

## **THE INFLUENCE OF THE SLAG COMPOSITION ON THE DESULFURIZATION OF NI-BASED SUPERALLOYS**

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### **Abstract**

The presence of sulfur in Ni-based superalloys is known to have detrimental effects on the oxidation resistance and the stress-rupture life of the final product. In most cases, sulfur originates from the raw materials, foremost nickel, iron and chromium. To decrease the concentration of sulfur to subcritical values below 10 ppm, it is common to perform an addition of NiCa and/or NiMg during primary melting in a vacuum induction furnace. As both calcium and magnesium display a significant degree of evaporation at the given process temperatures and pressures, the efficiency of this practice of desulfurization is comparably low and contamination of the furnace chamber by evaporated Ca or Mg can occur. Furthermore, the sulfidic products deposit on the crucible walls and may contaminate subsequent melts.

Hence, an alternative approach of removing sulfur during a pressure electroslag remelting step using different slag compositions and additives is currently under investigation at IME, RWTH Aachen University. The objective of this method is an increase of efficiency of the desulfurization by controlling activity levels and allowing for the use of low-grade, sulfur containing raw materials even for the production of high performance alloys. Moreover, remelting in a water-cooled copper crucible overcomes the issues caused by the interaction between NiCa/NiMg and the refractory material. In a first step, the effect on the desulfurization of slag mixtures containing varying amounts of metallic calcium or cerium oxide was studied experimentally. Several electrodes of alloy 718 were remelted in a 400 kW lab scale electroslag remelting unit at IME. The chemical composition of the metal and the adherent slag skin was analyzed in different heights of the ingot to illustrate the distribution of sulfur, calcium and cerium as a function of the process time. Furthermore, a structural investigation of selected slag and metal samples via SEM-EDX was carried out to obtain additional information about the mechanism of desulfurization. This paper presents the results of the conducted trials and the subsequent analyses. Finally, an outlook on intended investigations to further improve the removal of sulfur in the electroslag remelting process is given.

### **Introduction**

Since the development of the first nickel-based superalloys in the middle of the 20<sup>th</sup> century, various researchers have identified and studied several detrimental effects of sulfur on this class of materials. [1-5] Especially in alloys used for high temperature applications, the presence of sulfur is very critical as it forms low melting Ni<sub>3</sub>S<sub>2</sub> grain boundary films that lead to hot shortness even at low concentrations. Consequently, melting techniques like the addition of NiCa and NiMg in vacuum induction melting (VIM) had to be implemented to reduce the sulfur content below critical values and to modify the morphology of the

remaining sulfur into spherical and therefore less harmful MgS particles. [2,3] However, these practices can adversely affect the lifetime of the oxidic refractory lining due to the high oxygen affinity of calcium and magnesium. [6] Furthermore, the formed sulfides deposit at the crucible walls and can be absorbed by subsequent melts if the amount of desulfurization agents is not adjusted correspondingly. [7]

In consideration of the limits of desulfurization in VIM and the restrictions concerning the use of elements that change the morphology of sulfur in nickel-based superalloys, an alternative method of enhanced desulfurization in the electroslag remelting (ESR) process is currently under investigation at IME, RWTH Aachen University.

### **Fundamentals**

The ESR process is widely known to remove sulfur from nickel- and iron-based alloys. [2,6,8] Under inert gas atmospheres, the removal of sulfur is governed almost exclusively by the initial composition of the slag. To quantify the amount of sulfur that a slag can absorb, Kor and Richardson [9] have introduced a so-called sulfide capacity  $C_s$ , which was later modified by Hoyle [10], who stated that the sulfide capacity is defined uniquely by the composition of the slag. For various mixtures within the system  $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3$  the sulfide capacity was experimentally determined [9], but outside this common slag system, little information can be found with regard to the impact of slag constituents on the desulfurization.

