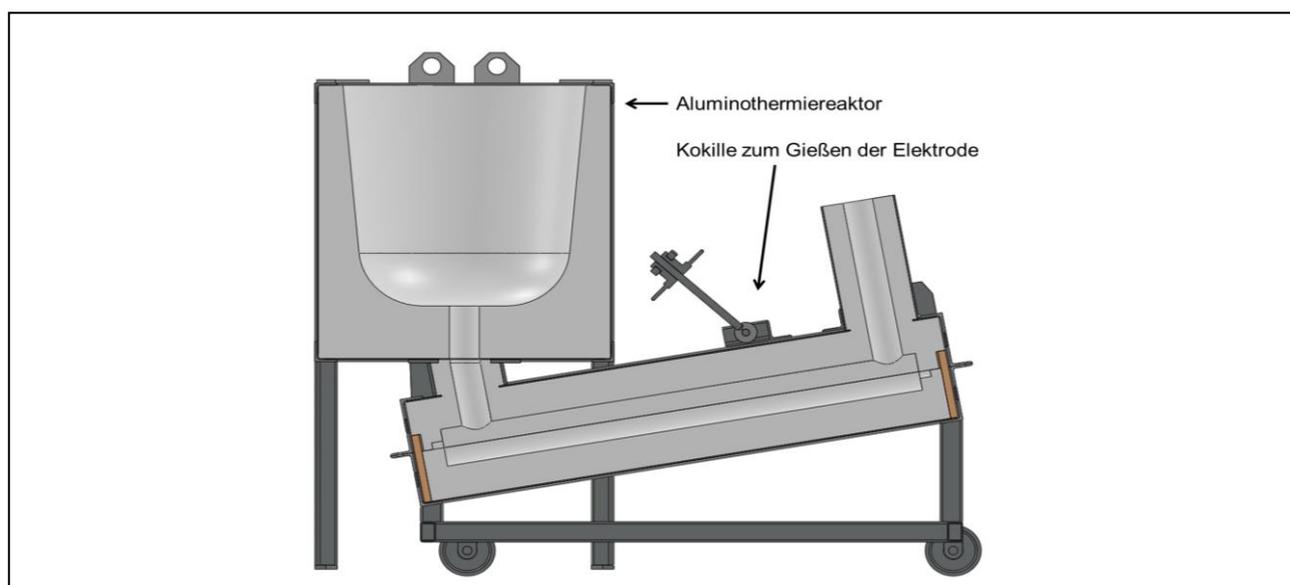


Figure 2: Schematic procedure of in-line aluminothermic process

The reaction vessel is modified with a bottom tapping whole and connected to the mould from the outer bottom side. Vessel and mould both are lined with refractory material. The tapping whole in the reactor bottom is covered with an Aluminium sheet to prevent filling the mould with input mixture. Depending on the thickness the sheet provides the required time for settling down of the metal phase before it is melted and allows filling the mould beneath with liquid melt phase. At the end of the mould there is an air outlet to prevent gas porosity within the final electrode. For in-line casting ATR experiment is performed with a total input charge of 115 kg.

The casted electrode has a diameter of 70 mm and a length of 1300 mm when completely filled. The electrode has to be finished by cutting the gate and cleaning the surface. After attaching the



stub and a further extension the electrode is prepared for inserting to the VAR process. Figure 3 shows the prepared electrode for the VAR process. The remelting experiment is performed in a VAR L 200 (ALD). The used copper mould has a diameter of 110 mm.

