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ABSTRACT

This report describes the technical results from the INGROS project. The project was a cooperation between Helsinki University of Technology, KTH, University of Oulu, Ovako Steel, Sandvik Steel, Rautaruukki Steel, Fundia Wire, Elkem, NTNU, Corus, and SINTEF. It was sponsored by the Nordisk Industrifond and Elkem.

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1 Summary

1.1 Goals of the project

The overall objectives of the project as described in the project proposal were as follows:

- 1) To develop new grain refiners for low alloy structural steels.
- 2) To develop new grain refiners for bearing steels and high-alloyed stainless steels.
- 3) To establish a Nordic network between the ferroalloy industry in Norway and the steel industry in Sweden and Finland. Included in the network are also the five Nordic academic institutions SINTEF, NTNU, KTH, UO and HUT.

1.2 Project organisation

A flow diagram of the project with the contributions from the companies/institutions from the different countries is shown in Figure 1. In the third year of the project, Corus joined the consortium. Corus has been working on inclusion engineering of steels for over a decade and has contributed by giving access to lab-scale equipment which was not available in the original project group. The co-operation with Corus will continue in 2004.

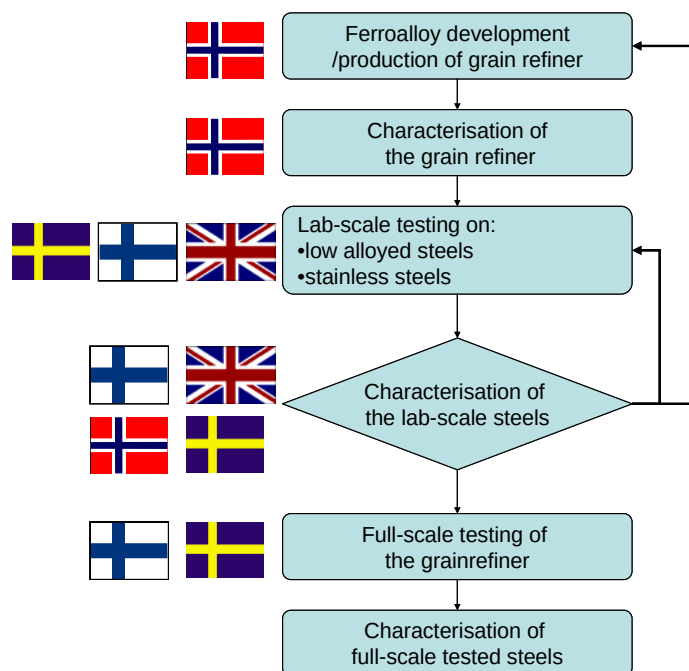


Figure 1. Flow diagram of the INGROS projects

1.3 Obtained results in relation to the goals

The first two goals, as described in §1.1, were fulfilled in the lab-scale experiments. Examples of the effect of the developed grain refiners on the microstructure of steels are shown in Figure 2. In Figure 2a and b, the effect on the solidification structure of stainless steels is demonstrated. In Figure 2c, it is demonstrated, that the grainrefiner facilitates the formation of inclusions that can nucleate ferrite. The scientific results of the project have been published in reports, on international conferences and on national seminars/workshops. The amount of scientific data which has been obtained in the experimental work for the INGROS project but which has not yet

been published is so substantial that it will most likely result in several scientific publications during the coming years.

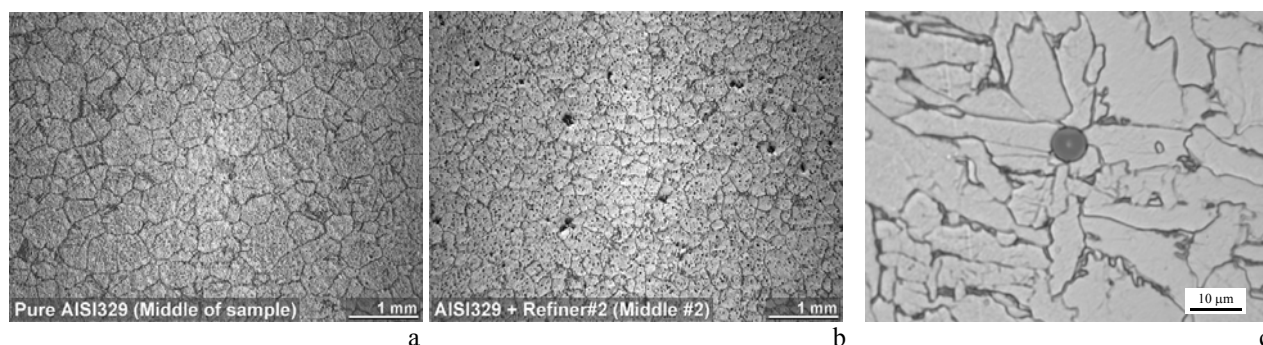


Figure 2. Examples of grain refinement: a) stainless steel without grain refiner, b) stainless steel with grain refiner, c) low alloyed steel with grain refiner.

The third goal was the establishment of a Nordic network. The project has definitely intensified the exchange of ideas between the Norwegian ferroalloy producer (Elkem) and the Swedish (Sandvik and Ovako) and Finnish (Rautaruukki and Fundia) steel producers/ferroalloy consumers. It also improved the relation between the academic environments in the Nordic countries. The project has resulted in an increased interest in the development of advanced ferroalloys. The coming five years, the Norwegian Research Council will support a project, called DISvaDRI, which aims at the development of such alloys. In addition, a proposal on grain refinement of steels has been sent to the European Research Fund for Coal and Steel (formerly ECSC). The participants in this project proposal include three of the partners from the INGROS project and three new partners: IRSID(France), CRM(Belgium) and Comdicast(Sweden). These companies have shown their interest in the scientific work done in the INGROS project and want to take part in further development.