Concerning the addition of oxidic and fluoridic compounds, the utilization of rare earth (RE) oxides up to levels of 40 wt.-% was found to have a beneficial influence on the removal of sulfur in the ESR process. The addition of RE elements in metallic form is generally feasible, too, but proved to be less efficient. [11] Due to its comparably high availability, cerium is the most common RE element for deoxidation or desulfurization purposes in metallurgy, often also used in the form of Ce-La mischmetal. [12] Experimental and theoretical investigations regarding the utilization of metallic cerium in VIM have shown that cerium forms stable oxides, sulfides and oxysulfides in the presence of oxygen and sulfur. [13] Pal et al determined the partition ratio between ceria-containing  $\text{CaF}_2$ -based fluxes and carbon-saturated iron in VIM and virtually no pickup of cerium by the metal was observed. [14] So far, no information about the mechanism of sulfur removal by  $\text{CeO}_2$  in ESR slags has been found in literature, but based on the above-mentioned results from investigations in VIM it is assumed that the slag absorbs the sulfur from the electrode in the form of thermochemically stable cerium oxysulfides.

As discussed above, the addition of metallic elements to ESR fluxes is generally feasible and presents a further method to increase the efficiency of desulfurization. Here, calcium is expected to show promising results, as it has already proven to be capable of removing sulfur in VIM. Furthermore, the general feasibility of remelting under calcium containing slags has already been demonstrated. [11,14-17]

### **Experimental Work**

The experimental investigations in the present work involved fabricating electrodes by vacuum induction melting, their subsequent remelting by chamber ESR as well as the sampling and analyzing of metal and slag after the trial. As the current stage of the investigation was exclusively focused on the influence of the slag chemistry on the desulfurization of the metal, aspects like energy efficiency, the loss of titanium due to oxidation and the economic feasibility of the slag constituents were disregarded in these trials.

### Fabrication of Electrodes by Vacuum Induction Melting

Seven electrodes of alloy 718 with 110 mm diameter and circa 600 – 800 mm length were cast in a 100 kg vacuum induction furnace at IME. Their compositions were within the specification limits of alloy 718 according to AMS 5562, only the sulfur content was adjusted to approximately 50 ppm to simulate the use of high sulfur containing raw materials.

### Electroslag Remelting

The remelting of the electrodes was carried out in a 400 kVA pressure electroslag remelting furnace with an average crucible diameter of 170 mm. An industrial process control unit ensured constant remelting conditions and allowed for the subsequent evaluation of the respective process characteristics. According to the findings in the preliminary work,  $\text{CaF}_2$ -based fluxes with additions of  $\text{CaO}$ ,  $\text{CeO}_2$  and metallic calcium were chosen for the study of desulfurization. To quantify their potential for sulfur removal, seven  $\text{CaF}_2$ -based slag mixtures with different combinations of these substances were prepared and used as process slags in the electroslag remelting process.

Two preliminary tests were carried out with quasi-binary mixtures of  $\text{CaF}_2/\text{CaO}$  and  $\text{CaF}_2/\text{Ca}$  (trials D1 and D2). As the mixture of  $\text{CaF}_2$  and Ca did not show sufficient efficiency of desulfurization despite a significant Ca-pickup of the ingot at the same time, Ca was thereafter only used in lower concentrations and in combination with  $\text{CaF}_2$  and  $\text{CaO}$  (trials D3 and D4). According to thermochemical calculations by FactSage 6.2,  $\text{CaO}$  decreases the activity of calcium in  $\text{CaF}_2$  and was therefore supposed to minimize the solution of Ca in the metal. In D5 to D7, the influence of  $\text{CeO}_2$  as a slag additive was investigated. Apart from D2 and D7, in all trials a  $\text{CaF}_2/\text{CaO}$  ratio of 4:1 was chosen to allow for a certain comparability of the results. The nominal composition of the utilized slag systems is given in table I.

