Sulphur Control in Nickel-Based Superalloy Production

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Abstract

The presence of sulphur 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 the sulphur content origins from raw materials, foremost chromium and iron. To decrease the concentration of sulphur to uncritical values below 10 ppm, it is common to perform an addition of Ca- and/or Mg-containing reagents during primary melting in a vacuum induction furnace. As calcium and magnesium exhibit a significant evaporation at the given process temperatures and pressures, the efficiency of this practice of desulphurisation is limited and a full removal of sulphur by this melt treatment is not possible.

Therefore, a novel approach, which is based on the desulphurisation during pressure electroslag remelting using active slags with different additives, is currently under investigation at IME Process Metallurgy and Metals Recycling at RWTH Aachen University. The objective of this method lies on an increased efficiency of the desulphurization to facilitate the use of low-grade, sulphur containing raw materials for the production of high performance alloys. This paper presents the results of the first fundamental trials in technical scale and gives an outlook on the future continuation of the investigations.

1   Introduction

Various researchers have studied the influence of sulphur on the mechanical properties of nickel-based superalloys thoroughly. [1-3] According to their findings, sulphur has a tendency for grain boundary segregation and is known to cause hot shortness in nickel alloys, since it forms a eutectic Ni_3S_2 phase with a melting point of 635 °C. This detrimental sulphide phase can already be found on grain boundaries at sulphur contents as little as 10 ppm. [1] Furthermore, sulphur promotes the

segregation of niobium to the interdendritic regions and the Laves phase. On the one hand, the latter is directly detrimental for the mechanical properties and on the other hand, its formation leads to a depletion of Nb in the matrix and therefore reduces the maximal possible amount of the beneficial γ'-phase in the alloy. [4]

In general, there are three common practices to avoid material failures of nickel–based alloys due to sulphur: the control of the sulphur content in primary melting by selection of raw materials with low sulphur levels, the desulphurization by metallurgical treatment and the compensation of sulphur by elements that reduce its harmfulness. [5] At first glance, the first practice might seem to be most straightforward, but since sulphur is a ubiquitous impurity in most chromium, iron and nickel containing raw materials, there is only a limited availability of high quality resources and their price is accordingly high. The removal of sulphur from nickel-based superalloys by means of metallurgical treatment is commonly carried out by addition of Mg- and Ca-bearing reagents to the melt during vacuum induction melting (VIM). On the one hand, a certain amount of S directly leaves the melt as MgS or CaS according to equation (1) and on the other hand, Mg changes the sulphur morphology from continuous grain boundary films to spherical sulphides upon solidification, which act far less detrimental to the mechanical properties. [2],[3]

$$Ca_{Metal} + S_{Metal} \leftrightarrow CaS_{Slag} \tag{1}$$
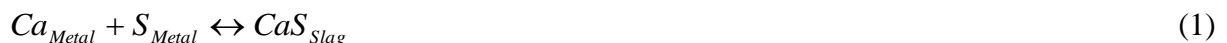
However, the formed sulphides deposit at the crucible walls and can be re-diluted in subsequent melts what leads to a possible enrichment of sulphur from heat to heat if the amount of desulphurization agents is not adjusted correspondingly. [6] Furthermore, the efficiency of the desulphurization is adversely affected by the high oxygen affinity and the significant vapour pressure of calcium at process temperatures and pressures in VIM, since calcium and magnesium react with the refractory lining or evaporate from the surface of the melt. [7]

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

2   Fundamentals of Desulphurization in ESR

The ESR process is widely known for its ability to remove sulphur from nickel- and iron-based alloys. [2,7,8] Oftentimes, the mechanism of desulphurization in ESR is described as an exchange of sulphur and oxygen between metal and slag as described in equation (2).

$$S_{Metal} + O^{2-}_{Slag} \leftrightarrow S^{2-}_{Slag} + O_{Metal} \tag{2}$$

However, it is obvious that the reaction depends on a sufficient supply of oxygen from the slag and that a certain oxygen pickup of the melt occurs. In open ESR furnaces, the S^{2-}-ions in the slag react

with atmospheric oxygen to SO_2 and the slag is continuously replenished with oxygen. Under inert gas atmospheres, this reaction is not possible and therefore the removal of sulphur is governed almost exclusively by the initial composition of the slag. To quantify the amount of sulphur that a slag can absorb, Kor and Richardson [9] have introduced a so-called sulphide capacity C_S, which was later modified by Hoyle [10], who stated that the sulphide capacity is defined uniquely by the composition of the slag. For various different mixtures within the system CaF_2-CaO-Al_2O_3 the sulphide capacity was experimentally determined [9], but outside this common slag system, only little information can be found with regard to the impact of slag constituents on the desulphurization.

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 sulphur 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 desulphurization purposes in metallurgy, often also used in the form of Ce-La mischmetal. [12] From experimental and theoretical investigations regarding the utilization of metallic cerium in VIM it is known, that it forms very stable oxides, sulphides and oxysulphides in the presence of oxygen and sulphur. As they have the lowest free energy of formation, the most probable compounds were found to be Ce_2O_3, Ce_2O_2S, CeS, Ce_2S_3 and Ce_3S_4, where the sequence, in which these compounds form, depends on the content of oxygen and sulphur in the metal. [13] So far, no information about the mechanism of sulphur removal by 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 sulphur from the electrode in the form of thermochemical stable cerium oxysulphides.

