



A first approach for electroslag remelting of CuCrZr alloys using pure copper as an example

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Abstract

The requirements for Cu-Cr-Zr alloys are constantly increasing. At the same time, conventional production processes such as melting and casting under controlled atmospheres like vacuum or high-purity inert gases are increasingly reaching their limits in terms of purity and non-metallic inclusions. For further refining of the alloy, electroslag remelting (ESR) is a suitable process, which has already been established for materials such as steel, nickel and titanium alloys. The ESR process is a secondary metallurgical process aimed at further purification after completion of the primary extraction or melting of recycled material and refining processes. The advantages of the ESR process are that macrosegregation can be almost completely eliminated, ensuring a more uniform chemical composition and a finer microstructure in ingots with fewer and evenly distributed non-metallic inclusions. In the ESR process, the heat generated in the slag melts a consumable electrode into a water-cooled copper mold. The metal droplets sink through the slag into the molten pool formed below the slag. Due to the interfacial reactions between metal and slag and between slag and atmosphere, as well as the remelting parameters, the metal is refined and solidified uniformly in the metal pool by a constant solidification rate. As a first step, the feasibility of remelting copper alloys and also Cu-Cr-Zr by ESR will be verified. For this purpose, the process is first considered thermochemically to determine the slag-metal reactions and then the experimental feasibility is tested. The focus is on the possible remelting and the observation of the behavior of non-metallic inclusions and the alloying elements.



1 Introduction

Due to constantly increasing demands on Cu-Cr-Zr alloys, conventional manufacturing processes such as melting and casting under controlled atmospheres such as vacuum or high-purity inert gases are increasingly reaching their limits in terms of purity and non-metallic inclusions. For the required refining, electroslag remelting (ESR) is a conceivable process, which has already been established for special alloys made of steel, nickel and titanium. In order to verify the feasibility of remelting copper, copper alloys and also, in particular, Cu-Cr-Zr by the ESU process, a large number of different parameters must be determined. These include the input materials such as alloy and slag to determine the equilibrium behavior of the components, as well as the settings and dimensions for the remelting process. In the first step, the remelting process from pure copper to a slag system based in the literature is considered thermochemically and tested experimentally in a first remelting test.

2 Cu-Cr-Zr ternary system

Copper and copper alloys are used for many applications because of their excellent electrical and thermal conductivity, corrosion resistance, ease of processing, and good strength and fatigue resistance. Among the numerous existing copper alloys, the research of Cu-Cr-Zr alloys has become a focus due to the combination of high strength and high electrical conductivity [1]. Application areas of Cu-Cr-Zr alloys are in the field of high-tech electrical products and used in rail transport [2-5]. The strength properties of CuCrZr alloy are due to the increased solubility of Cr in Cu at elevated temperatures due to the presence of zirconia [6]. The addition of zirconia increases the resistance to fatigue stress by reducing the stacking fault energy [7]. During the aging of CuCrZr alloys that follows after production, chromium precipitates are formed, which increase the strength and hardenability of the alloy due to the dispersion of the Cr precipitates formed. The resulting CuCrZr alloys have high electrical conductivity due to low electron scattering in solutes [8]. In this case, the concentration of the individual alloying elements is less than 1-2%, with the cumulative concentration of the alloying elements being less than 5% [6]. Furthermore, the low Cr content in the CuCrZr alloys prevents the formation of coarse chromium precipitates, which can lead to embrittlement of the alloy [9]. Coarsening of the Cr precipitates also reduces the electrical conductivity of the CuCrZr alloy [10]. In addition, the zirconia present increases the hardening of the alloy by improving the fine, homogeneous precipitation. Also, the ductility of the alloy is improved by preventing intergranular fractures [9].