1.4 Deviations from the original plan

During the course of the research project, several challenges were encountered which delayed the progress. The grain refiners for steels have shown their effectiveness in lab-scale experiments. However, the final properties of industrial scale grain refined steels have not yet been compared to the properties of the reference steels that have been produced.

The two main reasons for the delay were the following:

1. Complexity of alloy development. The whole concept of producing a grain refiner for steel, i.e. an alloy with a fine distribution of dispersoids, was the innovative aspect of the project and has been more complicated than originally anticipated. Twenty different alloys have been produced and characterised, but only four were promising enough to test further.
2. Difficulties with lab-scale steel casting experiments. It appeared to be tough to simulate industrial circumstances during lab-scale experiments. In order to form the right inclusions, one must have good control of the level of contamination, like oxygen and sulphur, during the melting.

Although the development of the grain refiners for steels has not yet been completed during the INGROS project, the feasibility of the concept has been proven. Several of the INGROS partners have already promised to put more resources into its development.

2 Input from the steel producers

The requests and requirements from the steel producers were collected and are summarised below:

1. Which steel grades are of interest for the tests:

Rautaruukki	037X (acicular ferrite), 056X, 026X, 094X (improved casting)
Fundia	prestressed concrete chain and cold heading steels
Ovako	0.2%C, 0.35%Si, 1.5%Mn, 0.25% Cr, 0.10%V
Sandvik	two austenitic and one ferritic stainless steel

2. Which properties are a measure for success:

Rautaruukki	037X: strength, toughness, impact ductility 056X, 026X, 094X: solidification structure, defects (slab inspection)
Fundia	Inclusion structure, toughness of wire rod
Ovako	Charpy V toughness, tensile strength, grain size
Sandvik	Dendrite spacing in bloom, grain size in billet, mechanical properties in billet

3. Which elements are critical and should be strictly controlled in the grain refiner:

Rautaruukki	see attachment
Fundia	O and N
Ovako	REM (oxides, sulphides)
Sandvik	O, S, P, Pb, Bi, C, B, Co, Cu, Nb

4. Process demands, limitations, dissolution rate and mixing behaviour of grain refiners:

Rautaruukki	-Addition amount may be 0,1-1 wt-%. -1 wt-% is about 31 kg/min (charge weight 125 t, casting time about 40 min). - Rautaruukki would prefer cored wire injection into the tundish.
Fundia	-Aimed Ti-content of steel 0.01-0.05 % -Addition as lumps (10-50 mm) in the ladle
Ovako	-Amount of FeCr: max. 100 kg (form: lumps or wire). -Minimum time between addition of grain refiner and start of casting should be > 5 minutes. -Grain refiners must be added in the ladle (not in the ingot).
Sandvik	Only way of adding in continuous caster would be by wire feeding, i.e. ferro alloy in the form of powder.

5. Miscellaneous point for discussion:

Rautaruukki	-Ce addition has been tried in the past (added as mischmetal): problems with inclusion growth and heterogeneous distribution.
Fundia	-Interested in Ti microalloying
Ovako	-What kind (composition and size distribution of inclusions) of grain refiners are there if we exclude REM ? -Is it possible to limit inclusion growth after addition of grain refiners (inclusion size should be <10 µm)?
Sandvik	

3 Ferroalloy development

3.1 Size and density of the inclusions in grain refiner No. 14B

The inclusions in grain refiner 14 are exclusively MnS inclusions. The inclusion size distribution in three samples (14-3, 14-4 and 14-6) of grain refiner 14 was first determined Table 1 list the statistical data on the inclusion distribution for both methods.

Table 1. Inclusion statistics in grain refiner 14, measured using SEM, automated image analyses.

specimen	Average diameter 3D (μm)	Area density $N_A(\text{No.}/\text{mm}^2)$	Volume density $N_v(\text{No.}/\text{mm}^3)$	Volume fraction(total)
14-3	0.47	125722	1.7×10^8	0.035
14-4	0.51	149982	1.9×10^8	0.056
14-6	0.97	3492	2.3×10^6	0.0046

4 Grain refinement of low-alloyed steel

4.1 Introduction

Within the framework of the INGROS project, three series of experiments, listed in Table 2, have been performed at Helsinki University of Technology.

Table 2. Overview of the experimental work done at HUT

	Date	Objective
First series (D1, D2, D3, D4)	June 2002	-Create active inclusions based on Ce-(oxy)-sulphides
Second series (1D3, 2D4, 3D3)	January 2003	-Reproduce the most successful steels from the first series
Third series (E1, E2, E3)	May 2003	-Test grain refiner 14D -Reproduce the most successful steels from the first series -Determine the maximum Ce addition

4.2 Experimental

4.2.1 Experimental apparatus and method

Lab-scale experiments were done in a 60 kW vacuum induction furnace. The base material was 037X pipe steel, which was provided by Rautaruukki. Charge weight was ca 6 kg. All heats were alloyed with Ce-containing preconditioner and Grain Refiner 14. Grain refiner 14D, which has a higher S content, e.g. a higher volume fraction of MnS, was used in the third series of experiments. The chemical compositions of the alloys are listed in Table 3. Note that the preconditioner in the second and third series of experiments has a lower Ce content than in the first series.

