Refining Potentials of the Electroslag Remelting Process Regarding Sulphur in Ni-Based Superalloys

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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 sulphur origins from the raw materials, foremost nickel, chrome and iron. To decrease the concentration of sulphur to uncritical values below 20 ppm, it is common to perform an addition of NiCa- and/or NiMg during primary melting in a vacuum induction furnace. As calcium and magnesium display a significant evaporation at the given process temperatures and pressures, the efficiency of this practice of desulphurisation is comparably low and a full removal of sulphur by this melt treatment is not possible.

Therefore, a novel approach, which is based on the desulphurisation by means of an active slag during pressure electroslag remelting (PESR), is currently under investigation at IME Process Metallurgy and Metal Recycling at RWTH Aachen. The objective of this method is to remove sulphur to extremely low concentrations at a higher yield for the desulphurisation agents at the same time. This paper presents the results of a first preliminary trial, which was conducted in order to obtain basic information about the behaviour of calcium and sulphur during remelting using a calcium-containing fluorine slag.

Keywords: electroslag remelting, desulphurization, calcium, active slag, Ni-based superalloys

1 Introduction

Various researchers have studied the influence of sulphur on the mechanical properties of nickel-based superalloys throughly [1][2][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]. Since sulphur is a ubiquitous impurity in nickel-containing raw materials, different possibilities have been investigated to reduce its level during the production of superalloys. One of the most common practices is the addition of NiMg and NiCa to the melt during vacuum induction melting (VIM) just before casting. On the one hand, a certain amount of S directly leaves the melt as MgS or CaS 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]. According to Siddall [3], an Mg to S ratio of > 1 is essential for good high temperature ductility. However, excess magnesium can form $MgNi_2$ laves phase, which degrades the creep rupture properties [2]. Therefore, it is essential to keep sulphur and magnesium levels in the alloy as low as possible, what can currently only be guaranteed by the use of raw materials comparably low in initial sulphur content. To be able to use raw or revert materials with higher sulphur concentration or to reach lower contents in the final ingots, new desulphurization practices need to be investigated.

2 Methodology and Materials

2.1 The Fundamentals of Desulphurization in Electroslag Remelting

Electroslag remelting is known to decrease the sulphur content of steel and nickel-based superalloys [2][4]. The mechanism of the desulphurization during the remelting process is mostly described as a reaction of sulphur with oxygen from the slag, here given by the following equation:

$$S_{Metal} + O^{2-}_{Slag} \leftrightarrow S^{2-}_{Slag} + O_{Metal} \qquad (1)$$

A_x: A dissolved in X

From the corresponding law of mass action (see (2)) one can conclude that high oxygen and low sulphur activities in the slag and low oxygen contents in the metal promote the desulphurization.

$$K = \frac{a(S^{2-}_{Slag}) \cdot a(O_{Metal})}{a(S_{Metal}) \cdot a(O^{2-}_{Slag})} \qquad (2)$$

K - Equilibrium constant /1, $a(X_Y)$ - activity of component X dissolved in phase Y /1

As a major result, in the literature many authors state that melting under air leads to better desulphurization than under argon atmosphere, since the sulphur in the slag can be oxidized by the atmospheric oxygen and leaves the system as SO_2 [5][6][7].

$$S^{2-}_{Slag} + \frac{3}{2} O_{2,Gas} \leftrightarrow SO_{2,Gas} + O^{2-}_{Slag} \qquad (3)$$

However, other authors [8][9] observed, that adequate desulphurization is possible under argon atmosphere, if slag systems with sufficient high sulphur capacities are utilized. The sulphur capacity of different slag systems was first systematically investigated by Kor and Richardson [10], who analyzed the sulphur content in various slag samples after reaching equilibrium with an exactly defined mixture of N_2, CO, CO_2 and SO_2. They introduced the indicator C_S for the sulphur capacity, which they defined as follows:

$$C_S = w(S_{Slag}) \cdot \sqrt{\frac{p(O_2)}{p(S_2)}} \qquad (4)$$

C_s - sulphur capacity
$w(S_{Slag})$ - weight percent of sulphur in the slag in equilibrium
p(X) - partial pressure of X

This formula was later modified by Hoyle [6] (see (5)), who states that sulphur capacity is a property of the slag, which is uniquely defined by its composition.