Table I: Nominal Composition of the Utilized Slag Mixtures

<b>Trial</b>	<b><math>\text{CaF}_2</math> / wt.-%</b>	<b><math>\text{CaO}</math> / wt.-%</b>	<b>Ca / wt.-%</b>	<b><math>\text{CeO}_2</math> / wt.-%</b>
D1	80	20	-	-
D2	95	-	5	-
D3	79,6	19,9	0,5	-
D4	78,4	19,6	2	-
D5	76	19	-	5
D6	64	16	-	20
D7	80	-	-	20

As calcium shows a significant vapor pressure at the given process temperature, the remelting was carried out under an atmosphere of 5 bar argon to minimize the evaporation. Consequently, all trials were conducted under that atmosphere to eliminate possible deviations in the results due to differences in the furnace pressure.

Despite the elevated pressure during ESR, calcium losses occur during the process due to evaporation, dissolution in the metal and reaction with S to form  $\text{CaS}$ . To compensate for these losses and to hold the activity of calcium constant, in D3 and D4 a mixture of 50 wt.-% Ca, 40 wt.-%  $\text{CaF}_2$  and 10 wt.-%  $\text{CaO}$  was fed into the slag during the melt by a screw conveyor. Pure calcium could not be used, as its morphology would have led to a choking of the screw conveyor. The expected Ca-losses due to evaporation were calculated beforehand with the aid of a model introduced by Stoephasius and Reitz in [15], whereas the losses due

to dissolution in the metal and reaction with S were estimated in consideration of the results from D2 and the given sulfur content of the electrodes.

#### Chemical Analysis of Slag and Metal

After the remelting trials, samples were taken from the produced ingots, the adhering slag skin and the slag cap on top of the ingots to observe possible changes in the chemical composition. If possible, the slag skin was carefully removed in sections of 20 mm height from the bottom to the top and afterwards pulverized in a ball mill to particle sizes below 90  $\mu\text{m}$ . The powder was then analyzed by titration to determine the CaO-content, x-ray fluorescence analysis (XFA) and a carbon/sulfur analyzer. The entire slag cap was first pre-crushed in a roll crusher and then a representative fraction was milled and analyzed in the same way as described for the slag skin.

From the edge of each ingot, a 40 mm wide slab was cut and divided into specimens with an approximate height of 30 mm. These samples were analyzed via XFA and spark discharge optical emission spectroscopy (SD-OES). Additionally, chips were drilled from the center of each sample to analyze the carbon and sulfur content.

#### Structural Investigation of Selected Slag and Metal Samples

To obtain additional information, selected slag and metal samples were analyzed by scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX). For the slag samples, a LEO 440 SEM was used, whereas for the metal samples a Zeiss Ultra 55 was used. Both devices were equipped with an EDX-unit by Oxford. Prior to the measurements, the slag samples were sputtered with palladium to avoid an electric charging of the samples. To ease the identification of particular areas with changes in the element distribution, backscattered electron imaging (BSE) was applied in most cases. Here, the local brightness of the picture increases with the atomic number of the existent elements. To determine the local composition of remarkable areas on the samples, integral as well as spot measurements were conducted.

## **Results**

#### Observations

In the course of remelting, significant differences between the utilized slag systems were observed with regard to furnace operation: While the addition of  $\text{CeO}_2$  to the slag didn't have an apparent effect on the process variables, the use of metallic calcium as a slag component caused a considerable decrease of the slag's specific electrical resistivity and severe fluctuations in the electrical parameters like the voltage and the current.

After opening the reactor, in all trials flue dust was found on top of the water-cooled copper mold, but in those with metallic calcium as a slag constituent, the amount was significantly higher. Furthermore, only in these trials a severe formation of sparks could be noticed during the stripping of the ingots. Beyond that, the surface quality of the ingots that were produced using the calcium-containing slag was inferior to the other ingots, which was presumably caused by the formation of a thicker slag skin between the ingot and the water-cooled copper mold.

#### Results of the Chemical Analysis

In the present investigation, the primary criteria for the assessment of the quality of the desulfurization agents are the remaining sulfur content in the ingot as well as the degree of contamination of the metal by slag constituents. Therefore, only the elements S, Ca and Ce, which are directly related to this reaction, will be discussed.