3 Electroslag remelting (ESR) process

The ESR process is a secondary metallurgical process aimed at further purification after completion of the primary extraction and refining processes. A major advantage of the ESR process is the removal of macrosegregation, ensuring a more uniform chemical composition and finer microstructure than ingots with fewer and more evenly distributed non-metallic inclusions. The ESR process consists of a water-cooled copper crucible in which heat is generated by applying an electric current in a liquid



slag phase, causing dropwise remelting of a self-consuming electrode [11]. Figure 1 shows a schematic design of the ESR process

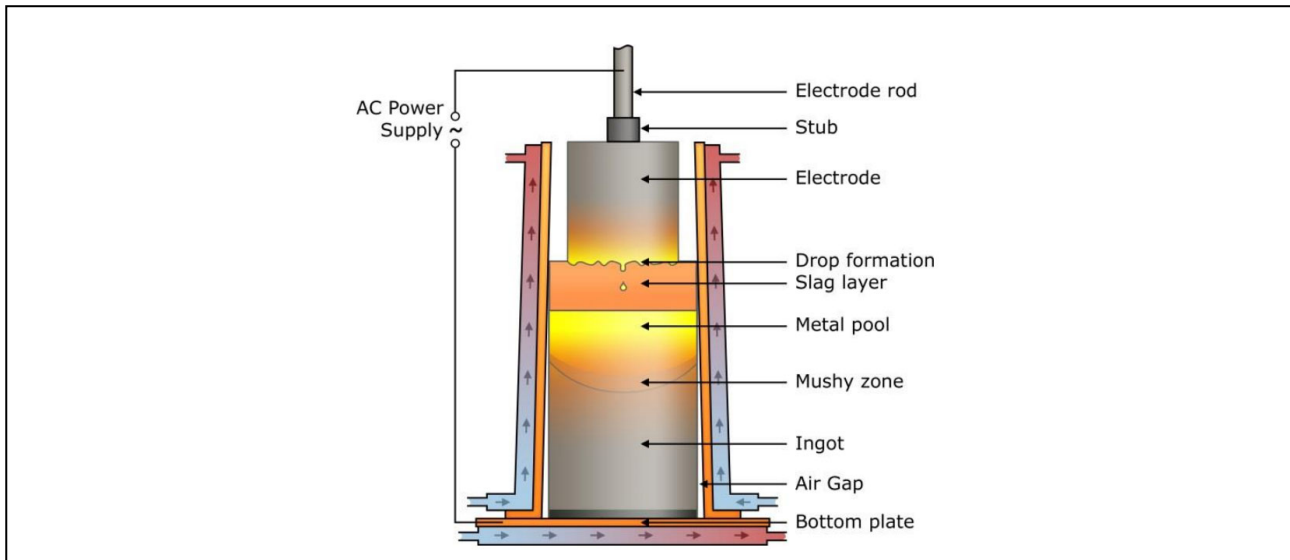


Figure 1: Schematic procedure of the ESR process [11]

Conventional production processes often reach their limits when it comes to manufacturing Cu-Cr-Zr alloys in applications where components made of these materials are subjected to high stresses. Melting and casting under controlled atmospheres such as vacuum or high-purity inert gases are currently the common processes for producing these alloys. Electroslag remelting is an alternative to vacuum processes and is characterized by flexibility of technological parameters and high quality of products. The ingots and materials produced by this process have microstructures with uniform density and high homogeneity, low segregation or voids, and few undesirable impurities or oxide inclusions [12]. Ahmadi et al [13] evaluated this process for stainless steel and concluded that ingots and feedstocks produced in this way have uniform density and microstructure, no segregation or voids, and no desired impurities or oxide inclusions. Prasad and Rao [14] addressed the recycling of light-weight, oxygen-free copper scrap with high conductivity using ESR technology and also used the same process to produce certain copper alloys such as Cu-Cr, Cu-P, and Cu-Ti from copper scrap.

4 Material and methods

Electroslag remelting for steel, nickel and titanium alloys is a widely researched field. In the field of copper and copper alloys, the field is just beginning to research. In general, there is no single alloy-slag system, but rather an adequate variety, which is selected according to various aspects of the alloy under consideration. During electroslag remelting, a wide variety of parameters are in equilibrium and influence the remelting process. Due to these interactions, it is important to consider the influence of individual parameters as individually as possible. In order to eliminate the influence of alloying systems on copper alloys, pure copper is remelted in the first step in the IME technical laboratory (Figure 2) via an open electroslag remelting process.