$$C'_S = \frac{w(S_{slag}) \cdot a(O_{metal})}{w(S_{metal})} \qquad (5)$$

For the ternary system CaF_2-CaO-Al_2O_3, which is one of the basic systems for remelting of steels and nickel-based superalloys, Kor and Richardson [10] plotted is sulphur capacity lines at 1500 °C (see Figure 1, left side). It is evident that calcium fluoride slags with approx. 15–40 wt.% CaO and only negligible contents of Al_2O_3 offer the highest sulphur capacity, whereas increasing amounts of Al_2O_3 decrease the sulphur capacity significantly. As Figure 1 (right) shows, the liquidus temperature of the slag system rises above 1600 °C for more than 25 wt.% CaO, what makes the utilization of such slags for the remelting of nickel-based alloys like alloy 718 (T_{liq}: 1335 °C [2]) unfeasible due to the resulting excessive overheat of the metal. Consequently, it would be advisable to use a slag mixture of CaF_2 with 15–25 wt.% CaO for a good absorption of sulphur into the slag.

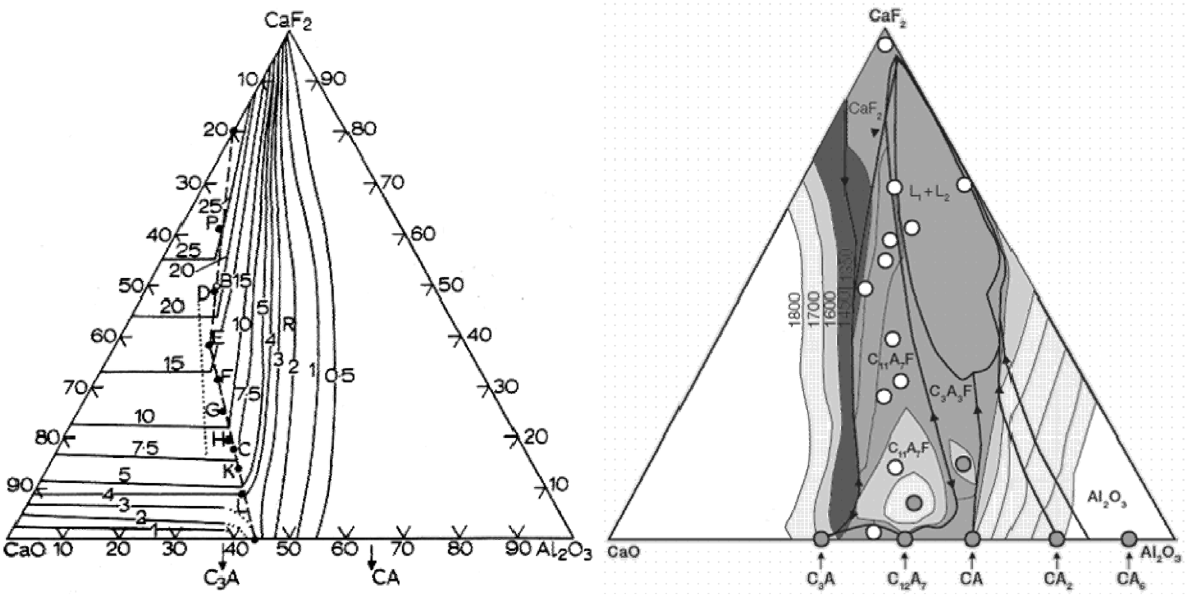

Figure 1: Left: Sulphide capacities in the ternary system CaF_2-CaO-Al_2O_3, the numbers on each line indicate C_S x 10^3 [10]; Right: Liquidus temperatures, phase existence ranges and selected commercially available slag mixtures (white circles)

Laboratory scale remelting trials of steel electrodes by Cooper and Kay [8] in CaF_2-slags containing different amounts of CaO showed promising results concerning the desulphurization (see Figure 2). The initial sulphur content of 0.13 wt.% in the electrode could be reduced to 0.02 –0.03 wt.% in the ingot by remelting under a slag containing 20 wt.% CaO. However, it must be considered that in nickel-based superalloys the initial sulphur content in the input material and the desired content in the ingot is significantly lower than in Cooper's experiments.

