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SLAG AS AN IMPORTANT PARAMETER FOR ELECTROSLAG REMELTING OF COPPER ALLOYS

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Introduction

Electroslag remelting has become established in the refining of steel and nickel metal alloys.^{1,2} It combines the refining of liquid metals through the use of a slag and the remelting parameters as well as the control of the solidification structure in one process.¹ In electroslag remelting, a self-consuming electrode is remelted by a slag to form a new ingot in a water-cooled mould, whereby the heat required for remelting is introduced by electricity in the slag via resistance heating.¹ This allows the removal of non-metallic inclusions and the removal of impurities such as oxygen to be combined with an improvement in the solidification structure and a reduction in the segregation of alloys.² The advantages are linked to high demands on the limited block weights, the complex plant technology and control, investigations and precise knowledge of the exact sequences of the metallurgical and physical processes as well as investigations into slag systems and their components.¹ A key factor in solving the challenges posed by increasing specialisation and the need for reliable metal alloys for critical components.³

At the IME Process Metallurgy and Metal Recycling, research was carried out in the field of electroslag remelting in the classic sub-atmospheric process, but also in a closed, controllable atmosphere, mainly on the alloy systems steel, nickel and titanium. In a new research step, the experience and advantages in the field of electroslag remelting are to be investigated for potential applications in the field of new alloy systems. In this approach, the decision is made to focus on the field of copper and copper alloys, as it covers various areas: a metal with significantly different properties than the alloys previously used in the ESR process, a wide range of use in various applications and a previously unexplored refining potential in the ESR process. This also involves the challenge of identifying suitable alloy systems, as an impurity such as a dissolved impurity or non-metallic inclusion has to be present for possible refining. In relation to the numerous possible copper alloys, this also results in a wide range of possibilities for the respective impurity challenges, although it must also be considered where refining of such alloys is necessary at all.

The use of copper as an electrode material also leads to the use of a new slag system due to the requirements for the slag used in electroslag remelting, caused by the

significantly lower melting point of copper compared to steel or nickel alloys. In addition to the remelting parameters, the slag used in electroslag remelting is the key factor because it enables the process through heat generation and, at the same time, the high contact surface between metal and slag results in the metallurgical refining process. There are a large number of different studies on the requirements and properties of slag systems, whereby the large number of different slag components with the resulting changes in properties and the challenge of characterising and measuring the properties of molten slag still reveal a huge need for research. The slags used in practice result from empirical findings and compromises between the functions of these in relation to the knowledge that has been built up and researched.⁴ In order to expand the knowledge of slag systems, properties such as physical properties, heat transfer, electrochemical properties and chemical properties are investigated both practically and theoretically.⁴ Furthermore, process properties such as thermal stability at process temperature, viscosity and interaction of slag with metal under different atmospheric conditions are investigated using partly theoretical and empirical approaches.^{5,6}

Due to this wide range of different requirements for the process and properties of the slag, the feasibility of a remelting test of copper at the technical plant at the IME was tested in an initial approach.⁷ Based on the successful feasibility, this contribution aims to provide initial findings for possible slag systems used for copper alloys during electroslag remelting.

Materials and Methods

Depending on the application and objective, there is not only one possible slag for remelting copper and copper alloys. Depending on the alloy system, the variety of possible slag components results in an almost infinite number of combinations for a new slag system. Therefore, the aim is to take a type of starting slag that can be adapted depending on the alloying element in the feed material and the type and quantity of impurities to be removed.

The challenge for a slag for the use of copper alloys in electroslag remelting is the low melting point of copper and copper alloys. For the process, the slag must be present in a molten state so that energy can be introduced into the system and the electrode material can be melted. This is also the only way to create a liquid-liquid phase interface between the slag and the metal and thus enable the refining process to take place. An important point that has been overlooked here is that some slags contain unmelted material and are present as a suspension, which is important for later investigations with regard to non-metallic inclusions.

In principle, the conventionally available slags consist of oxides such as aluminium oxide and calcium oxide and fluorides, with calcium fluoride being widely used. In order not to introduce any other compounds such as chlorides and without taking into account the challenges involved with handling and disposing of fluorides, an oxide-fluoride system is chosen. Either systems of oxides, fluorides and mixtures of both are considered.

As an approach for the melting point reduction for the remelting of copper alloys, the basic system $\text{Al}_2\text{O}_3\text{-CaO-CaF}_2$ is used with pre-melted WACKER Electroflux products ESR 2052 and ESR 3002. The slag system was chosen because it has a wide range of applications in the ESR process and can therefore be regarded as a functional and proven state-of-the-art slag system. Another aspect is that an approach involves establishing a slag system alongside copper as a new parameter in the ESR process, based on an operative slag, also considering the resulting conventional availability.

In the first step, a mixture of the two components is used to reduce the melting point and in the second step, the amount of calcium fluoride is gradually replaced by magnesium fluoride to further reduce the melting temperature (Figure 1). Due to the complex interactions and interrelationships, an empirical test of the influence of the interaction between oxides and fluorides is investigated and at the same time not influenced by any other component due to the magnesium oxide content in the input materials.