Table 3. Compositions of the alloys used in the experiments (wt.%)

	037X steel	Preconditioner 1st series	Preconditioner 2 nd and 3 rd series	Grain refiner 14B, 1 st and 2 nd series	Grain refiner 14D (S2), 3 rd series
C	0.0946		0.021		
Si	0.281	29.0	34	2.1	
Mn	1.080			2.1	3.14
P	0.013		0.009		
S	0.0048		0.001	0.5	1.2
Ce	0.002	21.0	13		
Al	0.038				
N	0.0036				
O			0.24	0.0120	
Fe	Balance	Balance	Balance	Balance	Balance

A summary of the experimental work done in the first series of experiments is listed in Table 4. A detailed description of the second and third series of experiments is given in Table 5. A weighed amount of 037X steel was melted in a vacuum furnace ($p < 1 \times 10^{-3}$ mbar). When the melting started, Ar was fed in ($p = 650$ mbar). After the metal had melted, the temperature (aim 1600°C) was measured by an immersion thermocouple and a sample was taken. Aluminium (150 ppm) was also added to all steels, except for steel 1D3, to compensate for the effect of the oxidised layer in the alloying device. Al was dropped into the melt with a piece of steel (037X). The preconditioner and the grain refiner were added with an alloying device. The alloying device used in the second series is shown in Figure 3. In the third series, the alloying device was slightly different. Powder and rods were both inside a cylinder. The device was ca. 100 grams lighter, so the temperature drop during alloying was smaller.

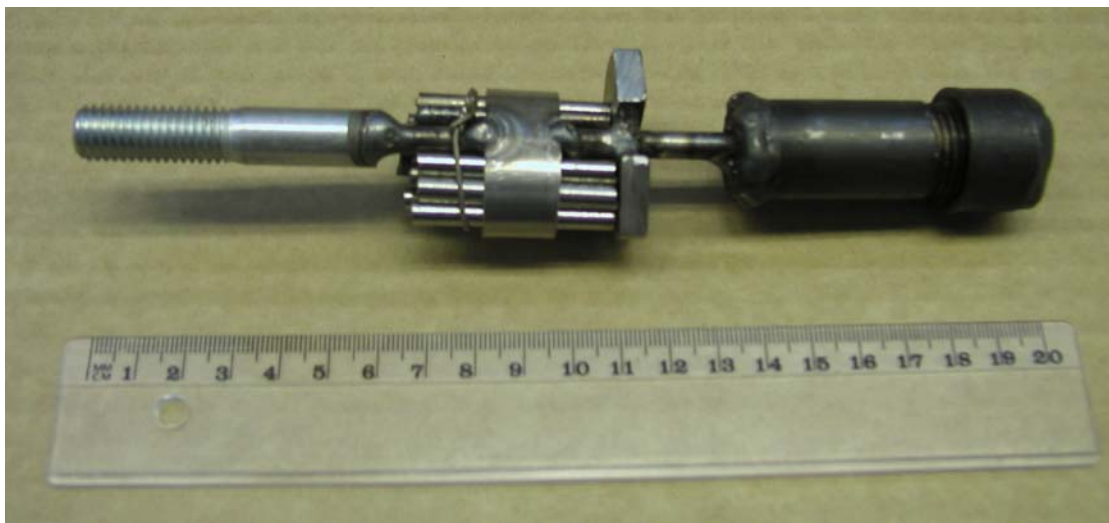


Figure 3. Alloying device used to add the preconditioner and the grain refiner.

The alloying device was preheated for 60 seconds above the melt after which the preconditioner containing cylinder was immersed into the melt. In experiments 1D3 and 2D4, the grain refiner rods were added 20 seconds later. In experiment 3D3 and the complete third series, the grain refiner rods were wrapped around the cylinder and immersed together at the same time with the preconditioner. Tapping was started 50-60 seconds after the last addition and took ca. 15-20 seconds.

Table 4. Summary of the experimental work in the first series of experiments

Trial No.	Target Ce (wt%)	Pre-conditioner 21wt%Ce (g/kg)	Grain Refiner 14B (g/kg)	Time between PC addition and tapping (min:sec)
D1	0.11	4.8	0	1:10
D2	0.11	4.8	5	3:53
D3	0.11	4.8	10	3:09
D4	0.10	4.8	15	1:50

Table 5. Description of the experimental work in the second and third series of experiments

Second series			
Experiment no.	1D3 (27.1. 2003)	2D4 (29.1.2003)	3D3 (28.1.2003)
Steel (037X)	6250 g	6040 g	6000 g
Preconditioner (ca. 13% Ce)	48 (7.3 g/kg)	46 (6.9 g/kg)	46 (7.1 g/kg)
Ce (100 % yield)	0.095 %	0.090 %	0.093 %
Ce in 037X	0.002 %	0.002 %	0.002 %
Grain Refiner 14B	64 (9.8 g/kg)	95 (14.3 g/kg)	62 (9.6 g/kg)
Alloying device (steel)	223 g	220 g	181+66 g
Steel from previous exp.	0 g (a new crucible)	281 g	142 g
Al + piece of steel (037X)	0 g	1 + 49 g	1 + 46 g
Total input	6585 g	6732 g	6544 g
Sample	33 g	36+17 g	36 g
Leftover from alloying device	10 g	32 g	57 g
Charge weight when alloyed	6542 g	6657 g	6451 g
Ingot weight	6400 g	6305 g	6170 g
Left in the crucible (approx.)	142 g	352 g	281 g
Progress of experiment	Time (minutes)	Time	Time
Vacuum pumps on	0	0	0
Diffusion pumps start	25	17	10
Power on (ca. 8×10^{-4} mbar)	32	22	13
Melting started, Ar in	52	42	30
Ar pressure 650 mbar	54	44	32
Everything melted, T measurement	60 1600°C (? , trouble)	47 1590-1600°C	40 1590-1600C
Sample	63	49	43
Al addition	No	51	44
Second sample	No	52	No
Preliminary work done	65	53	45
Preheating of alloying device starts	00:00 (min:sec)	00:00	00:00
Addition of preconditioner	00:55	01:00	01:00
Addition of grain refiner	01:15	01:20	01:00
Tapping started	01:45	01:50	01:45
Tapping finished	02:05	02:10	02:00
From the addition of preconditioner to the end of tapping	70 sec	70 sec	60 sec
From the addition of grain refiner to the end of tapping	50 sec	50 sec	60 sec