Figure 2: PESR (left) and ESR (right) furnace at IME Aachen [11]

Pure copper with a diameter of 100 mm and a length of 1,000 mm was used as the remelting electrode. Steel was used as the connection between the system and the remelting electrode to reduce heat transfer from the electrode out of the process. A mixture of CaF_2 :NaF (30:70) was used as slag for the process. For this purpose, a phase diagram was calculated using Factsage 8.0 (figure 3), a thermochemical simulation program, in order to select a slag mixture with a melting temperature below copper.

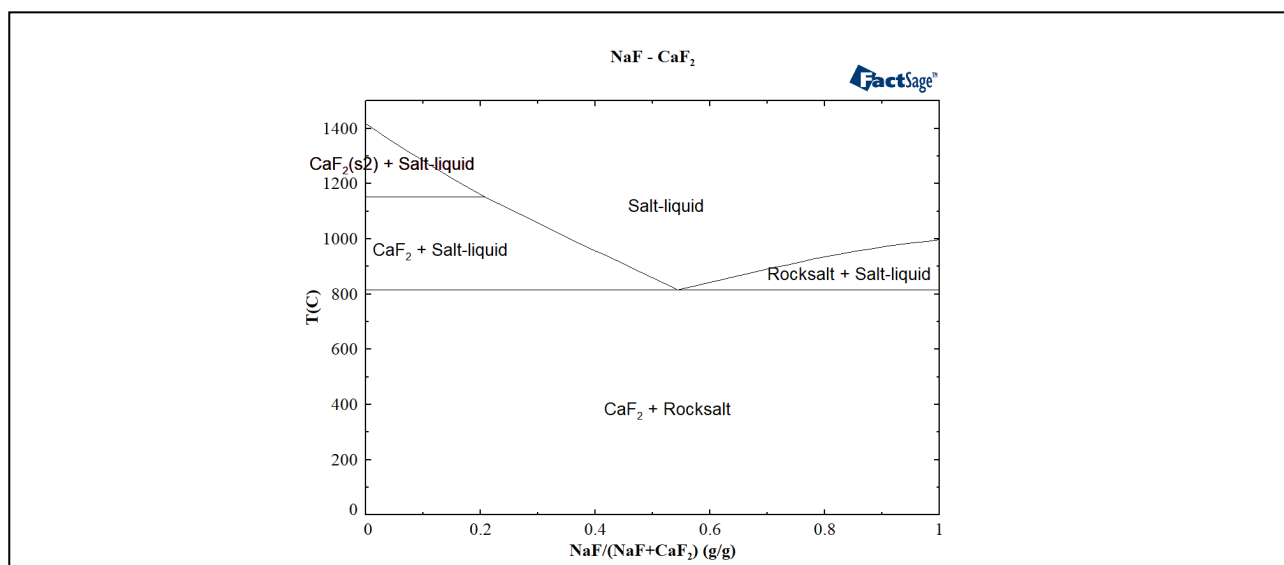


Figure 3: CaF_2 -NaF phase Diagram (Factsage 8.0)



5 Results and Discussion

The remelting process involves three phases: Start phase, remelting phase and hottopping. In the start-up phase, energy is introduced into the system via an open arc to melt slag. As soon as the tip of the electrode is immersed in the slag, the heat introduced by the current through the resistance of the slag is used to melt further slag via resistance heating. Meanwhile, the electrode is slowly pulled back so a slag bath can be formed. When the slag is completely melted, the electrode is continuously pushed to set a constant remelting process. This ends the start phase and the remelting process begins. During the remelting process, the electrode is continuously pushed forward and the set parameters are kept as constant as possible. At the end of the process, where the electrode becomes shorter and shorter due to the dripping process, a hottopping phase can be used in which the power is gradually reduced so that the process does not end suddenly. At the beginning of the process, the slag is completely melted. The slag components were not melted before, instead they were added to the process as pure substances. During the process, a thin layer of solid slag forms between the water-cooled mold and the molten metal. This can prevent interaction between metal and crucible material. Due to this effect, some slag always remains between the remelted ingot and the mold, causing the total amount of slag between the electrode and the ingot to decrease over the process. Furthermore, components from the slag can evaporate during the process due to the high temperature, which can also cause slag quantity and slag composition to change continuously during the process. To counter this, new slag can be added during the remelting process, which was not done in the first feasibility test in order not to influence the remelting process any further. The remelted ingot is shown in Figure 4. On the left is the bottom of the ingot, in the middle the ingot with slag layer and on the right without slag layer.