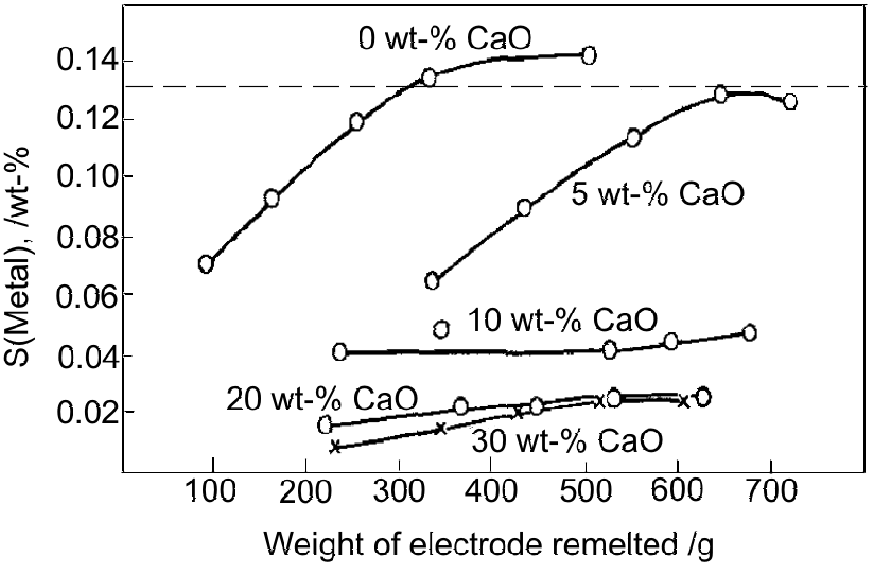

Figure 2: Results of laboratory scale ESR trials for desulphurization of steel electrodes with CaO containing CaF_2 slags [8]

Furthermore, the pickup of oxygen by the melt according to (1) should be kept as low as possible, as oxygen, like sulphur, can be detrimental for the mechanical properties of nickel-based alloys. For that reason, it might be advisable to accomplish at least a part of the desulphurization by means of an oxygen free reactant. Therefore, the approach of removing sulphur via addition of metallic calcium to the slag displays a possible alternative to the actual remelting practice. In the ladle metallurgy of steel [13] or the vacuum induction melting of nickel-based superalloys [2] the desulphurization by the addition of metallic calcium or calcium-containing alloys has been established for a long time. The effective mechanism can be described by the following equation:

$$Ca_{Slag} + S_{Metal} \leftrightarrow CaS_{Slag} \tag{6}$$

Anyhow, in the literature no information regarding the addition of metallic calcium to ESR slags for the purpose of desulphurization was found. However, for the remelting of titanium alloys the use of calcium as a slag component has proved to be feasible in principle [14]. Owing to the high reactivity of calcium, melting has to be carried out under an inert atmosphere like argon to avoid excessive oxidation by atmospheric oxygen. Furthermore, as Ca has a significant vapour pressure at process temperatures (for pure Ca: p_{Ca}^0 = 1.07 bar at 1500 °C [13]), the total pressure of the system should at least equal its vapour pressure in order to avoid boiling of the slag. As the work of Stoephasius et al [14] shows, the calcium losses decrease with increasing total pressure (see Figure 3) due to slowing down of evaporation kinetics with increasing inert gas pressure.