As already discussed above, the addition of metallic elements to ESR fluxes is generally feasible and presents a further method to increase the efficiency of desulphurization. Here, calcium is expected to show good results, as it has already proven to be capable of removing sulphur in VIM. Furthermore, the general feasibility of remelting under calcium containing slags has already been demonstrated. [11,14,15] The general mechanism of the desulphurization takes place analogously to the reaction shown in equation (1). Since calcium possesses a comparably high vapour pressure at typical temperatures in ESR, the remelting is preferably carried out under elevated pressure to reduce the losses due to evaporation. Still, as the evaporation cannot be suppressed completely, calcium has to be fed to the slag in the course of the melt to keep its activity constant. [14]

3   Experimental Work

The experimental investigations in the present work involved the fabrication of electrodes by vacuum induction melting, their subsequent remelting by chamber ESR as well as the sampling and analysis 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 desulphurization 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.

3.1   Manufacturing of ESR Electrodes by VIM

To obtain suitable electrodes for the study of desulphurization in ESR, six melts were carried out in a 100 kg VIM furnace at IME Aachen. Their compositions were within the specification limits of alloy 718 according to AMS 5562 (see table 1).

Table 1:   Specification limits for alloy 718 according to AMS 5562 (in wt.-%)

Element	Ni	Cr	Fe	Mo	Nb	Al	Ti
Lower spec. limit	50	17	Balance	2,8	4,75	0,2	0,65
Upper spec. limit	55	21	Balance	3,3	5,5	0,8	1,15

Only the sulphur content was adjusted to approximately 50 ppm, representing the use of raw materials high in sulphur. The precise sulphur content of the produced electrodes is given in table 2. All electrodes were 110 mm in diameter and approximately 600 mm in length, what corresponds to a respective weight of about 50 kg.

Table 2:   Initial sulphur content in ESR electrodes

ESR trial	D1	D2	D3	D4	D5	D6
S-content / ppm	83	48	50	50	50	63

3.2 Setup and Procedures of the Remelting Trials

The general operating principle of the electroslag remelting process has been described elsewhere. [2,10] The ESR unit at IME consists of an open and a closed melting station (see figure 1), what allows for operation under air atmosphere as well as under protective gas. The maximum applicable pressure is 50 bars, what facilitates the use of highly volatile elements like calcium or magnesium as slag components without excessive evaporation.

With a diameter of 160–180 mm, the tapered water-cooled copper mould of the closed remelting unit allows electrode diameters up to 110 mm, whereas the maximum length of the electrodes is restricted by the dimensions of the furnace chamber to 1 350 mm. For the open unit there are moulds with diameters between 90 and 150 mm available for electrodes up to 1 510 mm in length. Both remelting stations are operated by means of an industrial standard process control unit, which gives the possibility of recording and analyzing process variables like melt rate, electrode position or electrical data. The input of melting power is controlled through a thyristor and allows for currents up to 5 kA and operating voltages to the extent of 80 V.
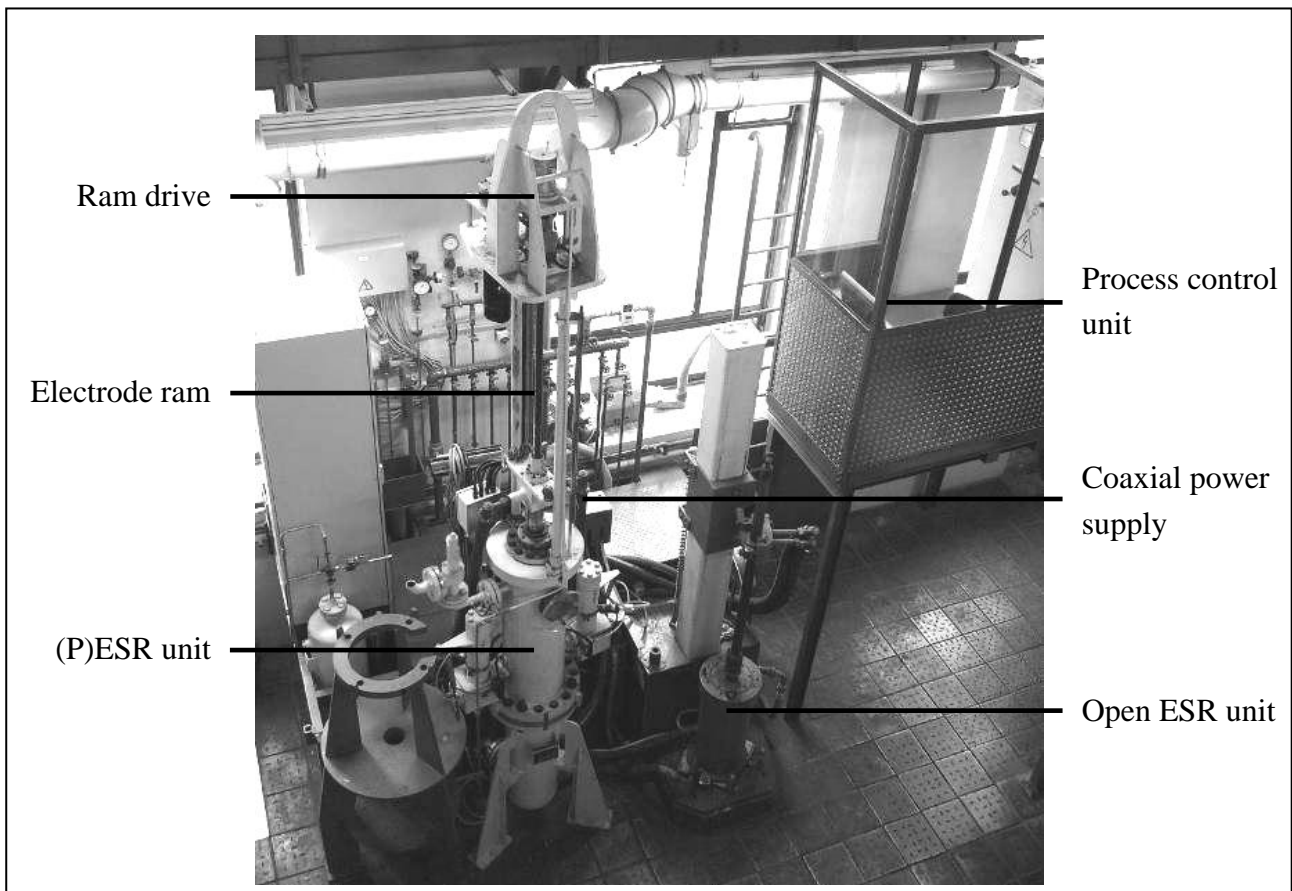
Figure 1:   (P)ESR unit at IME Process Metallurgy and Metal Recycling