Figure 4: Remelted Ingot, left: bottom side, middle: with slag skin, right: without slag

During the remelting process, different values are monitored and recorded: Time, electrode position, speed, power, current, voltage, resistance. These values can be used during the remelting process to control and adjust it. At the beginning of the process, these values are adjusted, but especially in the



start-up phase, a safe start-up process must be checked and carried out by the operator of the unit. In order to evaluate the melting process for copper in a first step, several parameters were varied during the process. Due to the strongly varying start process, the start phase is not considered. During the start-up phase, the slag is initially partial and finally completely melted, while the speed of the electrode changes from pulling dynamically to pushing and a constant resistance is established. A uniform remelting process can be set via the constant resistance. If the resistance rises sharply, the electrode loses contact with the slag; if the resistance falls, the gap between the electrode and the ingot narrows and a short circuit may occur. The resistance is largely dependent on the properties of the slag system. If the composition of the slag changes, the resistance of the slag also changes. At the beginning of the remelting process, the power is set higher than for the rest of the remelting process in order to melt the slag. When a uniform resistance has been established, the remelting process is started and the power is switched to remelting power. Figure 5 shows the start of the remelting phase. A constant resistance, uniformly increasing feed rate and constant power show a steady remelting process.

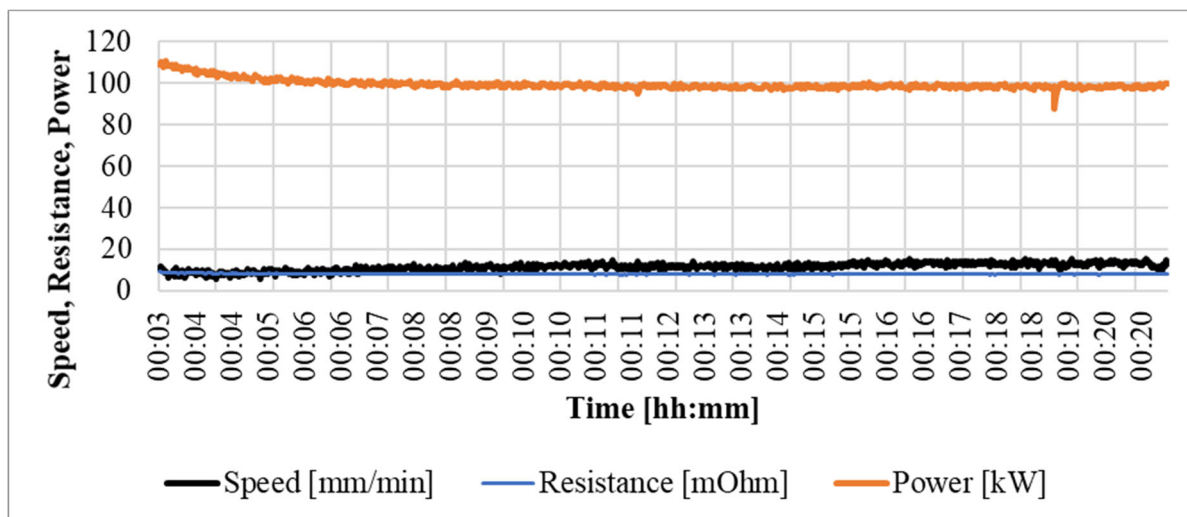


Figure 5: ESR furnace at IME Aachen [11]