Table 5. Continued

Third series			
Experiment no.	E1 (21.5.2003)	E2 (22.5.2003)	E3 (23.5.2003)
Steel (037X)	6150 g	6145	6040
Preconditioner (13% Ce)	29 (4,6 g/kg)	44 (6,8 g/kg)	89 (13,6 g/kg)
Ce (100 % yield)	0.062 %	0.090 %	0.178 %
Ce in 037X	0.002 %	0.002 %	0.002 %
Grain Refiner 14D (S2)	40 (6,3 g/kg)	53,3 (8,3 g/kg)	34 (5,2 g/kg)
Alloying device	129	136,9	152
Steel from prev. exp.	0 (new crucible)	100 (approx.)	300 (approx.)
Al + piece of steel	0,8 + 26,5	0,75 + 29,9	0,75 + 25
Total input	6375,3	6510	6640
Sample	34	35	34
Leftover from alloying device	41,8	51	51
Charge weight when alloyed	6299,5	6424 (approx.)	6555 (approx.)
Ingot weight	5850	5750	6066
Progress of experiment	Time (minutes)	Time (minutes)	Time (minutes)
Vacuum pumps on	0	0	0
Power on	22 (9 x 10 ⁻⁴ mbar)	19 (5 x 10 ⁻⁴ mbar)	16 (9 x 10 ⁻⁴ mbar)
Melting started, Ar in (650mbar)	48	63	40
Everything melted	58	67	45
T measurement	61 (1600)	70 (>1600)	46 (1560)
		71 (1600)	47 (1570)
			49 (1580)
			50 (1600)
Sample taken for O analyses	62	73	51
Al addition	63	74	52
Preliminary work done	64	75	54
Preheating of alloying device starts	00:00 (min:sec)	00:00	00:00
Addition of preconditioner and grain refiner	01:00	01:00	01:00
Tapping started	01:45	01:45	01:40
Tapping finished	01:55	02:00	02:05
From the alloying to the end of tapping	55 sec	60 sec	65 sec
Comment	There was brownish dust in the furnace that smelled like sulphur.	Bigger amount of brownish dust.	Heavy boiling and a lot of dust.

4.2.2 Heat treatment and characterisation

In order to examine the efficiency of the different inclusions as nucleation sites for ferrite, the steels were subjected to thermal treatment. The thermal cycle, as shown in Figure 4, had a peak temperature of 1350°C and a cooling time between 800°C and 500°C of 40 seconds. The steels D1, D3 and D4 were also subjected to a shorter thermal cycle with a peak temperature of 1350°C and a cooling time between 800°C and 500°C of 20 seconds. After heat treatment the microstructure was examined by optical microscope and the inclusions were characterised using a Hitachi 4300 Field Emission SEM.

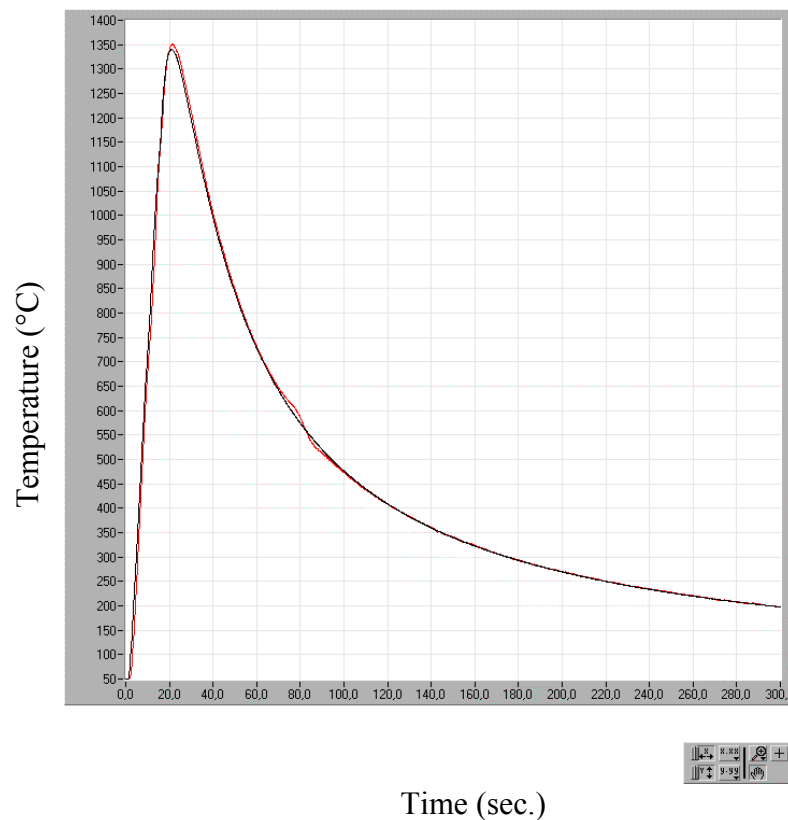


Figure 4. Thermal cycles with $T_{peak}=1350^{\circ}\text{C}$ and $\Delta t_{8/5}=40$ sec.