From the fundamentals in chapter 2 it is expected that the presence of CaO, CeO_2 or elemental calcium in the slag shows a beneficial effect on the desulphurization of nickel-based superalloys. To quantify their potential for sulphur removal, six 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 CaF_2/CaO and CaF_2/Ca (trials D1 and D2). As the mixture of CaF_2 and Ca did not show sufficient efficiency of desulphurization despite a significant Ca-pickup of the ingot at the same time (see chapter 4.2.1), Ca was thereafter only used in lower concentrations and in combination with CaF_2 and CaO (trials D3 and D4). In D5 and D6 the influence of CeO_2 as a slag additive was investigated. Apart from D2, in all trials a CaF_2/CaO ratio of 4:1 was chosen to allow a certain comparability of the results. The nominal composition of the utilized slag systems is given in table 3.

Table 3:   Nominal composition of the utilized slag mixtures

Trial	CaF_2 / wt.-%	CaO / wt.-%	Ca / wt.-%	CeO_2 / wt.-%
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

Despite the elevated pressure in PESR, calcium losses occur during the process due to evaporation, dissolution in the metal and reaction with S to 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.-% CaF_2 and 10 wt.-% 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 [14], 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 sulphur content of the electrodes.

As the use of calcium as a slag component necessitates remelting under inert gas and elevated pressure to avoid excessive oxidation and evaporation, all trials were conducted under an atmosphere of 5 bars argon. After the starting phase, in which the initial mixture of solid slag components completely melted, the melting phase commenced. In this stage, the input of energy was controlled through a melting power controller, whereas for the regulation of the immersion depth of the electrode into the slag the resistance swing controller was applied. Near the end of the melt, the so-called hot-topping phase was initiated, in which the melting power was decreased gradually to minimize the shrinkage cavity in the final ingot.

3.3   Sampling and 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. The slag skin was carefully removed in sections of 20 mm height from the bottom to the top (see figure 2, bottom left) and afterwards pulverized in a ball mill to particle sizes below 90 μm. The powder was then analyzed by titration to determine the CaO-content, x-ray fluorescence analysis (XFA) and a carbon/sulphur analyzer. The entire slag cap was first pre-crushed in a jaw crusher and then a representative fraction was milled and analyzed in the same way as described for the slag skin.

From ingot D2, chips were drilled every 20 mm as shown in figure 2 (top left) and analyzed by flame atomic absorption spectrometry (FAAS) for calcium. As this method proved to be time-consuming and only revealed information about one element at a time, the procedure of sampling and analysis was modified for the following trials: From the edge each ingot, a 40 mm wide slab

was cut and divided into specimen with an approximate height of 30 mm according to the illustration in figure 2, right. The so produced samples were analyzed via XFA, spark discharge optical emission spectroscopy (SD-OES) and from the centre of each sample chips were drilled for the analysis for carbon and sulphur.
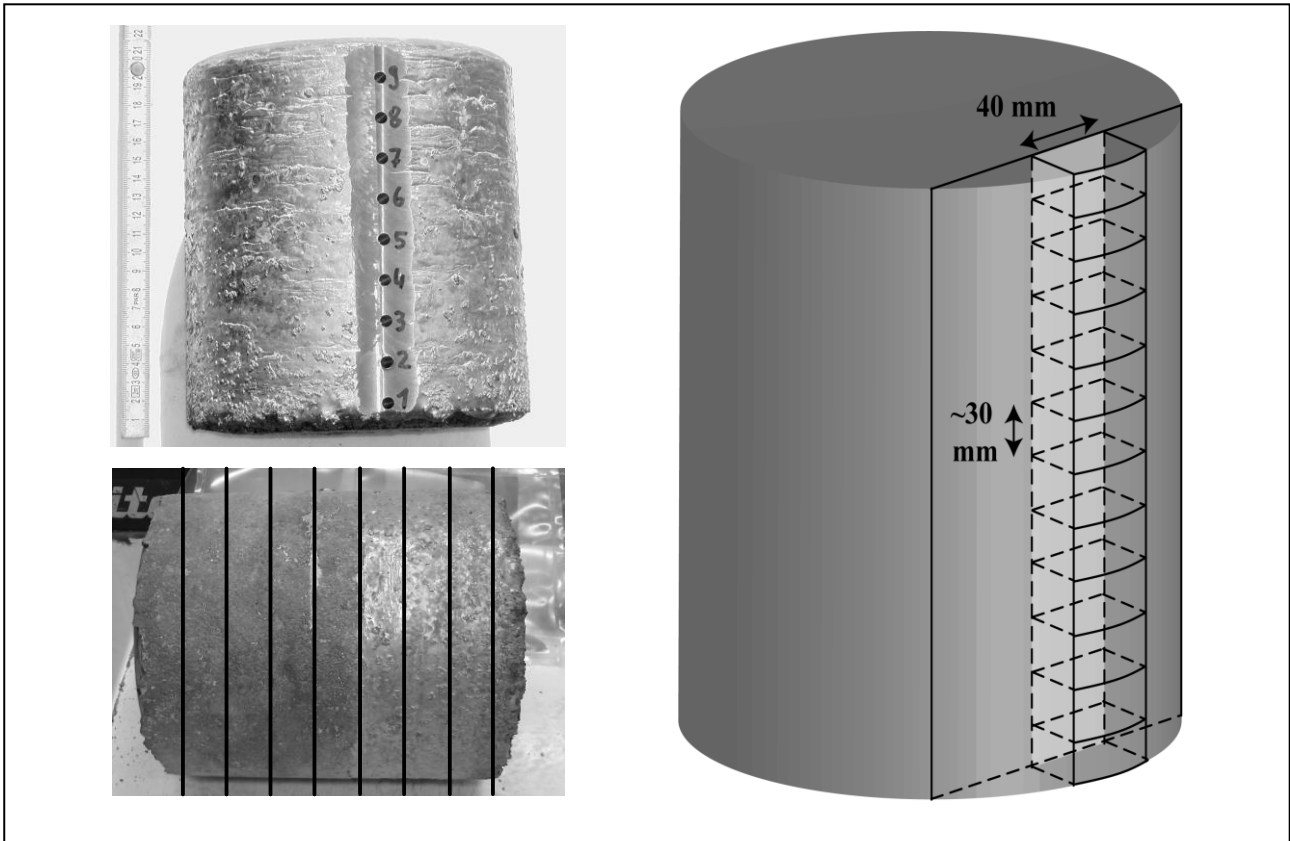