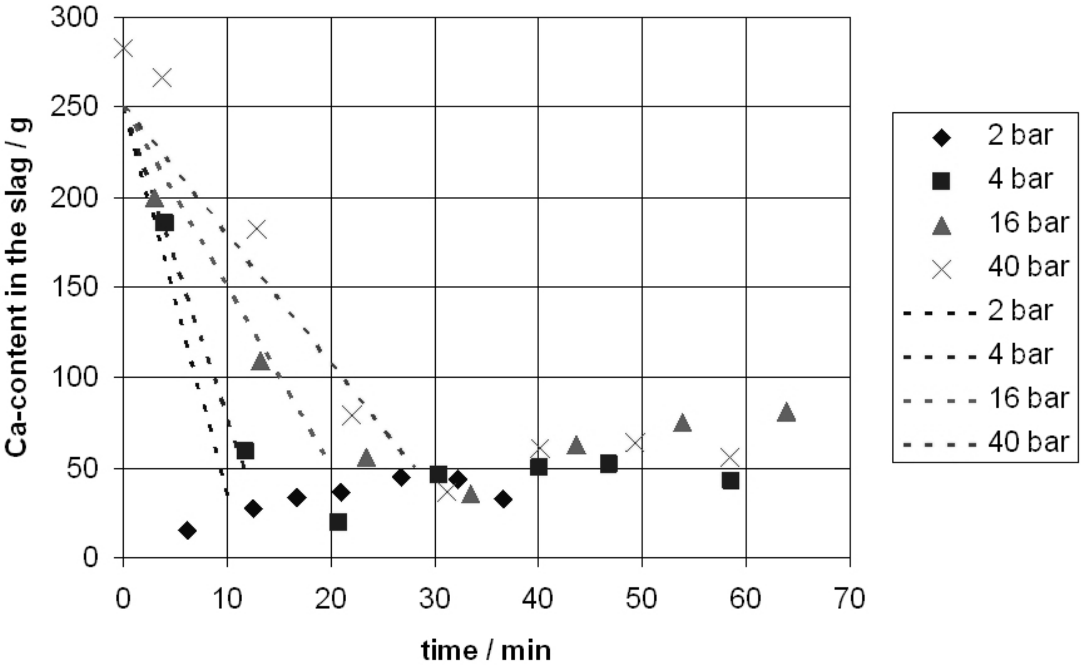

Figure 3: Experimental (points) and theoretical (dashed lines) evaporation of calcium [14]

2.2 Experimental Work

Based on the previously described fundamentals, a first preliminary trial was carried out to determine the principle behaviour of Ca during the remelting of Ni-based superalloys and to evaluate its influence on the desulphurization. To minimize the parallel reaction of sulphur with CaO, the binary system CaF_2-Ca was chosen as slag system.

2.2.1 Primary Materials

For the remelting trial in the ESR process an electrode of alloy 718 was produced by vacuum induction melting at IME. The composition was within the specification limits of this alloy according to AMS 5562 (see Table 1); only the sulphur content of the metal was adjusted to 48 ppm in order to simulate the utilization of raw materials with high sulphur level. With 3 ppm the initial calcium level of the metal was negligible. The dimensions of the nearly cylindrical electrode were approximately 110 mm in diameter and 650 mm in length at a weight of around 47 kg.

Table 1: The compositional range of major elements in Alloy 718 according to AMS 5662

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

In total, 4 kg of slag were utilized. The initial mixture contained 95 wt.% of a commercially available fluoride flux with > 97 wt.% CaF_2 (1–2 wt.% CaO) as well as 5 wt.% of calcium granules with an average grain size of approx. 1 mm.

2.2.2 Experimental Setup and Procedures

The general operating principle of the electroslag remelting process has been described elsewhere [2][6]. The ESR unit at IME consists of an open and a closed melting station, giving the possibility to conduct trials under air atmosphere as well as under protective gas (see Figure 4). Maximum applicable pressure is 50 bars, what facilitates the use of highly volatile elements as calcium or magnesium as slag components.

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 1350 mm. For the open unit there are moulds with diameters between 90 and 150 mm available for electrodes up to 1510 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 drive speed or electrical values. 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.

