Role and Effects of Slag Components in ESR Processes

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The electroslag remelting process (ESR) is a well-known refining process suitable for the production of high quality metals with advanced properties. Typical applications are the field of the aviation- or energy-sector for example. For many years the ESR process is under investigation at the IME, RWTH Aachen University. After a short review of the ESR process fundamentals, this paper gives an overview on various components used in slag systems, their necessity for and their effects on the process itself.

One of the most commonly used slag system consists of varying amounts of the components CaF₂, Al₂O₃ and CaO. It is well known that this system is suitable for a wide range of steel and nickel alloys. Additionally there are some other additives like MgO, SiO₂ or TiO₂ whose influence on refining capabilities and chemical or thermochemical behavior are stated out.

Otherwise, while focusing on the before mentioned slag system, the remelting of titanium and its alloys need different slag systems usually containing CaF₂ and varying amounts of NaF or MgF₂ for example. The influence of these components are also reviewed in this paper.

Lastly, some characteristics of the laboratory scale ESR furnace and some examples about recent research activities at the IME are presented.

1 Introduction

Steadily increasing demands on the quality of metals regarding purity and solidification structure are demanding subsequent processing steps. The reason is that the possibilities of conventional manufacturing processes are limited because of reactions of molten metal with the crucible refractory lining for example [1]. These subsequent processes belong to the special metallurgy. One of this processes is the electroslag remelting (ESR), which was originally developed for the refining of high grade steels and alloys [2]. Nowadays there is a wide range of Materials processed by this technology, including superalloys, titanium, aluminium or even copper. [3]

Materials produced by ESR can be used in many different fields of technology, for example in aerospace applications, power generation, military uses, oil and gas extraction facilities or the manufacturing of tool materials. [3][4]

The utilized slag in this process plays an important role in minimizing detrimental parameters such as nonmetallic inclusions or gas content. The refining mechanisms could be divided into physical or chemical phenomena, but even a combination between both is possible. A suitable choice of slag components can modify the slag behavior in the desired way as different components have different impacts on slag properties like electrical conductivity, viscosity or the ability to react with impurities or soluted gases. Today the most qualified materials usable for slag construction are fluorides, oxides or a mixture of both. It is important, hereby, to adjust the slag matching the properties of the remelted metal to avoid undesired reactions. [5][6][7]
2 Fundamentals

In the ESR process the metal to be refined is an electrode dipping into the slag medium. The whole process is carried out in a water cooled copper crucible. An electrical current flow is applied through the electrode and subsequently the slag medium, ingot and bottom plate of the crucible. Since the slag has a lower electrical conduction than the metal, it is heated through resistance heating up to temperatures above the liquidus temperature of the metal. A thin film of liquid metal is continuously formed at the tip of the electrode. Out of this film molten metal droplets will detach and sink through the slag medium due to their higher density. Eventually these droplets will form a liquid metal pool under the slag which is then solidified with a well-defined structure due to the high cooling rate [3]. A visual presentation of the ESR process can be seen in Figure 1.

![Figure 1: Principal functionality of the ESR process][8]

The most important refining mechanisms (besides the chemical deoxidation or desulphurization during the liquid phase of the metal) are the dissolution of impurities prior the formation of the liquid metal film, the ad- or absorption of impurities out of the liquid metal film and the precipitation and growth of new impurities during solidifying of the ingot. [9]

3 Slag systems and their required properties

The most important part of the ESR process is the (molten) slag medium itself. Some of the basic purposes are [3]

- Acting as heating element via Joule heating
- Acting as solvent for nonmetallic inclusions
- Refining the metal
- Protection of the liquid metal from atmosphere

Moreover it is widely accepted that every slag system should have basic properties, some of which are listed below: [2][10]
- Slightly lower liquidus temperature than the metal
- Sufficient thermal stability at process temperature
- Appropriate electrical and thermal conductivity
- Low viscosity

The purposes of the solid slag skin between ingot and mould are different from these ones of the liquid slag bath and are therefore excluded in this paper.