Figure 2:   Systematic sampling of slag and metal (top left: sampling of ingot D2; bottom left: sampling of the slag skin; right: sampling of ingots D1 and D3-D6

4   Results

4.1   Observations

In the course of remelting, significant differences between the utilized slag systems were observable with regard to furnace operation: While the addition of 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 considerable changes and fluctuations in the electrical parameters like the electric resistivity, the voltage and the current. The characteristics of the resistivity in trials D6 (top) and D3 (bottom) is shown in figure 3 and it is apparent, that the mean electrical resistivity is significantly lowered by the addition of metallic calcium to the slag. Furthermore, the trend shows considerable fluctuations that were consequently observed in the characteristics of current and voltage, too.
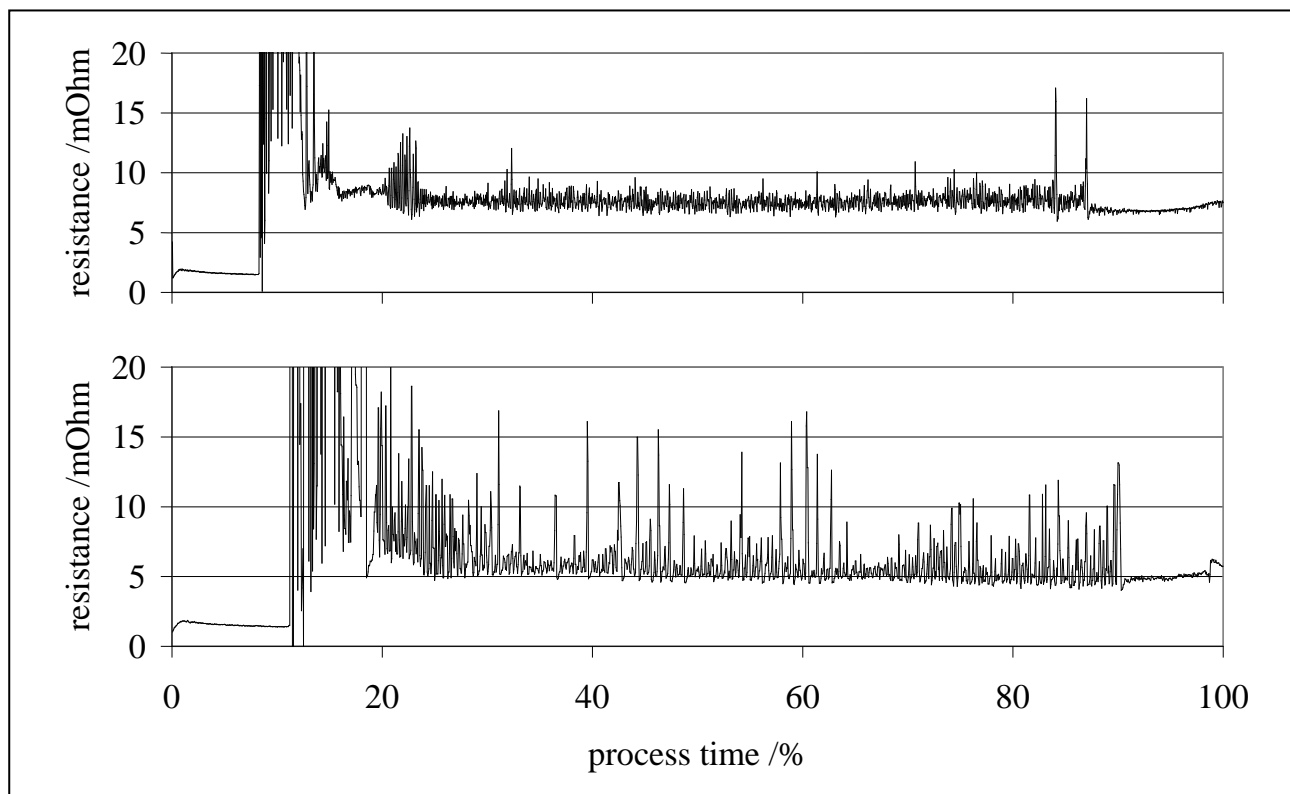
Figure 3: Trend of the resistance during trial D6 (top) and D3 (bottom)

After opening the reactor, in all trials flue dust was found on top of the water-cooled copper mould, 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.