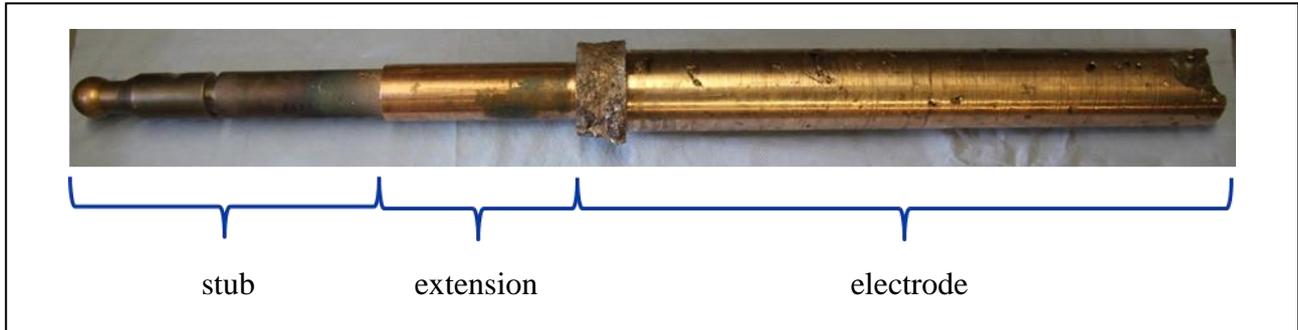


Figure 3: Aluminothermic produced electrode prepared for the VAR process

5 Results

The observations of the preliminary trials have shown that the loss of trials targeting CuCr25 is higher than targeting CuCr15. Despite adjusting the reaction heat of the various trials it is obvious the reaction eq (2) poses more heat per mol Al. The turbulence of reaction raises with higher amount of Cu in the target product. Figure 4 shows the result of selected trials with different methods of charging Chromium. It can be seen that charging with over stoichiometric ratio of Cr_2O_3 the remaining Al content is strongly reduced. Furthermore, higher Cr content in target alloy results in higher Al content.

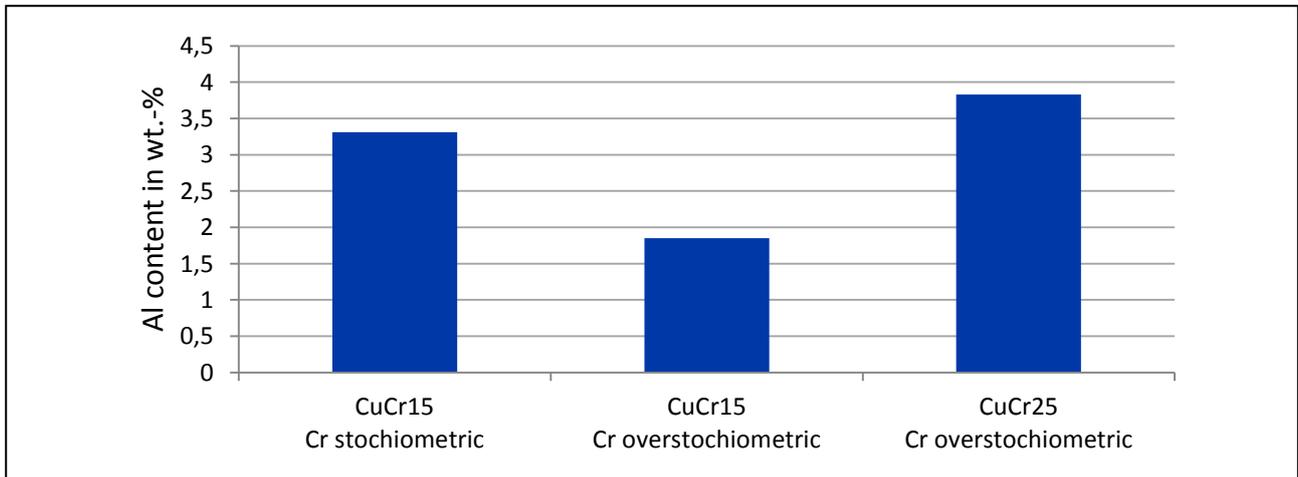


Figure 4: Al content of preliminary trials

Compared with previous trials shown in table 1 the optimized ATR mixture presents a Cu-Cr material with 1,85 wt.-% Al content instead 4,3 wt.-%. The possibility of further decreasing of Aluminium in the Cu-Cr material is given by the subsequent VAR process by evaporation. Minor amounts in the electrode can be even completely eliminated. In order to verify the results of the



preliminary trials the optimized mixture with over stoichiometric Cr_2O_3 and target alloy CuCr15 is performed as up scaled trial with total load of 115 kg. The recovery is significantly higher than in small scale trails as well as the metal yield. Figure 5 shows the result of SEM image with analysed composition of the different phases. It is remarkable that the Cr-rich phase solidifies in dendritic structure. The oxide particles mainly mixed phase of Al_2O_3 and CaO are entrapped between the dendritic arms.