As Figure 1 illustrates, in all trials the average sulfur content was reduced below 20 ppm and in D6 and D7 even below 10 ppm. That corresponds to desulfurization efficiencies between 70 and nearly 90 percent, when the desulfurization efficiency is defined as the quotient of the removed sulfur and the initial sulfur content in the electrodes. However, due to variations in the initial sulfur content of the electrodes in trials D1 and D7, an absolute comparability between the particular experiments is not fully given. Nevertheless, it can be observed that the trials with ceria allowed for the lowest sulfur contents in the final ingots.

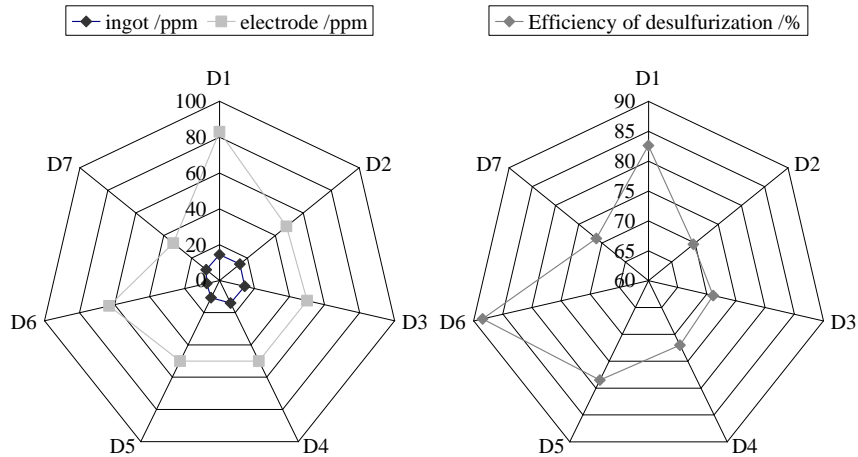


Figure 1: Left: average sulfur content in the metal before and after remelting (in ppm). Right: efficiency of desulfurization (in %).

To quantify the degree of contamination by the desulfurization agents, Figure 2 shows the contents of calcium and cerium in the ingots. In all trials, only the respective desulfurization agent could be found in the metal, the other reagent was below the detection limit. With average Ca contents between 38 and 535 ppm, significant differences in the degree of contamination were observed in the trials with metallic calcium, whereas the pickup of cerium in trials D5 to D7 was more uniform with 200 to 330 ppm.

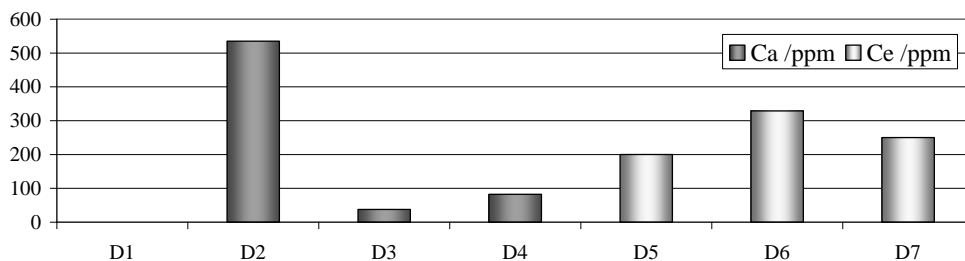


Figure 2: Average content of Ca and Ce in the ESR ingots.