With regard to the slag skin adhering to the ingot, several differences could be observed. On the one hand, with up to 2 mm the thickness of the slag skin was significantly higher in the trials with metallic calcium in the slag compared to approximately 0.1 to 0.2 mm in all other trials. On the other hand, in experiments with CeO_2-containing slags the slag skin adhered strongest to the surface of the ingots and could only be removed by intense application of force. During subsequent milling, the calcium-containing slag showed the highest fraction of metallic particles.

Presumably as a consequence of the thick slag skin and the non-uniform process variables, the surface quality of the ingots produced by remelting under slags containing metallic calcium was significantly lower than in the other trials.

4.2   Chemical Analysis

As the focus of the current investigation lies exclusively on the desulphurization of the metal, only the elements S, Ca and Ce, which are directly related to this reaction, will be discussed in the following paragraphs.

4.2.1 Chemical Analysis of the Metal

Figure 4 shows the distribution of sulphur as a function of the height in the produced ingots. It is evident, that the sulphur content was decreased to 20 ppm or less in all trials. With 6 – 8 ppm, the lowest values were achieved in D6 with a slag mixture that contained 20 wt.-% CeO_2. In most trials, a certain fluctuation of the sulphur content is apparent, only D4 and D6 remain within a tight variation limit of maximum ± 1.5 ppm.
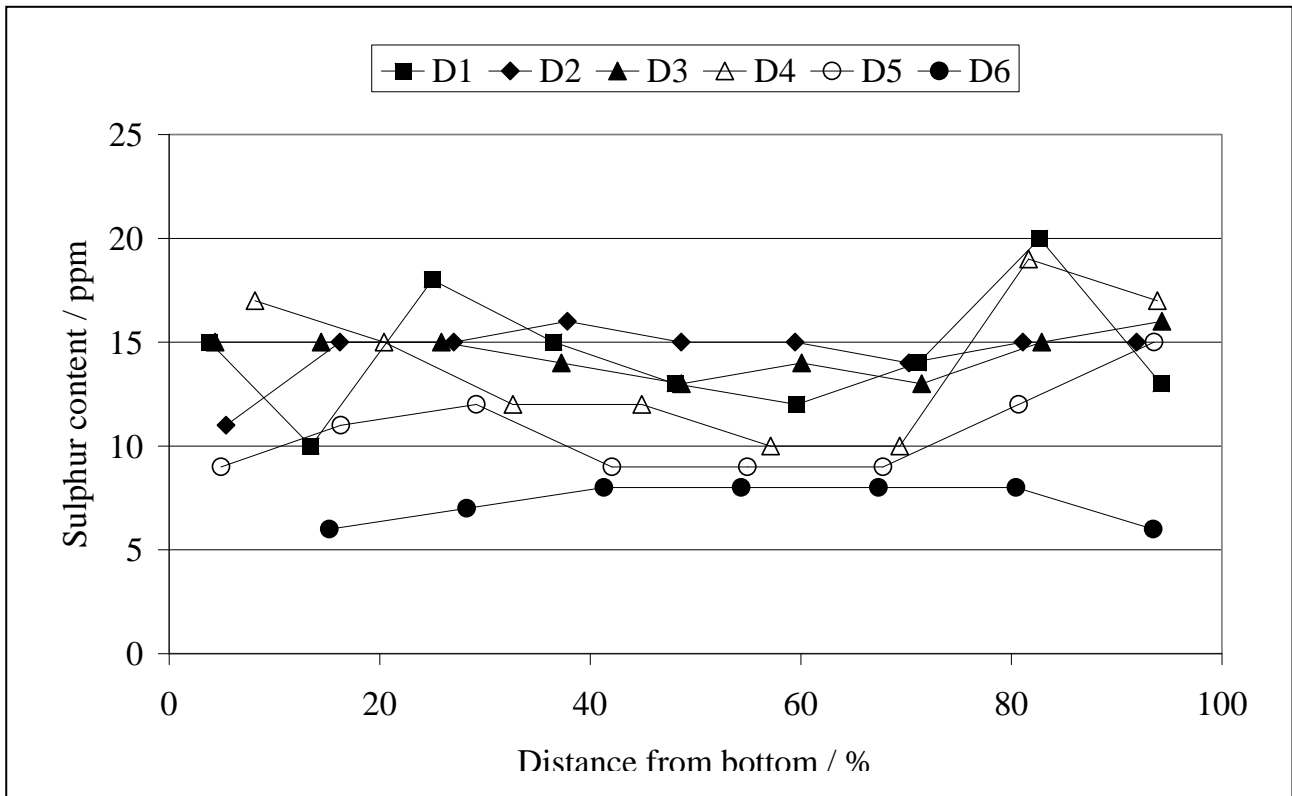