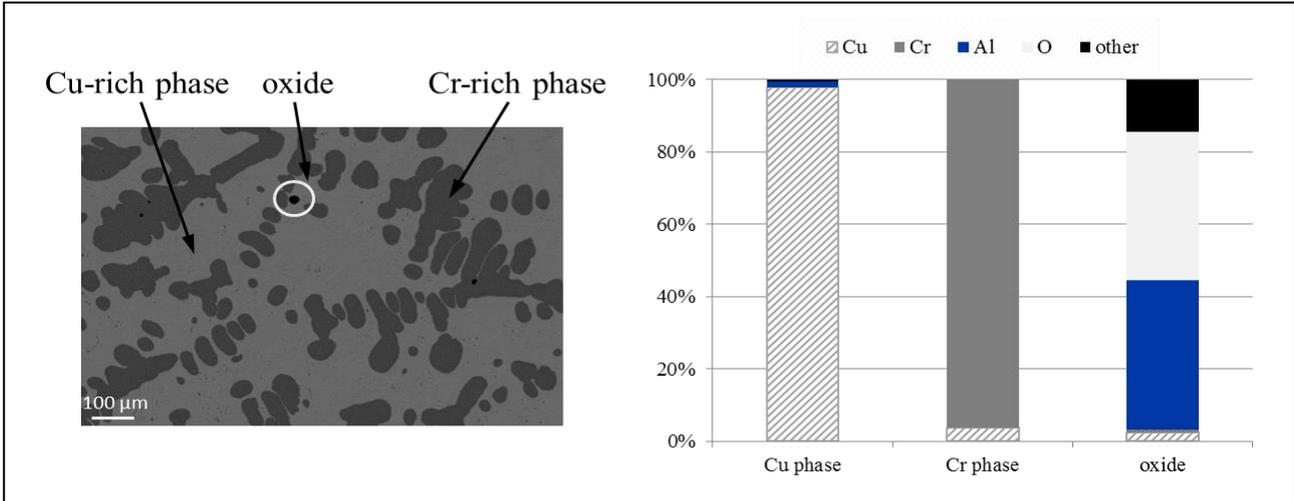


Figure 5: SEM image (left) with XRD results of selected phases (right) of up scaled experiment

Since the results of the preliminary trails and the up scaled were promising the developed mixture is applied for the ATR experiment with in-line casting. The beginning of the reaction, ignition and propagating of reaction was similar to the up scaled experiment without casting. After a few seconds dust came out through the air outlet of the mould confirming the melting of the Al sheet. During the further progress heavy turbulence occurred and a lot of material was spread out through the air outlet. Figure 6 shows the product of the ATR in-line casting experiment with casting gate.



Figure 6: Metal product of ATR in-line casting untreated and prepared for VAR process

It is obvious that the mould was not filled completely with metal due to the heavy metal loss. In order to reduce the turbulence of the experiment regarding the casting period it is recommended to



examine the thickness of the Aluminium sheet. Figure 7 shows the analysing results of the produced electrode compared to the preliminary trials in small scale. Is it remarkable that the Chromium content within the electrode is higher than the Chromium content in the casting gate. Furthermore, the amount of other elements mainly Aluminium and oxides are decreased significantly at the up scaled experiments compared to the small scale 25 L trial. This proportion varies between 1,3 wt.-% (electrode gate) and 1,1 wt.-% (electrode bottom) and can be removed easily during VAR process by flotation and evaporation.