### Results of the Structural Investigation

Due to the elevated cerium content in the metal, a structural investigation of selected slag and metal samples was conducted to obtain additional information about the mechanism of the cerium pickup. Figure 3 shows two backscattered electron images of samples from the slag skin in trial D7. The left sample corresponds to a height of approximately 110 mm in the ingot, the right sample was taken at 240 mm. In the left picture, which is representative for the overall appearance of the sample, a nearly homogeneous looking, smooth ground layer (A) with coexisting extensive brighter (B) and darker areas (C) on top can be observed. The approximate composition of these areas was locally determined by EDX spot measurements

and is given in Table II. According to the atomic mass, the brighter areas contain high amounts of cerium, whereas the darker areas mainly consist of Ca and F. In the second sample, corresponding to a height of 240 mm in the slag skin, instead of the extensive bright areas only few bright spots with very limited spatial extension can be found. The right image, which was taken at a higher resolution, shows the structure of these bright spots, which predominantly seem to form near hair-line cracks in the ground layer. The chemical composition of the ground layer is given in Table II as D and approximately matches the composition of the ground layer in the first sample.

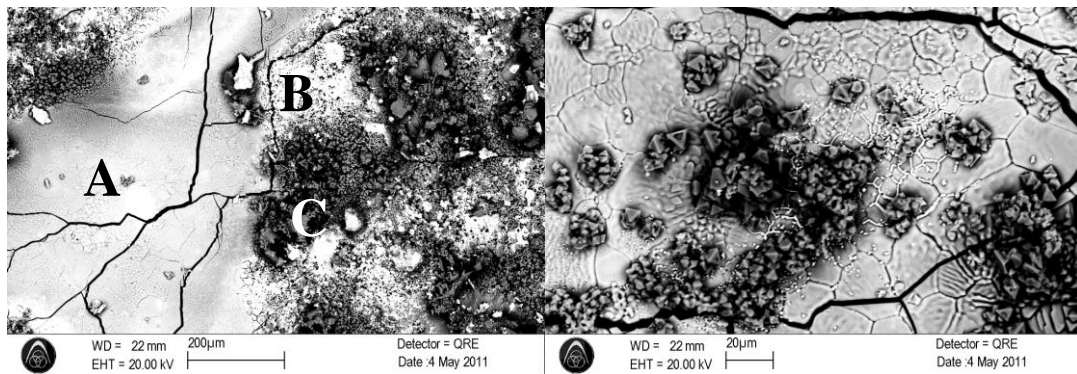


Figure 3: SEM backscattered electron images of the slag skin in different heights (left: ~ 110 mm; right ~240 mm)

Table II: EDX Spot Measurements of Selected Areas

Area	Element					
	O	F	Al	S	Ca	Ce
A	2.94	49.33	-	-	36.51	11.21
B	13.06	11.48	1,84	0.35	11.97	61.31
C	-	43.63	-	-	56.37	-
D		42.75			44.29	12.96

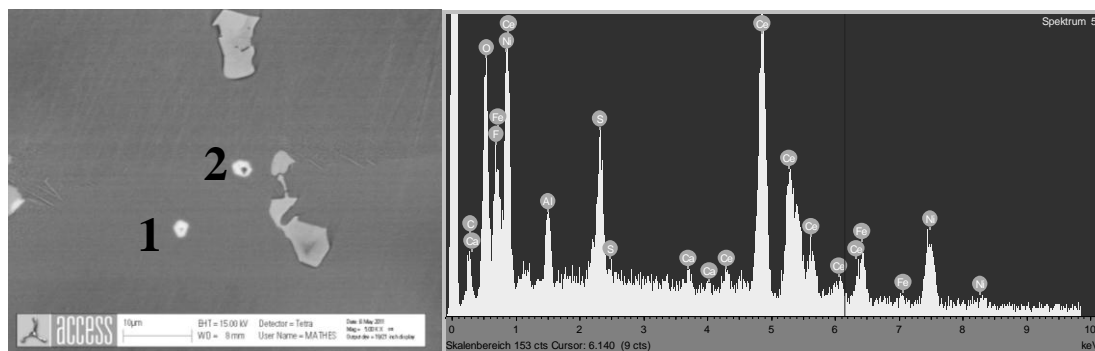


Figure 4: SEM backscattered electron image of a metal sample with corresponding element spectrum

The SEM analysis of ingot D7 revealed the existence of cerium-containing, non-metallic inclusions that often contained significant amounts of O, Ca, F and S. The SEM backscattered electron image in Figure 4 shows two of these inclusions, marked by the numbers 1 and 2. On the right, the corresponding element spectrum of inclusion 1 is given.