4.3 Results and discussion

4.3.1 Chemical analyses

The chemical analyses of the steels are shown in Table 6. There is a significant loss of aluminium in every experiment. The yields of the additions are listed in Table 7. In the 1D3 experiment, both the yields of Ce and S are significantly lower than in the other experiments. The reason is probably a poor temperature control caused by a malfunctioning of the immersion thermocouple, i.e. the melt was too hot. Also the nitrogen level is higher in the 1D3 experiment. The yield of S is almost 100 % in experiments 2D4 and 3D3. The Ce yield is over 50 % in experiment 3D3, in which the preconditioner and the grain refiner were added simultaneously. Because of this high Ce yield in experiment 3D3, it was decided to add the preconditioner and grain refiner simultaneously in the third series (E1, E2 and E3). The high Ce yield was, however, not reproduced in the third series. The high O content in steel E1 might be coming from the new crucible and/or insulation mass. Steel E2 and especially E3 have a very low S yield. In steel E3, all the S added through the grain refiner was lost. It is unlikely that this has something to do with the higher S content in the grain refiner used in the third series, since steel E1 has a high S yield.

Table 6. Chemical composition of the steels (wt.%)

Trial	C	Mn	Si	Ce	S	O	N	Al
D1	0.086	1.04	0.402	0.056	0.0071	0.0040	0.0038	0.006
D2	0.086	1.02	0.435	0.006	0.0080	-	0.0053	0.004
D3	0.076	1.04	0.417	0.018	0.0090	0.0030	0.0040	0.009
D4	0.080	1.06	0.404	0.035	0.0133	0.0033	0.0035	0.007
1D3	0.080	1.000	0.526	0.011	0.0060	0.0038 ¹	0.0083	0.005
2D4	0.076	1.020	0.533	0.037	0.0120	0.0044 ²	0.0064	0.009
3D3	0.090	0.997	0.529	0.054	0.0096	0.0037 ³	0.0039	0.009
E1	0.0685	0.97	0.414	0.023	0.0127	0.0092 ⁴	0.0072	0.007
E2 ⁷	0.0620	1.01	0.507	0.026	0.0108	0.0047 ⁵	0.0082	0.009
E3	0.0652	0.952	0.732	0.068	0.0044	0.0044 ⁶	0.0091	0.011

¹ 0.0076 wt% O in the melt before preconditioner/grain refiner addition

² 0.0045 wt% O in the melt before Al addition, 0.0054 wt% O in the melt after Al addition before preconditioner /grain refiner addition

³ 0.0043 wt% O in the melt before preconditioner/grain refiner addition

⁴ 0.0073 wt% O in the melt before preconditioner/grain refiner addition

⁵ 0.0066 wt% O in the melt before preconditioner/grain refiner addition

⁶ 0.0066 wt% O in the melt before preconditioner/grain refiner addition

⁷ Average of two analyses, Ce varies from 0.019 to 0.032 wt%, the other elements show no significant scatter

Table 7. Yields of the additions

	D1	D2	D3	D4	1D3	2D4	3D3	E1	E2	E3
Ce	51 %	5 %	16 %	34 %	10 %	37 %	55 %	35 %	34 %	36 %
S	-	128%	84 %	113 %	25 %	99 %	100 %	104 %	59 %	<0 %
Si	87%	111%	98%	88%	91 %	91 %	93 %	85 %	95 %	93 %

4.3.2 Microstructure

The microstructure after heat treatment is shown in Figure 5 to Figure 13. The micrographs show that the potency of the inclusions to nucleate ferrite differs significantly between the steels. In the first series, the inclusions in steels D3 and D4 are capable of nucleating ferrite, while the inclusions in steel D1 appear to be inert. The inclusions in steel D1 have generally a faceted shape, while the inclusions in steels D3 and D4 are globular. A rough estimate of the inclusion size distribution in the optical microscope reveals that the inclusions in D1 are, on the average, smallest. The largest inclusions are observed in steel D4, where the maximum diameter is about 7 μm . It is clear from the micrographs that

In the second series, steel 2D4 contains clearly inclusions with the largest potential to nucleate ferrite, while the inclusions in steel 3D3 show no signs of nucleating ferrite. The inclusions in steel 1D3 show occasionally signs of nucleating ferrite.

In the third series, only steel E1, shown in Figure 11, contains significant amounts of acicular ferrite. Steel E2, shown in Figure 12, contains some acicular structure, but no clear nucleation events associated with inclusions were observed. Steel E3, shown in Figure 13, shows no signs of intergranular nucleation of ferrite by inclusion.