As mentioned above, the choice of components in a used slag has to be adjusted to address different metals and their corresponding specific characteristics such as oxygen affinity for example. There are many materials suitable as slag components but almost all slags have the basis calcium fluoride (CaF₂). Regarding the remelting of titanium and its alloys, the slag consists nearly completely of pure CaF₂. The two most common additives are lime (CaO) and alumina (Al₂O₃) [2]. Figure 2 shows the ternary phase diagram consisting of these three ingredients. [11]

![Figure 2: Ternary phase diagram CaF₂-Al₂O₃-CaO [11]](image)

### 3.1 Vapor pressure

Due to the high process temperatures, the vapor pressure plays an important role in adjusting slags for the ESR process. The utilized components must not evaporate at prevalent temperatures so their corresponding vapor pressure should be low. CaF₂ has the lowest vapor pressure of all fluoride components which could be used for the ESR process and is in combination with the positive effect on the liquidus temperature the most used fluoric component. But other fluorides like BaF₂ and MgF₂ can also be used because their vapor pressure are not significantly higher. Negative aspects of the usage of CaF₂ are the low viscosity and high electrical conductivity (see chapters 3.2 and 3.3) which have to be kept in mind regarding remelting of steel or nickel-based alloys. In these cases oxide components have to be added to CaF₂, which are mostly Al₂O₃ (viscosity, el. conductivity) and CaO (basicity, desulphurization). This explains
the wide usage of this slag system. Nevertheless the vapor pressures of these additives have also be sufficiently low. Figure 3 shows the vapor pressure of different oxides as a function of temperature. It can be seen that the vapor pressures of oxides used in the ESR process are sufficiently low. [10]

Figure 3: Vapour pressures of different oxides compared to CaF$_2$ [10]

3.2 Viscosity

The viscosity is generally viewed as the degree of friction between two interacting layers of liquids. Since molten slags are considered to be ionic liquids, the viscosity is strongly dependent on the size of the slag ions as well as the electrostatic interactions. [13]. The easiest and most common way to describe the phenomenon of viscosity is the tendency of a pure SiO$_2$ melt to form three-dimensional SiO$_4^4$ tetrahedral networks. In these melts the silicon atoms respectively the tetrahedrons are bonded through so called bridging oxygen where the oxygen is electrically neutral. Pure SiO$_2$ melts have a very high viscosity which can be decreased by adding basic oxides because of their tendency to break the silicate network into smaller entities. This breakdown leads to an increase in electric negative O$^2$-ions, so called free oxygen. Free oxygen ions have a higher mobility within the melt which is resulting in a lower viscosity. More precisely, the cations of basic oxides, e.g. Ca$^{2+}$ or Na$^{2+}$ are responsible for the breakdown of silicate networks as they tend to form bonds with the bridging oxygen of the network-tetrahedrons in the form of O$^2$ -- Ca$^{2+}$. There are some elements with an amphoteric character whose cation can be integrated into the silicate network but need other cations in their immediate neighbourhood to provide electrical neutrality. [12]

In the ESR process, however, slags are compiled mostly on a basis of CaF$_2$. The amount of silica, if it is added at all, is relatively small. Fluoric ions show the tendency to act as networking breakers [14] so the viscosities of melts on fluoric basis are relatively small, see Figure 4 for an example of a simple CaF$_2$ melt. This figure shows the effect of the addition of varying amounts of just Al$_2$O$_3$ which is of particularly interest regarding typically used ESR slags.
Figure 4: Viscosity of pure, liquid CaF$_2$ and its change as a function of the amount of Al$_2$O$_3$ [15]

The viscosity of liquid slag systems is temperature dependent. In [11] it can be seen that it decreases significantly in the temperature range of 1350 to 1375 °C while the intensity of this decrease depends on the amount of CaF$_2$. A further increase of temperature has still its impact on viscosity, but not that strong. This observation is confirmed in [14] but it has to be noted that this study investigated fayalitic slag systems with an eye on the CaF$_2$-content. The temperature dependence of molten slags can be described by the Arrhenius-relationship as follows: [16]

$$\eta = A_\eta \exp\left(\frac{E_\eta}{RT}\right)$$

(1)

$\eta$ = viscosity, $A_\eta$ = frequency factor, $E_\eta$ = activation energy for viscous flow, $R$ = gas constant, $T$ = temperature

Kato et al. [16] investigated slags with varying amounts of CaO, SiO$_2$ and Al$_2$O$_3$. They conclude that the activation energy for viscous flow increases with the addition of Al$_2$O$_3$ and SiO$_2$ but decreases with the addition of CaO. This fits the before mentioned characteristics of several slag components and can explain the increase in viscosity shown in Figure 4 as Al$_2$O$_3$ is amphoteric but acts as network builder in fluoric slags whereas CaO works as network breaker. Their results also indicate the decrease of viscosity with the addition of several fluoride compounds whereby CaF$_2$ is the most efficient one followed by MgF$_2$, AlF$_3$ and NaF.