### Discussion

With regard to the removal of sulfur from the electrodes, the ceria containing slags proved to be most efficient, whereas the combination of 20 wt.-% CeO<sub>2</sub> and 16 wt.-% CaO (D6) leads

to even lower sulfur contents in the metal than the quasi-binary mixture of  $\text{CaF}_2$  and 20 wt.-%  $\text{CeO}_2$  (D7). This can either be attributed to the additional reaction of  $\text{CaO}$  with  $\text{S}$  to form  $\text{CaS}$  or to the increased activity of  $\text{CeO}_2$  as shown in the ternary iso-activity diagram by Wang et al [18]. The increased activity of ceria could also be responsible for the higher cerium level in ingot D6 compared to D7. The structural investigation of the slag skin from D7 leads to the conclusion that at least in this trial predominantly a slag layer of  $\text{CaF}_2$  with approximately 12 wt.-%  $\text{Ce}$  solidified first, followed by a layer in which  $\text{Ce}$ - and  $\text{CaF}_2$ -rich phases formed. Whilst in the lower part of the slag skin extensive bright areas with high cerium levels were found, only a few very small, bright particles existed in the upper region of the slag skin. The cause for this structural change might be a depletion of the slag due to the transfer from cerium to the metal in the cause of the melt. This is supported by the chemical analysis of the metal, as the contamination in the lower part of the ingot was with 300 ppm higher compared to 200 ppm in the upper part. There is virtually no difference in the sulfur content in the metal samples (10 ppm in the lower part and 9 ppm in the upper part). In light of this, it might be favorable to avoid the formation of particles high in cerium by lowering the ceria content in the slag to an optimum level. Anyhow, the existence of cerium-containing, non-metallic inclusions in the ingots generally discourages the use of ceria as a slag component, as their high density ( $7.13 \text{ g/cm}^3$  for pure  $\text{CeO}_2$  [19]) hinders their removal by vacuum arc remelting (VAR). However, the observations that many of the inclusions contained significant amounts of sulfur and that the sulfur content in the metal was considerably decreased support the statement by Li et al [13] that cerium forms stable sulfides and oxysulfides and is therefore an effective desulfurization agent from a thermochemical point of view.

In the present investigation, the desulfurization with metallic calcium as a slag constituent was least efficient and the sulfur content did not fall below 10 ppm in any sample, although particularly in trial D2 a significant pickup of calcium by the metal occurred. Whereas the calcium pickup of the metal could be successfully reduced by lowering the concentration of  $\text{Ca}$  in the slag and decreasing the calcium activity by the addition of  $\text{CaO}$ , the desulfurization efficiency could not be influenced by these measures. As the transport of  $\text{Ca}$  into the metal does not seem to be the limiting factor for the removal of sulfur, further investigations have to be carried out to identify the relevant parameters. As the use of calcium was linked with unstable remelting conditions and non-uniform ingot surfaces, there is also the need for optimization with regard to the general usability of this slag system for ESR.

### Conclusions

The results of the present investigation show that both cerium oxide and calcium are generally feasible for the desulfurization of nickel-based superalloys. However, both slag constituents lead to a significant contamination of the ingots and it has yet to be investigated if subsequent VAR can reduce their contents to subcritical levels. If the latter should be the case, then the slag chemistry will be further adjusted to improve the efficiency of desulfurization with preferably low contamination of the metal by unwanted constituents. The improvement of the process slag systems will be additionally supported by thermochemical calculations of the desulfurization and solution reactions. Afterwards, when the mechanism is largely understood, additional aspects of the process, such as the energy efficiency, the loss of titanium or the economic feasibility of the slag components, will be addressed.

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