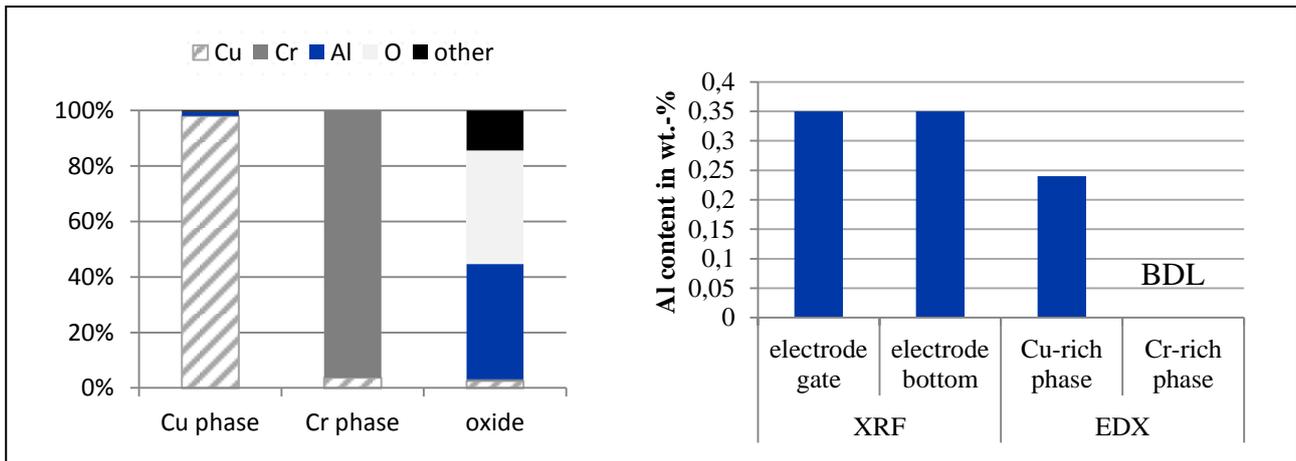


Figure 7: Analysing results of produced electrode

Figure 7 shows the Aluminium content of the electrode analysed via XRF and EDX. Starting from 4,3 wt.-% at previous trails the electrode obtains 0,35 wt.-% Aluminium and hereby fulfills the initial objective of reducing the remaining Aluminium amount completely.

The product of the subsequent VAR experiment obtains no surface defects and has no shrinkage cavity. The cross section of the ingot shows grey particles that indicate a segregation of the Chromium. The particles occur mainly in the center of the ingot and the amount decreases towards both sides. The segregation happens because of the temperature gradient inside the ingot due to water cooled copper mould. The amount of Cu-Cr alloy was not enough to form a controlled solidification during remelting. Two main parameters have to be adjusted for the next VAR trials, length of electrode and melt rate.

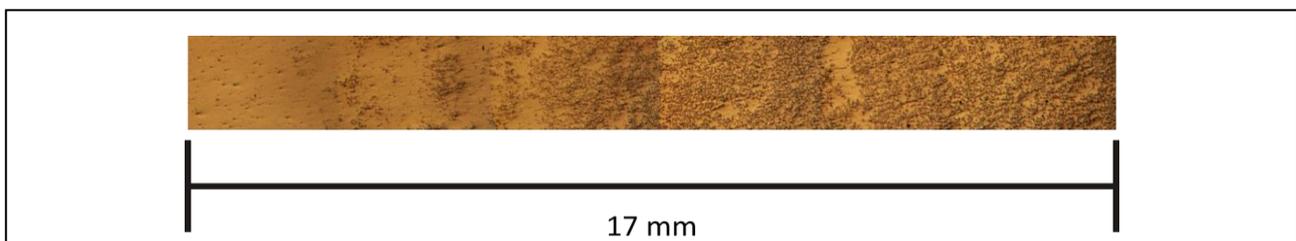


Figure 8: Remelted Cu-Cr alloy



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