Two parameters are directly influenced by the slag viscosity which makes knowing the effects of additions mentioned above very important. On the one hand a low viscosity promotes a high stirring of the slag bath mainly due to electromagnetic forces. This makes it easier to reduce the gas content of the slag at the interface of slag and
gas/atmosphere. The second point of importance regards the velocity of the molten metal droplets through the slag bath. For a sufficient amount of time that the droplet needs to stay in the slag medium for an optimal refining the viscosity should be in a specified range and not be too low. [10]

3.3 Electrical Conductivity

The necessary heat for remelting metals via ESR is generated through Joule heating, see equation 2. [10] Therefore choosing a slag has to be carried out in regard to its electrical conductivity. Some papers postulate that this conductivity of pure, liquid CaF₂ is too high [17] so that the slag cannot be heated sufficiently. Otherwise remelting of titanium and its alloys is carried out under nearly pure CaF₂ which proofs that it is indeed possible. [18][19] However, the electrical conductivity can be adjusted by adding different ingredients to the slag. This plays an important role regarding the energy efficiency of the remelting process as a high electrical conductivity lead to an insufficient heat generation.

\[ I = \frac{V \cdot A_{eff} \cdot x}{l} \quad (2) \]

\( I \) = current, \( V \) = potential across slag, \( A_{eff} \) = effective cross-sectional area of resistor (in this case the slag bath), \( x \) = specific electrical conductivity, \( l \) = length of resistor (slag bath)

Hara et al.[17] investigated different Additives and their impact on the electrical conductivity of CaF₂. They observed a decrease in conductivity when adding those Additives. The strongest influence, according to the authors, in terms of a decrease have acidic oxides, \( \text{Al}_2\text{O}_3 \), \( \text{ZrO}_2 \) or \( \text{TiO}_2 \) for example followed by \( \text{BaO}, \text{MgO} \text{ BaF}_2 \) and \( \text{MgF}_2 \), in that order.

As can be seen in Figure 5 only CaO has a negative impact on the electrical conductivity of CaF₂. Chiho et al. [20] investigated some more additives but in contrast to Hara et al. they carried out their experiments directly on slags used in the industry.
(CaF$_2$-Al$_2$O$_3$ and CaF$_2$-Al$_2$O$_3$-CaO). The results can be seen in Figure 6. Compared to the results of Hara et al. they confirmed the behavior of TiO$_2$ and MgO when adding more than one mass-% of either ingredient. But at lower contents these oxides first increases the electrical conductivity to a certain peak and would therefore have a negative effect on the energy efficiency of the ESR process. When looking at elements like FeO (not depicted here) or MnO they found an overall increase in conductivity of molten Slags with the before mentioned composition. It has to be stated out here that the results in Figure 5 are given for mol-% whereas those ones in Figure 6 are in mass-%. So they have to be converted for a directly comparison but are suitable to show the general behavior of additions regarding the specific elements.

Investigating a silica-based slag, Segers et al. [21] found that a substitution of CaO with MgO, at a fixed amount of other ingredients has no significant effect on the electrical conductivity. Otherwise a substitution of SiO$_2$ with Al$_2$O$_3$ leads to a significant drop in conductivity. When Si is present in metals, there will be a formation of SiO$_2$ in the ESR process, according to the equilibrium between Si, Al and O at given temperatures (see eq. 10, chapter 3.5).