To investigate the effect of power on the remelting process, the power was adjusted from 100 kW to 105 kW for a period of approximately 12 minutes after 20 minutes of process time. Figure 6 shows this adjustment in the remelting protocol. A direct increase in feed rate can be noted with the increase in power. Because the resistance is set, the electrode must be moved forward more quickly when more power is applied. Several small power drops are observed in comparison with the lower power. This means that the power drops briefly for a short interval, but is then directly adjusted again. This can be explained by small irregularities in the electrode or mold or other influences on the remelting process. Over the entire duration of the melting process, a continuous increase in the speed of the electrode can be observed, which results from the electrode becoming shorter. In order to further observe the effect of the reduction of power in the process, the power was reset to the original value after 33 minutes of process. This shows only a short reduction in the speed of the electrode follows. Figure 7 shows the end of the remelting process. Here the protocol shows that for the set power with



the resistance the speed of the electrode must be strongly increased, which points to the end of the electrode and therefore the process. From minute 36, at the same power and resistance, the feed rate drops to 0, since all the copper has been remelted there.

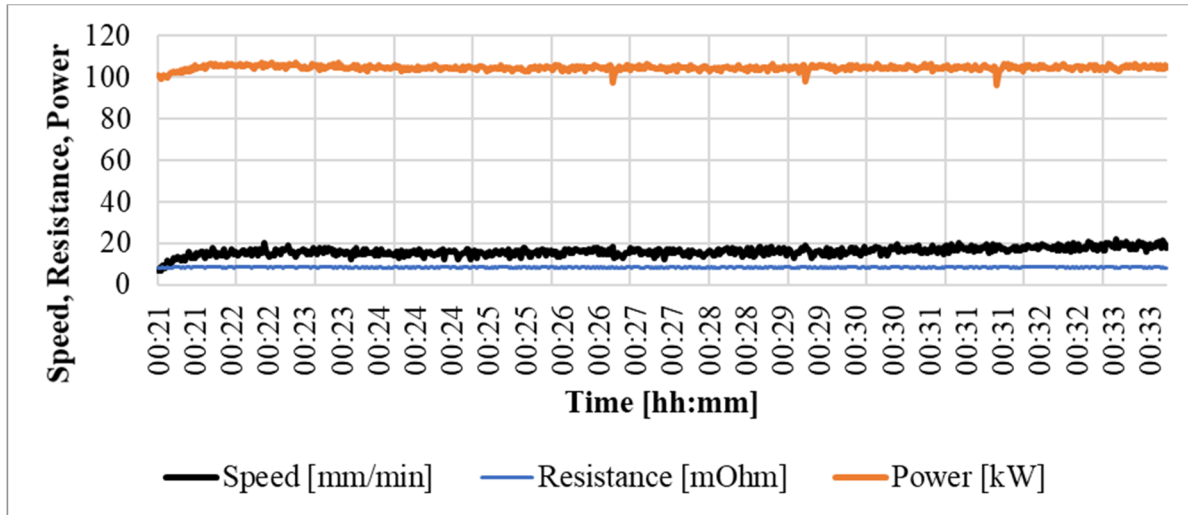


Figure 6: ESR furnace at IME Aachen [11]