Figure 4:   The distribution of sulphur in the remelted ingots

Beside the initial sulphur content in the electrodes and the mean sulphur content in the remelted ingots, figure 5 gives the efficiency of desulphurization for the conducted trials. The latter is here defined as the ratio of the removed sulphur and the initial sulphur level in the electrodes. The highest efficiency of desulphurization was observed in D6 followed by D1 and D5, what means that the trials with metallic calcium as desulphurization agent show the lowest desulphurization efficiency.
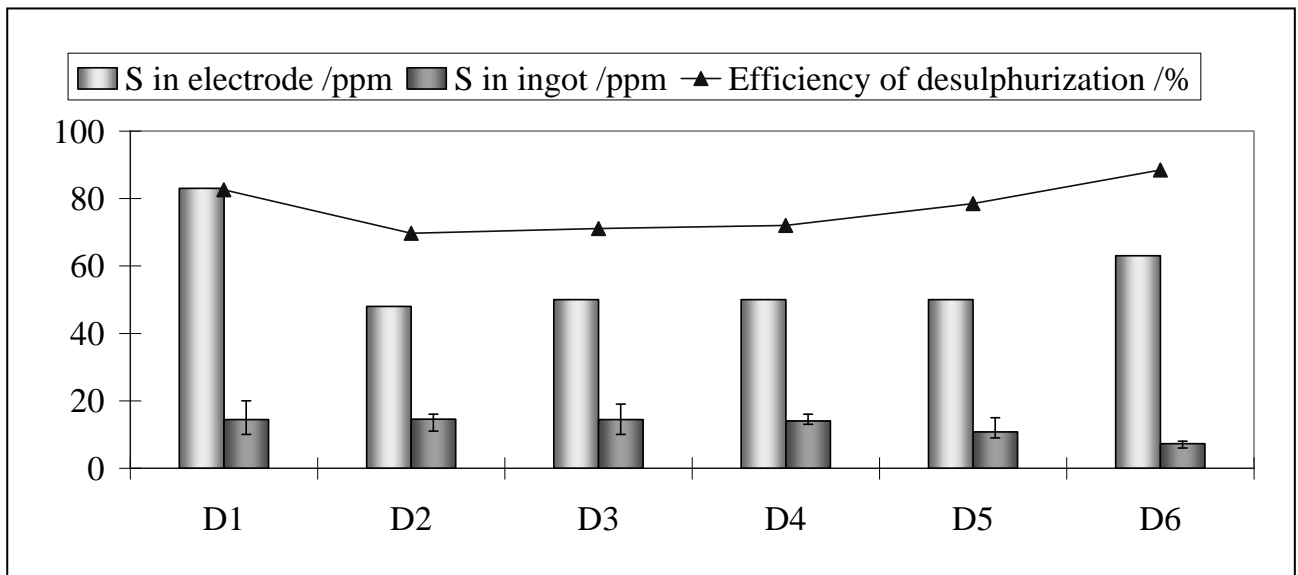
Figure 5: Mean sulphur content in the metal and the efficiency of desulphurization

The results of the analysis for calcium and cerium in the metal samples are presented in figure 6. Whereas in trial D1 virtually no pickup of calcium occurs, in D2 the calcium content drops in the course of the trial from initially 1300 below 600 ppm. In D3 and D4 the calcium level increases from 30 to 50 ppm and from 40 to 110 ppm respectively. According to the analysis, the cerium content in D5 and D6 adds up to 200 and 300 to 400 ppm respectively.
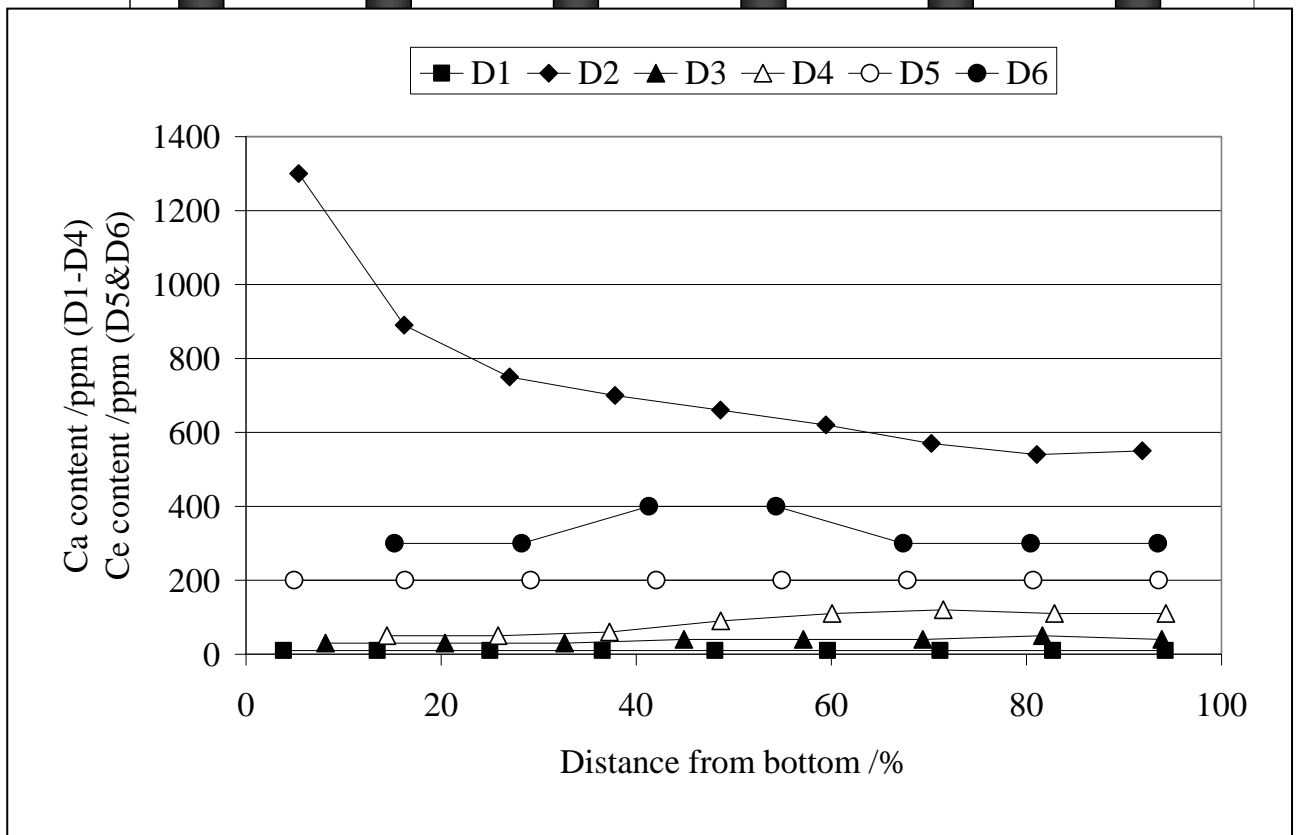