Due to the highly interdependent character of the ESR process and the continuous loss of slag to the slag skin the electrical conductivity changes during the process. This is particularly interesting whilst remelting steels or iron alloys, as iron is continuously oxidized. The iron oxide subsequently alters the electrical conductivity as mentioned above. [20] Besides these effects, desired reactions of the ESR process should be taken into account. The desulphurization is one of those reactions. CaO is widely used as slag ingredient because of its strong affinity to react with Sulphur to form CaS. On the other hand, CaS leads to a decrease in electrical conductivity. [17] Lastly, it is known that the dependency of the electrical conductivity, comparable to the viscosity, and temperature follows an Arrhenius relationship, which leads to a decrease of the conductivity at high temperature, especially at those ones needed for the ESR process.

### 3.4 Basicity

The basicity is a measurement of the mass of basic acting components related to the mass of acidic acting ingredients of slag systems. This relationship plays an important role regarding refining characteristics, the desulphurization for example. Traditionally the basicity is described by the ratio CaO/SiO$_2$. Basic acting oxide components tend to disintegrate into their cations and oxygen-anions (Ca$^{2+}$ and O$^{2-}$ for example). The amount of free O$^{2-}$-ions will therefore increase with increasing basicity of the slag. [22]

One problem with describing slags through the silicate network theory (see chapter 3.2) is the disregard of varying influences of different slag cations. To address this problem, the so called optical basicity $\Lambda$ has been introduced. With the help of this optical basicity the structure of a slag can also be described. Furthermore it considers the different influences of different slag ingredients. It can be expressed as follows: [12]

$$\Lambda = \frac{\sum(X_1n_1A_1+X_2n_2A_2+X_3n_3A_3+\cdots)}{\sum(X_1n_1+X_2n_2+X_3n_3+\cdots)}$$  

$\Lambda$ = optical basicity, $X$ = mole fraction, $n$ = amount of oxygen atoms in an oxide (e.g. n=2 for SiO$_2$)

If there are cations in a network which need a balancing of electrical charge through other cations, there will be introduced correction terms which need to be taken into
account. Usually the mole fraction of the element which is needed for balancing another element is subtracted from the mole fraction of the element which is in need of this balancing. Is, for example, Al₂O₃ the element which will be balanced with BaO the following correction term occurs: [12]

\[ X_{BaO}^{korr} = (X_{BaO} - X_{Al_2O_3}) \] (4)

\[ X^{korr} = \text{correction term, } X = \text{mole fraction} \]

It has to be mentioned here, that the authors does not give any information on how these two equations are related to each other.

The basicity is practically important regarding the oxygen content of steels or burn off of alloy elements like manganese. Both parameters decrease with increasing basicity as can be seen in [6]. Contrarily silicon will be increased with increasing basicity which can has therefore a maximum value. With regard to other parameters like the electrical conductivity this basicity maximum will also be reasoned. Moreover, Birol et al. [23] found out that the electrical conductivity is directly related to the optical basicity such that both parameters will increase if one of these parameters increases.

### 3.5 Influence of additives on the materials quality

The aim of the ESR process is to increase the quality of the desired metals/alloys. Due to different activities of every participating element in this process interactions between certain elements are unavoidable. This can be undesired in terms of alloying elements but regarding impurities these interactions are of a very important nature. Simplified, the activity of a certain element is the degree of its “free” concentration within a metallic melt. This concentration is available for chemical reactions but it has to be noted that activities are dimensionless per definition. The activity of a certain element in a multicomponent, liquid alloy can be expressed as: [22]

\[ a_i = \gamma_i x_i \] (5)

\[ a_i = \text{activity, } \gamma_i = \text{activity coefficient, } x_i = \text{mole fraction} \]

If the desired metal/alloy can be considered as a diluted solution, the activity coefficient can be expressed as a fixed activity coefficient \( f_i \), whereby equation 5 is changed as follows:

\[ a_i = f_i x_i \] (6)

Moreover, interaction coefficients between single elements have to be considered in multicomponent systems. This is needed to address the phenomenon that dissolved components influence each other and alter their according activities. For multicomponent systems the interaction coefficient can be expressed as [24]

\[ \log f_i = e_i [\%i] + \sum e^j_i [\%j] \] (7)

in which \( e_i[\%] \) represents the interactions parameter of an element i which is influenced by another element j, for which applies [24]

\[ e^j_i = \frac{d \log \gamma^0_i}{d[\%j]} \] (8)
Titanium is generally remelted under a slag consisting of nearly pure CaF$_2$. Because of the high oxygen affinity of this element, oxidic components cannot be used in order to prevent an oxygen pickup into the ingot. It was shown at IME in previous publishings that the ESR process can reduce the oxygen content by adding metallic calcium as deoxidizer. But it has to be noted that the addition of pure Ca leads to a pickup of Ca into the ingot.[18] It is also shown in this publishing that hydrogen can be almost entirely removed. The character of the ESR process itself leads furthermore to an even distribution of dissolved nitrogen.