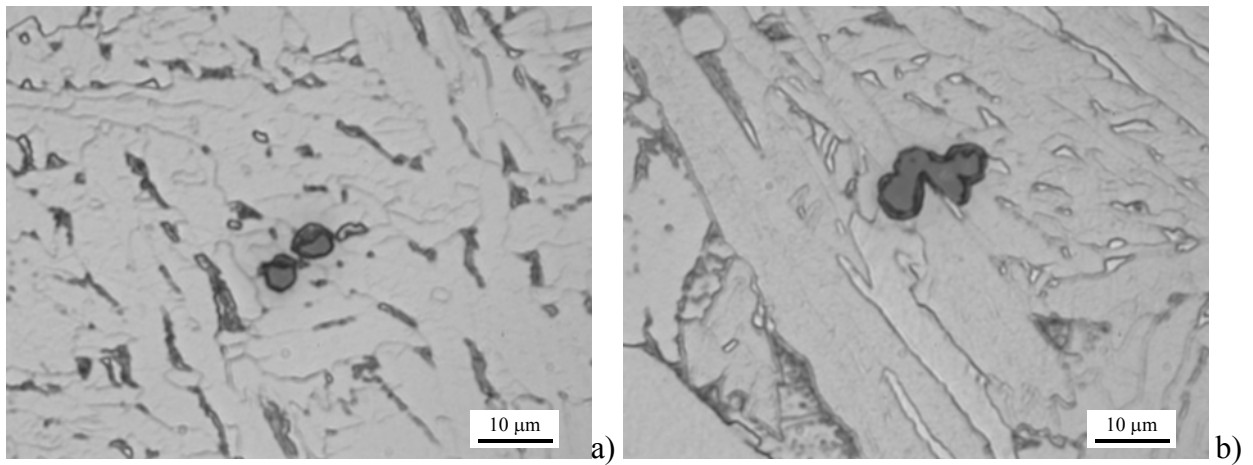


Figure 5. Microstructure of steel D1, after a heat treatment at $T_{peak}=1350^{\circ}\text{C}$ and a) $\Delta t_{8/5}=40$ sec, b) $\Delta t_{8/5}=20$ sec.

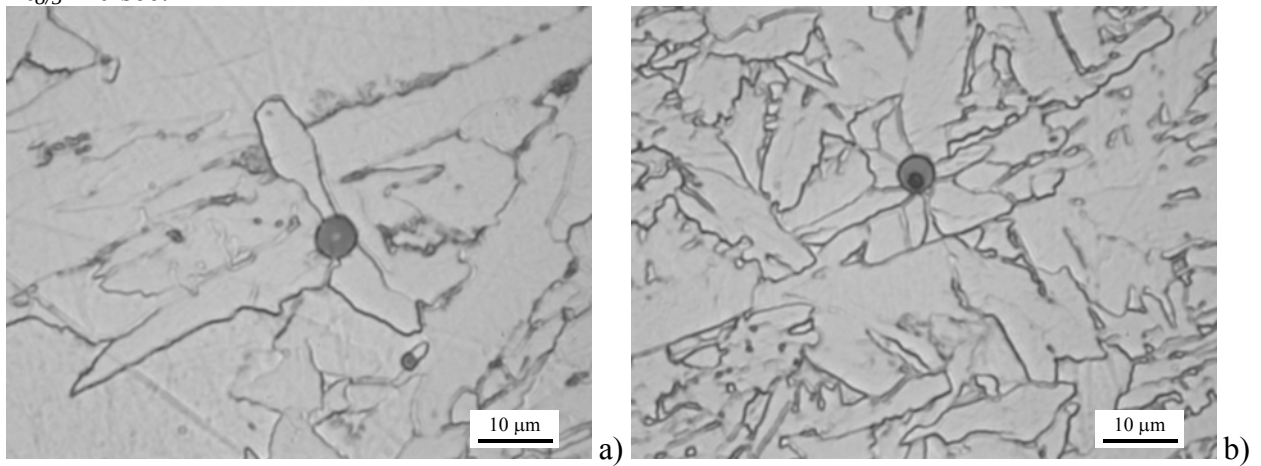


Figure 6. Microstructure of steel D3, after a heat treatment at $T_{peak}=1350^{\circ}\text{C}$ and a) $\Delta t_{8/5}=40$ sec, b) $\Delta t_{8/5}=20$ sec.

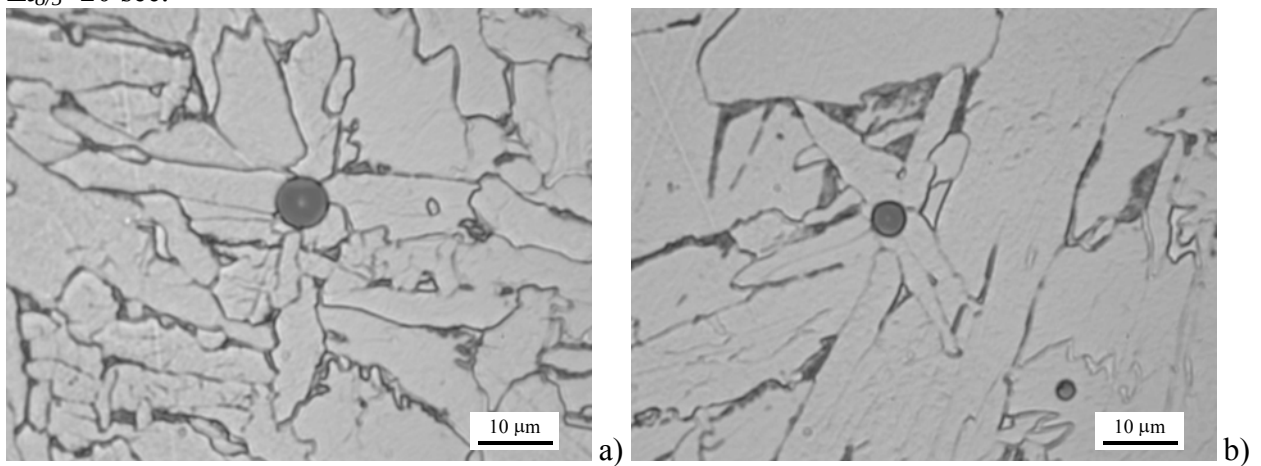


Figure 7. Microstructure of steel D4, after a heat treatment at $T_{peak}=1350^{\circ}\text{C}$ and a) $\Delta t_{8/5}=40$ sec, b) $\Delta t_{8/5}=20$ sec.