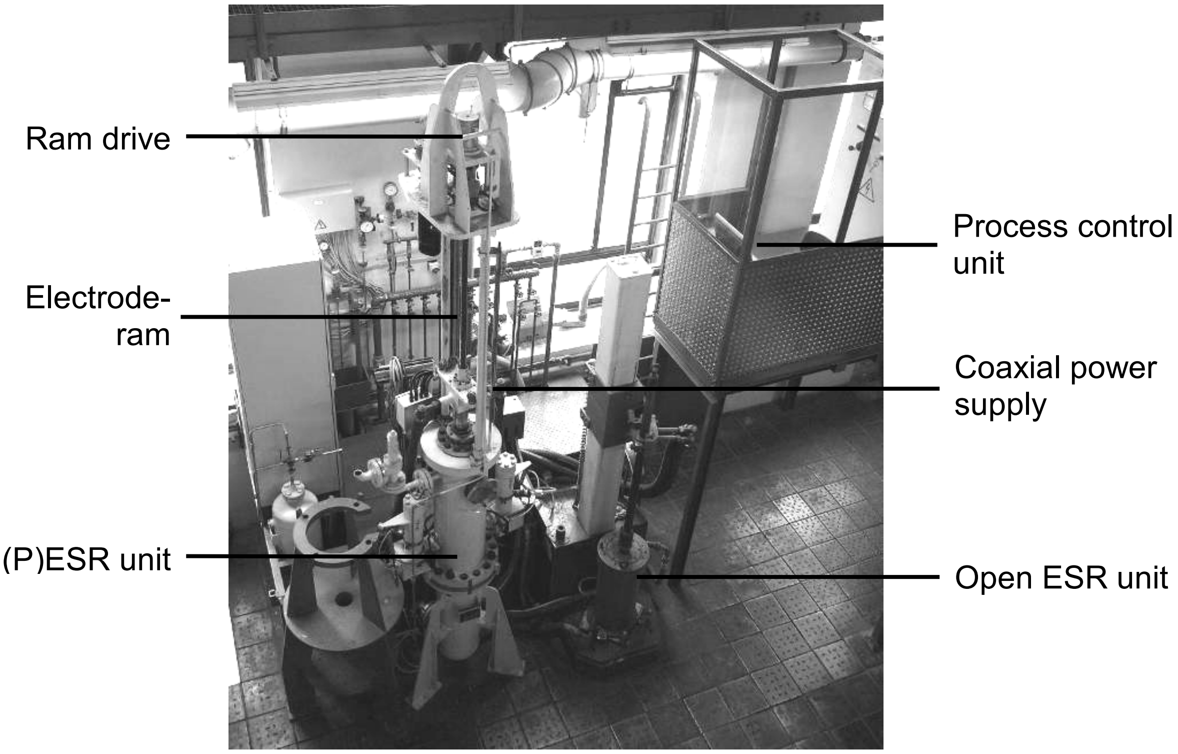

Figure 4: (P)ESR unit at IME Process Metallurgy and Metal Recycling

The trial was conducted under an atmosphere of 5 bars argon to minimize the evaporation and oxidation of calcium and other volatile or reactive constituents. After the start-up phase, in which the initial mixture of solid slag components completely melts, 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. The average melting power was 121 kW at an average swing of 3.2 mΩ. 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.

2.2.3 Sampling and Analysis of Metal and Slag

To observe the distribution of sulphur on metal and slag during the course of the trial, samples were taken of the slag skin adhering to the ingot and also from the ingot itself. The whole slag skin was removed in sections of 20 mm height from the bottom to the top, so that nine slag samples were obtained in total. These samples were each crushed in a ball mill to particle sizes below 90 μm, before a representative amount was taken for the analysis of sulphur and the determination of CaO by titration and the rest was compacted for X-ray fluorescence analysis (XFA). As the following Figure 5 shows, nine metal samples for analysis of sulphur and calcium were drilled at intervals of 20 mm, correlating with the position of the previously taken slag samples.

Figure 5: Position of the metal samples in the final ingot

For the determination of the chemical composition of the slag, a PANalytical Axios XFA and a LECO CS400 carbon/sulphur analyzer were utilized. As the XFA measurement of elements with atomic weights smaller than that of sodium is afflicted with uncertainty, the fluorine and oxygen contents of the slag cannot be directly determined via XFA. Acting on the assumption, that sulphur in the slag exclusively exists as CaS and that metallic calcium has fully oxidized before the analysis, sulphur and lime were quantified via LECO carbon/sulphur analyzer respectively titration first. Thus, the calcium existing as CaS and CaO could be subtracted from the total calcium analyzed by XFA and the remaining calcium was assumed to be CaF_2. All other metallic elements in the slag are assumed to have formed oxides. The metal samples were measured via LECO sulphur analyzer for sulphur and inductively coupled plasma optical emission spectrometry for calcium.

3 Results

The remelting process was carried out without any significant differences to trials without metallic calcium as a slag component apart from the fact that the electrode swing was approximately threefold higher. During the stripping of the ingot, a slight reaction of calcium with atmospheric oxygen was observed and the inside of the furnace chamber was covered with a comparatively large amount of flue dust. The initially solid slag cap started to decompose shortly after exposure to the atmosphere.