In the aerospace sector, TiAl is an important alloy to decrease weight while providing high strength. But at working temperatures over 700 °C the oxidation resistance decreases significantly. To overcome this problem, besides further alloying with metals like niobium for example which is restricted to a magnitude of roughly 2 weight-% [19], there are some suggestions to micro-alloy TiAl with fluorine. [25] Nafziger [26] gives some examples which fluorine-containing components are worth considering to overcome this challenge. Some of these suggestions are CaF$_2$, MgF$_2$, BaF$_2$ or LaF$_3$. The ESR process indeed can help to carry out this fluorine pickup but not by using pure CaF$_2$ which has no [19] or just a small effect. [18] Spiess et al. [19] tried to substitute CaF$_2$ with MgF$_2$ and observed a small increase in fluorine pickup which is not enough to have a noticeable effect on the oxidation resistance. Thereupon they proposed the usage of NaF for fluorine pickup due to its more positive delta H value. This has to be further investigated.

With regard to Ni-based superalloys or steel the slag systems usually differs from that used for titanium. Though the base component is CaF$_2$ as well, varying amounts of Al$_2$O$_3$ or CaO are added to increase the effectiveness of the process and to enhance chemical refining. With the addition of CaO to the slag, not just the basicity will be raised but also the sulphur content of the metal will be lowered. Due to the high affinity of Ca for sulphur, an exchange reaction as follows will be fostered: [27]

$$[S] + (CaO) = [O] + (CaS)$$ \hspace{1cm} (9)

\[\] = diluted in the metal, (,) = liquid

It should be mentioned here that this reaction needs a low oxygen activity which is no problem in the ESR process. With this reaction, the achievable sulphur can be lowered beneath 0.004 weight-% which is needed for maraging steel for example. [28] To achieve this low content, a sufficient amount of CaO should be added to the slag. Miska [29] proposed that this content should around 24 weight-%. During the remelting operation the slag enriches with CaS and is not saturated at the end of remelting.

Another possibility of desulphurization is the utilization of rare earth elements as slag components. The reason is their high affinity to sulphur as it is reported in [30] or [31]. A practical investigation on the desulphurization characteristics was carried out in [32] where slag systems containing either CaO or CeO$_2$ were used. Every slag was able to reduce the Sulphur content, regardless which constituent was used. The usage of CeO$_2$, however, resulted in the lowest Sulphur contents.

Furthermore, rare earth oxides can be used as a substituent for Al$_2$O$_3$ as can be seen in the work of Mitchell. [33] This is due to the fact that rare earth oxides show a similar behavior regarding the electrical conductivity and leads to a decrease in that conductivity, like Al$_2$O$_3$ does. Moreover they show the behavior of forming complexes
with oxygen and sulphur which decreases the sulphur content in the remelted metal as stated out above.

The oxygen content is related to the content of \(Al_2O_3\) in the slag. The addition of rare earth oxides can reduce its content to a certain level according to [34]. This is due to the lowered activity of \(Al_2O_3\). “Classic” components like MgO can help to reduce the oxygen content of the ingot. In coherence with a relatively high content of rare earth oxides the decomposition of MgO into magnesium and oxygen is not as strong as the decomposition of \(Al_2O_3\) which leads to a lower oxygen content.