Figure 6: Distribution of Ca in ingots D1-D4 and Ce in ingots D5&D6

4.2.2   Chemical Analysis of the Process Slag

The chemical analysis of the slag skin and the slag cap on top of the ingots shows considerable fluctuations in the sulphur content (see figure 7). While the sulphur level in the slag skin usually lies between 200 and 500 ppm and doesn't exceed 800 ppm in any sample, the level in the slag cap is with 860 to 1500 ppm significantly higher. Regarding the general distribution of sulphur in the slag skin, no definite trend could be identified.
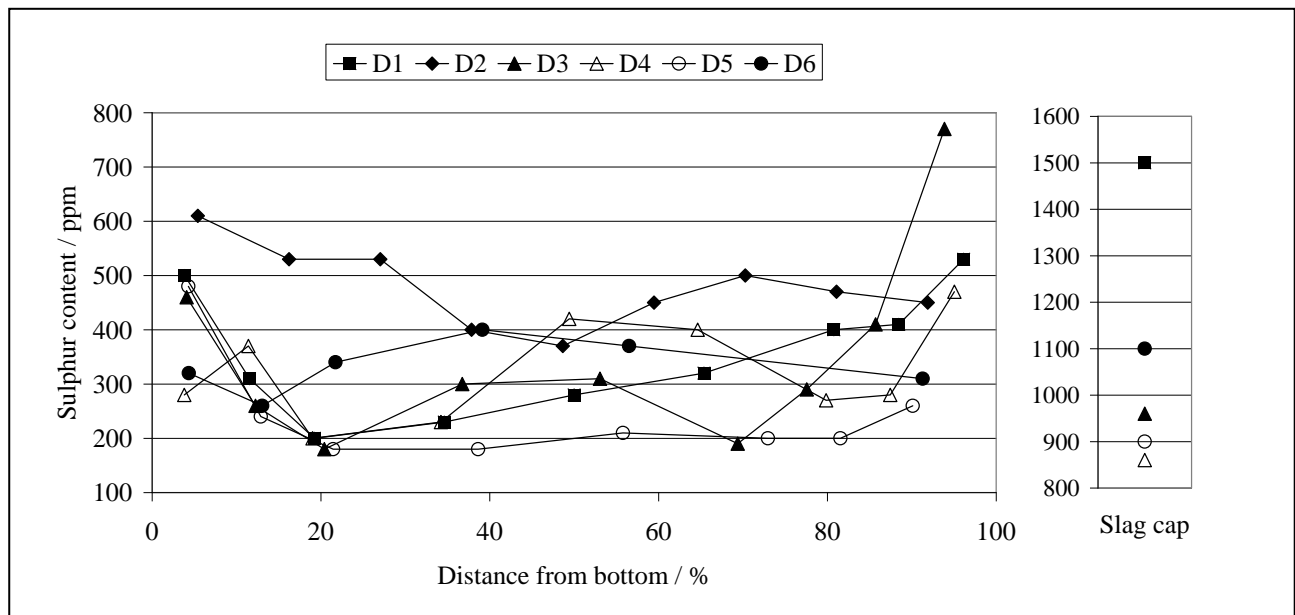

Figure 7:   The distribution of sulphur in the process slag

The chemical analysis of the slag skin revealed abnormal fluctuations of more than 100 percent for the relevant elements Ca and Ce and their compounds. As these large fluctuations within very short distances appear to be unrealistic, it is assumed that the amount of slag was not sufficient for reliable analyses of the chemical composition of the slag.

5   Discussion

With regard to the removal of sulphur from the electrodes, CaF_2-CaO-CeO_2 seems to be the most efficient slag system that was examined in this work, whereas the efficiency of desulphurization increases with increasing CeO_2 content in the slag. In trial D6 the sulphur level in the ingot is throughout below 10 ppm and therefore fulfils the requirements considering the removal of sulphur. However, the significant pickup of cerium up to levels between 300 and 400 ppm in the remelted metal has to be taken into account with regard to its influence on the mechanical properties of the material. Here, it has to be clarified whether cerium is solved in the metal or exists in the form of non-metallic inclusions like oxides, sulphides or oxysulphides that contain chemically bonded cerium. Until now, that question could not be answered yet, but as cerium was introduced into the process in oxidic form and generally forms very stable compounds with sulphur and/or oxygen, there seems to be a certain probability that at least a part of it exists as non-metallic inclusions. The latter