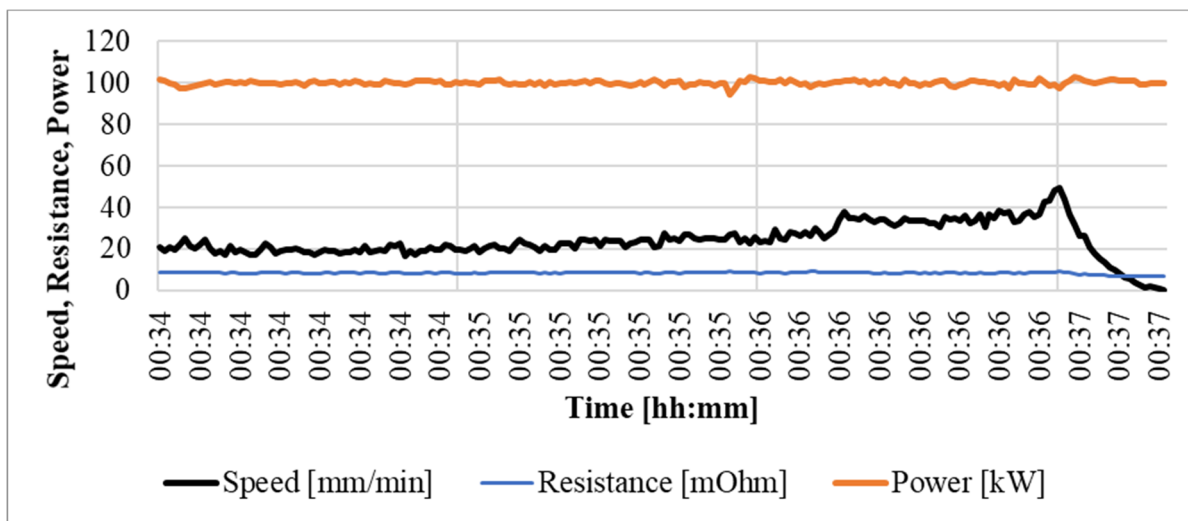


Figure 7: ESR furnace at IME Aachen [11]

In order to evaluate the remelting process in addition to the melting protocol, the remelted ingot was cut into different pieces and analysed under an optical microscope. Figure 8 shows an inclusion in the copper matrix. This is a picture of the start of the remelting process. The process is very turbulent due to recurring arcs, which can lead to irregularities in the remelting process as well as swirled slag inclusions. Furthermore, this disturbs the uniform solidification structure.

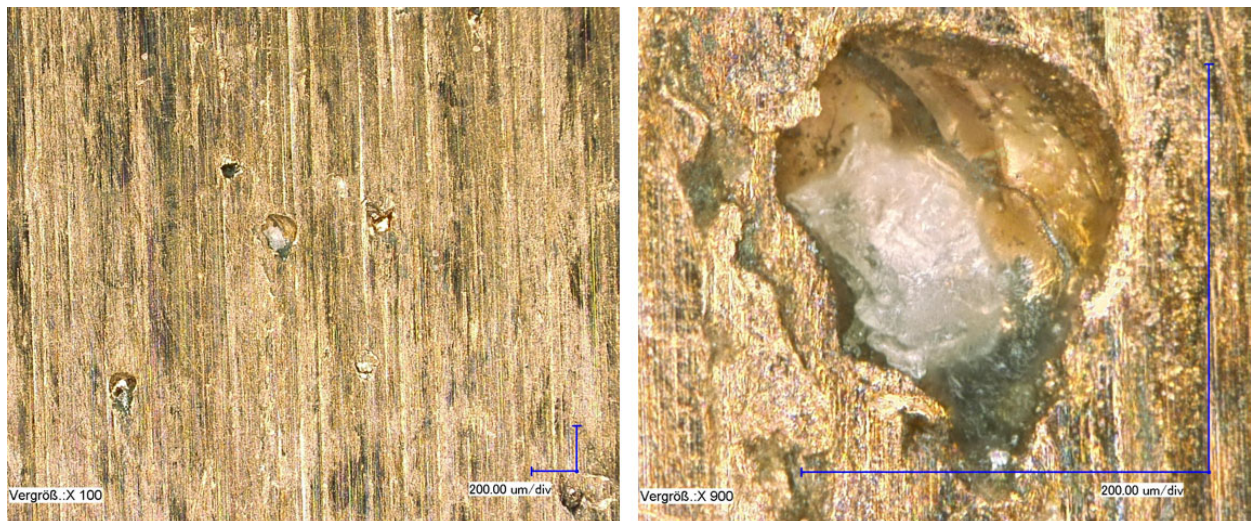


Figure 8: Optical image of an impurity in the remelted copper

6 Conclusion and outlook

Due to the low melting temperature and the high thermal conductivity of copper, the remelting of copper requires a challenging electroslag remelting process and the required slag. An initial proof-of-concept trial showed that remelting of pure copper is possible. This poses the challenge of the further process for copper alloys, especially CuCrZr. Thermochemical simulation has to be used to determine possible slag systems and to verify them experimentally through equilibrium tests, which can be used in the ESU process and at the same time allow a suitable refining effect for the alloy system. Afterwards, the resulting slag has to be tested and optimized in the ESR process and the influence and refining possibilities have to be analyzed.

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