Typically the alloy which shall be remelted has a low oxygen content. As long as there are no strong deoxidizing agents within the slag system, this content is not really influenced. What is influenced, however, is the amount of alloyed elements like titanium or silicon which depends on the amount of certain slag components. It was found that aluminium and silicon as well as aluminium and titatnium react with each other in order to reach a chemical equilibrium. Investigating steel, Radwitz et al. [35] showed that equation 10 will occur during ESR processes, using CaF\(_2\)-\(Al_2O_3\)-CaO slags, as long as there are small amounts of SiO\(_2\) residues in the slag. The result of this equation is a loss of silicon in the steel and a pickup of aluminium.

\[
3 [\text{Si}]_{\text{steel}} + 2 [\text{Al}_2\text{O}_3]_{\text{slag}} \leftrightarrow 4 [\text{Al}]_{\text{steel}} 3 [\text{SiO}_2]_{\text{slag}} \tag{10}
\]

Pateisky et al. [5] compiled a similar equation for the reaction of titanium with aluminium:

\[
3 [\text{Ti}]_{\text{steel}} + 2 [\text{Al}_2\text{O}_3]_{\text{slag}} \leftrightarrow 4 [\text{Al}]_{\text{steel}} 3 [\text{TiO}_2]_{\text{slag}} \tag{11}
\]

These two reactions make it clear that the chemical composition of an alloy can be controlled with a suitable choice of slag constituent. Adjusting the slag in order to reduce or rise specific activities can result in no loss or pickup of alloying elements under or above certain limits. Moreover the pickup of undesired elements can be prevented.

4 Conclusion

The utilized slag system in the ESR process plays an important role for the process efficiency on the one hand and the refining of the desired metal / alloy on the other hand. The choice of suitable additives can adjust properties of the slag system towards more efficient electrical conductivity or viscosity. The chemical refining abilities can also be influenced in that way that proper degassing or desulphurization can take place. But even the loss of alloying element can be prevented by conditioning the slag with certain additives. These highly flexible possibilities of adjusting slag systems make the ESR process a suitable and versatile way to produce high quality materials.

5 Presenting the Institute for Process Metallurgy and Metal Recycling (IME)

The institute under the guidance of Prof. Dr.-Ing. Dr. h. c. Bernd Friedrich has a wide range of experience regarding the ESR process. The basis therefore is the operation of two laboratory scale ESR furnaces at the institute, one of which is a classic open atmosphere ESR, the second one a closed chamber ESR. The latter is capable of remelting electrodes under vacuum conditions or (pressurized) inert gas atmosphere.
up to 50 bar. Both furnaces can be seen in Figure 7, Table 1 shows some important operating parameters.

Figure 7: The pilot scale ESR and (P)ESR furnaces at IME

Table 1: (P)ESR parameters at IME

<table>
<thead>
<tr>
<th>Technical Data</th>
<th>Molds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transformer with 2 taps</td>
<td><strong>ESR</strong></td>
</tr>
<tr>
<td>(1) $U_{\text{max}} / I_{\text{max}}$</td>
<td>85 / 5</td>
</tr>
<tr>
<td>(2) $U_{\text{max}} / I_{\text{max}}$</td>
<td>66 / 6</td>
</tr>
<tr>
<td>$P_{\text{max}}$</td>
<td>~ 400 kW</td>
</tr>
<tr>
<td>Control and data logging</td>
<td>ALD</td>
</tr>
<tr>
<td>$P_{\text{operation}}$</td>
<td>up to 50 bar</td>
</tr>
<tr>
<td>$\phi_{\text{electrode}}$</td>
<td>~100 – 110 mm</td>
</tr>
<tr>
<td>(P)ESR</td>
<td></td>
</tr>
<tr>
<td>160 – 180 x 890 mm</td>
<td></td>
</tr>
</tbody>
</table>

In the recent years many research projects were carried out at IME in order to get a deeper understanding of the process itself, interactions between participating components (metal, slag etc.), kinetics and so on. Some examples for these research activities are listed below.

- Synthesis of high-strength steel
- Deoxidation of oxygenous TiAl
- Refining of titanium scrap
- Influence of process parameters
- Investigation of slag systems
When the electrodes are not provided by project partners, the IME is able to cast its own electrodes out of scrap material or pure components. The furnace for such casting operations is a 100 kg vacuum induction furnace. Molds are either made of grey cast iron or are water cooled copper molds. The workshop of the institute combines two of these ingots and weld a stub on them to produce a full ESR electrode. After the ESR process the ingot can be grinded down to a specific diameter and is able to function as a subsequent electrode for the vacuum arc remelting (VAR) process which is also operated at IME. With these furnaces it is possible to carry out the whole so called triple melt process on a laboratory scale. This can provide outstanding possibilities if it is not desired or possible to investigate these processes on an industry scale.

References