can possibly be removed by flotation during vacuum arc remelting, whereas the evaporation of solved cerium seems unlikely due to its comparably low vapour pressure at the given temperatures. The effect of solved cerium in superalloys has been studied by various researchers before. For example, for the iron-nickel-based alloy Udimet 901, Cosandey et al [16] discovered a maximum solubility of 100 ppm Ce in the as-cast condition. Above that level, Ni_5Ce starts to form at grain boundaries what results in the loss of high temperature ductility and forgeability. On the other hand, below 100 ppm, residual cerium was found to improve the creep ductility of the alloy. According to Woo and Nishimoto [17], the addition of up to 0.3 wt.-% improves the weldability of cast alloy 718 and decreases the amount of laves cluster and sulphur segregation at the grain boundaries. These two examples show that the presence of solved cerium in superalloys can be both detrimental and beneficial for selected material properties depending on its content, which therefore has to be controlled carefully.

With regard to the efficiency of desulphurization, the mixture of 80 wt.-% CaF_2 and 20 wt.-% CaO showed promising results, too. However, the initial sulphur content in the utilized electrode was significantly higher than in the other trials and after remelting the resulting mean sulphur level in the ingot was 4 to 7 ppm higher than in the trials with cerium oxide. As the activity of sulphur decreases with declining concentrations in the metal, the difficulty of sulphur removal increases from a thermochemical point of view. Therefore, in further experiments it has to be investigated, which final sulphur content in the ingots could be realized with an initial sulphur content of 50 ppm in the electrodes.

The lowest desulphurization efficiency and the highest remaining sulphur contents in the ingots were found in the trials with metallic calcium as desulphurization agent. Apart from that, the use of calcium was linked with unstable remelting conditions and non-uniform ingot surface qualities as a result. The fact, that during the stripping of the ingots in these trials a severe formation of sparks could be noticed, leads to the conclusion that metallic calcium was still existent in the system after remelting. Either that implies that calcium was evaporated, condensed on the water-cooled crucible walls and not fully re-solved in the melt or that the charged amount of calcium was not consumed completely during the desulphurization reaction. The corresponding investigation has not been finished yet, but if the latter was the case, it has to be determined, what the limiting factor for the desulphurization is and how the degree of the chemical reaction can be improved in future trials. If an underestimation of the evaporation of Ca is responsible for the comparably low efficiency of desulphurization in these trials, the feeding rate and the furnace pressure have to be adjusted accordingly. However, the fact that in trial D4 the calcium content in the metal was increased up to 110 ppm in the course of the melt leads to the conclusion, that the transport into the metal and the evaporation of calcium should not have been the limiting factors for the desulphurization.

The particular high calcium levels in the trial with 5 wt.-% metallic Ca in the slag seem abnormal in relation to the trials with 0,5 and 2 wt.-%, what might be attributed to the different analytical method. Therefore, the samples from this trial will be rechecked by SD-OES to have comparable results by consistent characterisation techniques. As the cerium content in the ingots of D5 and D6 only

varies in steps of ±100 ppm, these values will also be double-checked by inductively coupled plasma OES to verify their reliability.

It appears remarkable that in all trials the sulphur content in the slag cap on top of the ingots is significantly higher than in the slag skin between the ingot and the water-cooled copper mould (see figure 7). As the currently applied analytical methods were not capable of identifying differences with regard to the chemical composition apart from sulphur, it is planned to carry out x-ray diffraction analysis and scanning electron microscopy with energy dispersive x-ray analysis of the slag samples to determine the existent phases and thereby reveal a possible explanation for the non-uniform distribution of sulphur in the slag.

6   Summary and Outlook

Six electrodes with comparably high sulphur levels of approximately 50 ppm were produced by VIM and remelted in a labscale 300 kW-PESR furnace under different process slags and elevated pressure. The influence of different slag constituents on the efficiency of desulphurization was studied. Therefore, the content of sulphur and desulphurization agents in the final ingots was quantified by chemical analysis and compared to the initial levels in the electrodes. The highest efficiency of desulphurization was obtained with the slag system CaF_2-CaO-CeO_2 and sulphur levels below 10 ppm were achieved throughout the electrode. However, a significant pickup of cerium up to 400 ppm was measured in the ingots. So far, it could not be identified if cerium is solved in the metal or exists in the form of non-metallic inclusions, but if the latter proves to be the case, trials in a vacuum arc remelting furnace will follow to investigate the possibility of removing these inclusions. The desulphurization with metallic calcium was not as efficient as with CeO_2, but as Ca has a comparably high vapour pressure, solved excess calcium might be removed during VAR in opposition to cerium. Nonetheless, the calcium content in the final ingots should be kept as low as possible, as high calcium levels in VAR electrodes are supposed to interfere with the formation of the arc.

Where it seems beneficial, the current investigation will be extended by SEM analysis of slag and metal samples to obtain additional information about the distribution and the form of sulphur, cerium and calcium in both phases. When the examination of the six ingots and corresponding slag samples as well as possible subsequent remelting trials by VAR will be finished, the slag chemistry will be further adjusted to improve the efficiency of desulphurization without contaminating the metal with unwanted constituents. The improvement of the process slag systems will be additionally supported by thermochemical calculations of the desulphurization reaction. Afterwards, when the mechanism is entirely understood, additional aspects like the energy efficiency, the loss of titanium or the economic feasibility of the slag components will be addressed.

Thus, in future an increased efficiency of desulphurization in the ESR process might facilitate the use of raw materials with comparably high sulphur content or enable lower sulphur levels in the final ingots to obtain even better material characteristics than today.

7   Acknowledgements

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