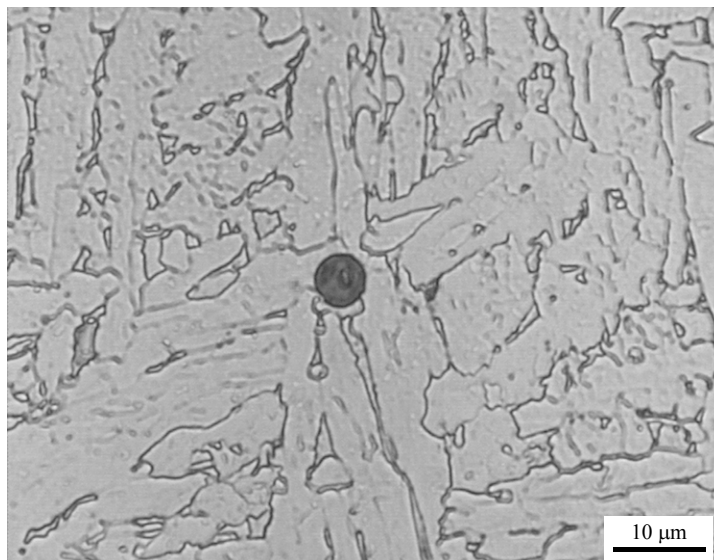


Figure 8. Microstructure of steel 1D3, after thermal cycling at $T_{peak}=1350^{\circ}\text{C}$ and $\Delta t_{8/5}=40$ sec.

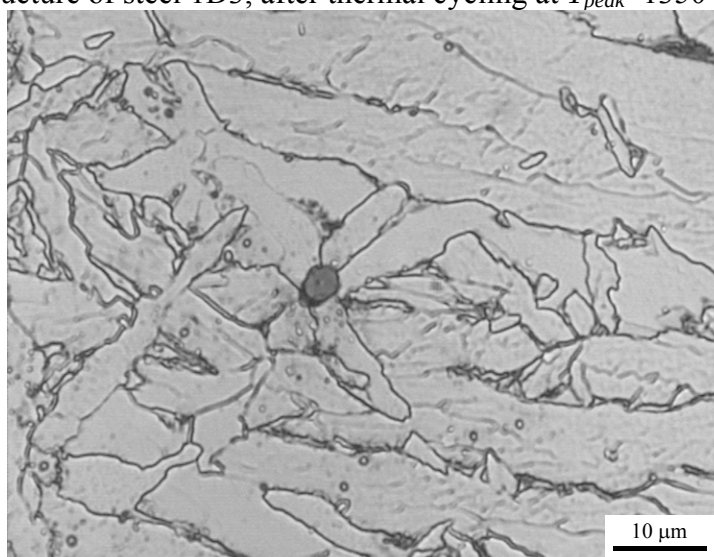


Figure 9. Microstructure of steel 2D4, after thermal cycling at $T_{peak}=1350^{\circ}\text{C}$ and $\Delta t_{8/5}=40$ sec.

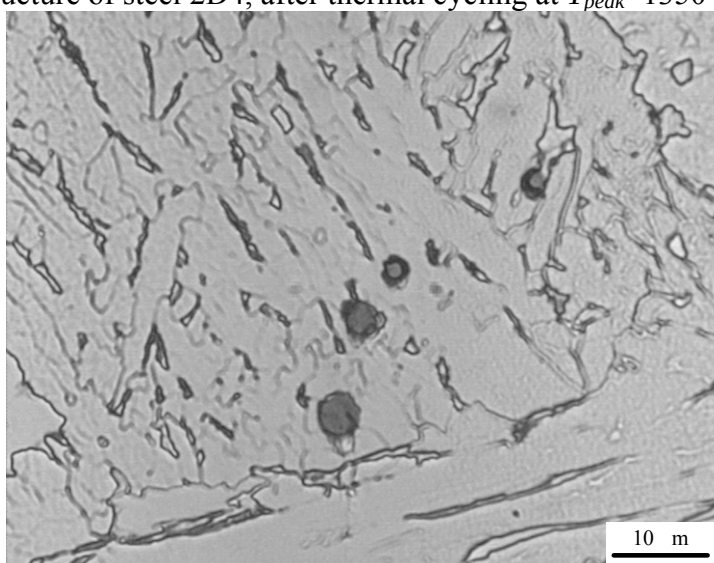


Figure 10. Microstructure of steel 3D3, after thermal cycling at $T_{peak}=1350^{\circ}\text{C}$ and $\Delta t_{8/5}=40$ sec.