Figure 6 illustrates the analyses of the metal and slag samples. CaO content in the slag drops within the first three samples from initially 4.91 wt.% to approx. 2 wt.%, where it remains almost constant until the end of the melt. That is in good accordance to the trials carried out by Stoephasius et al. [14]. In general, the characteristics of the Ca distribution in the ingot looks similar to that of CaO in the slag (representing Ca during melting), only the decrease from bottom to top is steadier and Ca does not reach a constant level in the metal. The sulphur content in the slag first declines from 0.06 wt.% in the first sample to 0.04 wt.% in the middle of the ingot before it increases to 0.045–0.050 wt.% again. Compared to the initial sulphur level in the electrode of 48 ppm, the content in the refined metal could be decreased to 11 ppm in the first sample and 14–16 ppm in the rest of the ingot. That equals a sulphur removal of 77 respectively 67 %.

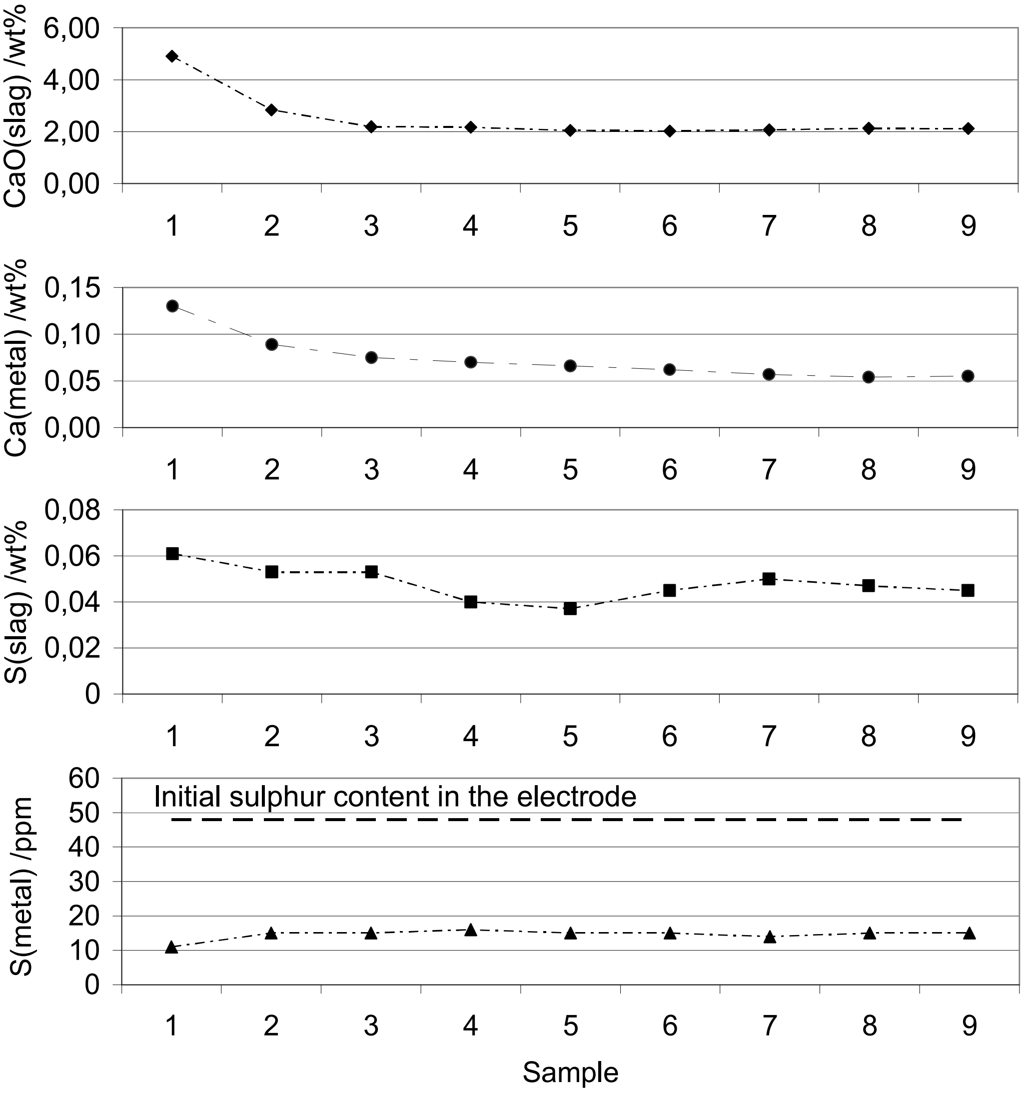

Figure 6: Results of the chemical analyses of the metal and slag samples

4 Discussion

From the results of the chemical analyses shown in Figure 6, several conclusions can be drawn. Since the highest calcium content in the metal is observed in sample 1, the dissolution of calcium from the slag into the liquid metal phase occurs apparently fast and is therefore unlikely to be the rate-determining step of the desulphurization. Consequently, the formation of CaS according to the reaction mechanism given in (6) is enhanced, what is supported by the high sulphur content in the slag and its low concentration in the metal. As calcium evaporates from the slag in the course of the trial, the calcium content in the metal is reduced as well and therefore the efficiency of the desulphurization abates. Hence, the sulphur level in the metal increases from 11 to approx. 15 ppm where it remains until the end of the trial.

Since the sulphur concentration in the ingot is always significantly lower than in the electrode and the total mass of the slag cap on top of the ingot decreases during remelting due to the formation of the slag skin between ingot and mould, the sulphur content in the slag would be supposed to increase with time. The fact, that it does not, raises the question if sulphur leaves the slag into the gas phase. This could either happen through reaction with remaining oxygen in the atmosphere according to the mechanism in Equation 3 or by evaporation in the form of a compound with a comparably high vapour pressure. As the total mass of sulphur removed from the metal equals 1.12 g, 0.07 mole oxygen would be sufficient to transform it completely into SO_2. For the given volume of the furnace, that amount of oxygen corresponds to a remaining gas pressure of less than 50 mbar before the inlet of Ar, what is considered a realistic value. However, the presence of calcium would rather cause the formation of CaO as the Gibbs free energy for that reaction is far more negative and the concentration of calcium in the slag outweighs that of sulphur by far at the beginning of the trial. According to the fundamentals presented in chapter 2.1, the formation of CaO would lead to a higher sulphur capacity of the slag, but it still cannot explain the nonexistent increase of sulphur in the slag. Therefore, the evaporation of sulphur in the form of a compound with high vapour pressure seems to be more likely at the moment.