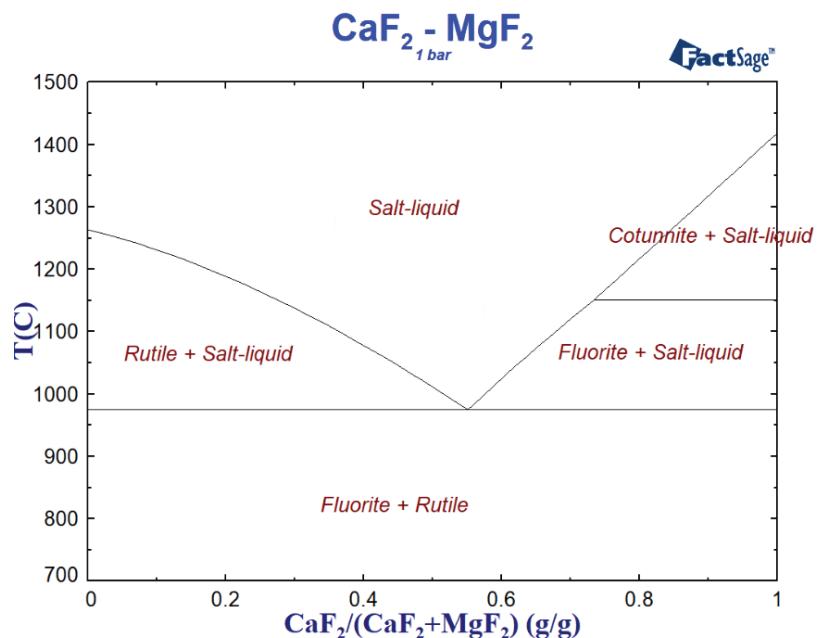


Figure 1: $\text{CaF}_2\text{-MgF}_2$ phase diagram at a pressure of 1 bar (calculated with Factsage 8.3)

In order to investigate the interaction between the slag components in a first step, mixtures are melted. For this purpose, the slags were melted in a graphite crucible in a vacuum induction furnace. Once it was visually visible that the slag had completely melted, it was poured into a steel crucible.

Results and Discussion

The slag systems were successfully melted. It has been shown that targeted temperature monitoring and adjustment required for melting the slag during the melting process is difficult and requires further modification of the setup. Thus, the temperature could not be measured during the experiments. Furthermore, it became apparent during the tests that parts of the slag evaporate when the slag is not yet completely melted, which must also be taken into account when designing the tests precisely in the future. In order to determine which components evaporate during the melting process, the condensates of the vapours must be analysed in future. This will allow for predicting and adjusting potential slag behaviour for later application in the ESR process. In addition, a partially solid residue remained at the bottom of the crucible after pouring, which also requires a closer examination of the mixing and melting behaviour of the feed components.

Table 1 shows the input mixtures used for the experiments with the respective results for aluminium calcium and magnesium via inductively coupled plasma optical emission spectrometry and for fluorine via ion-selective electrode. Homogeneous samples from the cast material from the mould were used for the analysis. It can be seen that with increasing additions of magnesium fluoride, the proportions of aluminium and calcium decrease, while the contents of magnesium and fluorine increase. The gradients for the magnesium content in the molten slag tend to increase linearly on average, while the magnesium content increases more per trial.

Table 1: Feedstock of the VIM melting tests and analyses of the melted slag systems

No.	Input material			Composition of molten slag system			
	ESR 3002 [g]	ESR 2052 [g]	MgF2 [g]	Al [%]	Ca [%]	Mg [%]	F [%]
1	500	500	0	11.3	44.0	1.59	18.9
2	500	450	50	11.9	42.6	2.83	18.6
3	500	400	100	11.6	41.0	4.66	19.0
4	500	350	150	11.1	38.3	5.82	19.7
5	500	300	200	10.1	36.8	7.18	20.8
6	500	250	250	8.65	37.3	7.42	22.8

Conclusion

The approach of replacing calcium fluoride with a lower-melting fluoride shows that it is possible to reduce the melting temperature, but that further investigations are necessary. In addition to the chemical analysis, other properties such as the determination of the melting temperature and melting behaviour are required.

Furthermore, it seems reasonable to investigate an optimised composition in the Al₂O₃-CaO-CaF₂ system with regard to the lowest possible melting temperature and then to investigate the effect on the melting point by adding additives. A purely oxidic and fluoride-containing alternative with a change to materials that are not commonly used in electroslag remelting could probably also be investigated.

A major challenge will be not to set the requirements for the slag system too high in order to keep flexible options open, although they must be limited so that the number of options does not become too large and a possible application can ultimately be found. The challenge here is also the possibility of carrying out melting tests: While many options can be carried out in slag melting tests, carrying out experiments on electroslag remelting is much more complex in comparison.

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