The calcium level of 0.05–0.13 wt.% in the ingot must be regarded as critical, since the presence of excess calcium leads to the formation of Ni-Ca phases, which dramatically increase the brittleness of the alloy [1]. However, trials by Samuelson [13] show, that by subsequent vacuum arc remelting a decrease of calcium contents down to 5–10 ppm is possible and that these concentrations can be achieved independently from the initial calcium level in the electrode. Yet, it has to be investigated, how the evaporation of such comparably high calcium contents affects the vacuum arc remelting of nickel-based superalloys.

Although the utilized slag system has not been optimized yet with regard to the calcium fraction or the sulphur capacity, the use of calcium as a desulphurizing agent seems to be very promising since a relative sulphur removal by 67 to 77 % was obtained. For comparison, Eissah and Mohammadi [5] achieved for the remelting of steel a relative sulphur removal of 33 to 68 % by the use of CaF_2-based slags without addition of calcium and Elliot et al [15] reports a desulphurization efficiency of 50 % for nickel-based superalloys in industrial conditions. The absolute sulphur level in the ingot of 11 to 16 ppm might just not fulfil the requirements for critical applications, but considering the high sulphur content in the primary electrode and the not yet optimized slag system, the utilization of calcium containing slags for desulphurization of nickel-based superalloys in electroslag remelting seems promising for further investigations. On the one hand, the presented approach might allow the fabrication of superalloys with extremely low sulphur contents or on the other hand, it might facilitate the use of cheaper raw materials with higher initial sulphur contents.

5 Summary and Outlook

To investigate the general behaviour of calcium and its effect on the desulphurization during electroslag remelting of nickel-based superalloys, a first trial with a CaF_2 slag containing 5 wt.% of metallic calcium has been carried out at IME. Sulphur contents of 11 to 16 ppm in the final ingot were observed what equals a relative sulphur removal of 67 to 77 %. However, the desulphurization was attended by a significant dissolution of the calcium in the metal. Therefore, the possibilities for the removal of calcium by vacuum arc remelting need to be evaluated in the future. Furthermore, an optimization of the slag system with regard to the calcium content and the sulphur capacity will be carried out to allow even better desulphurization ratios. To obtain a more uniform removal of sulphur, a continuous addition of calcium to the slag will be under investigation as well.

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