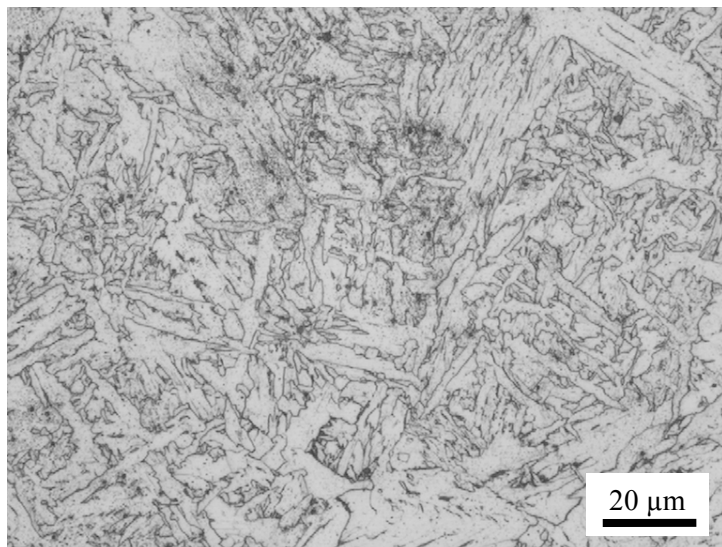


Figure 11. Microstructure of steel E1, after thermal cycling at $T_{peak}=1350^{\circ}\text{C}$ and $\Delta t_{8/5}=40$ sec.

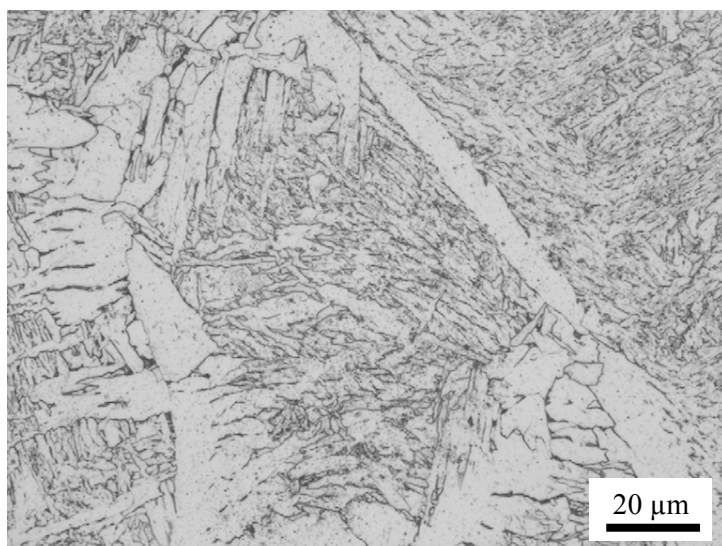


Figure 12. Microstructure of steel E2, after thermal cycling at $T_{peak}=1350^{\circ}\text{C}$ and $\Delta t_{8/5}=40$ sec.

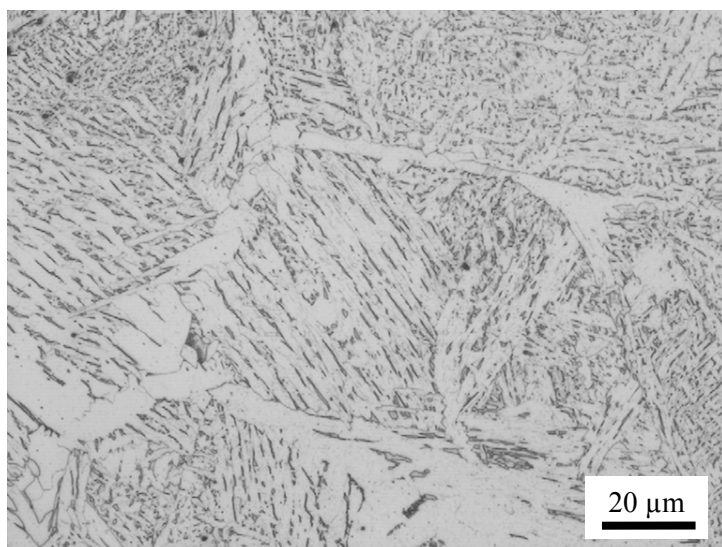


Figure 13. Microstructure of steel E3, after thermal cycling at $T_{peak}=1350^{\circ}\text{C}$ and $\Delta t_{8/5}=40$ sec.

4.3.3 Inclusion characterisation

Steel D1

The FEG SEM investigations were performed to investigate the inclusion composition. Figure 14 shows a backscattered electron image of three inclusions in steel D1. The inclusions in this steel consist of one phase. The composition, as measured by EDS, is shown in Table III.1.

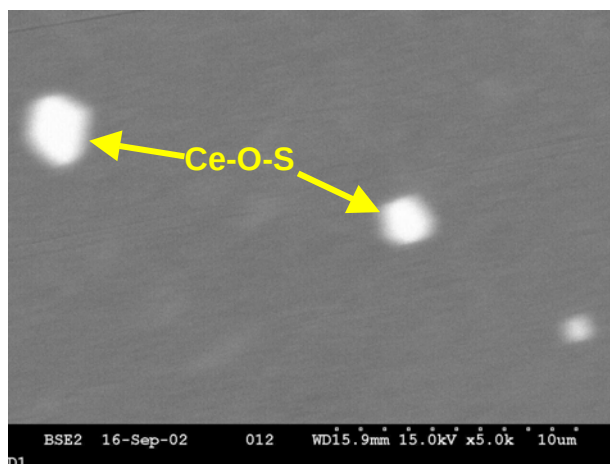


Figure 14. Backscattered electron image showing single phase inclusions in steel D1

Table 8. Quantitative EDS analyses of the inclusions in steel D1

At%	Ce	O	S
	36.7	41.2	22.1
	44.8	24.0	31.2
	38.3	41.8	20.0
	38.4	42.0	19.6
	41.3	36.9	21.8
	41.5	33.4	25.0
	37.2	43.2	19.6
	42.0	26.4	31.6
	40.2	40.8	18.9
	39.7	42.2	18.0
	39.0	41.8	19.1
average	39.9	37.6	22.5
standard deviation	2.4	6.8	4.8

Steel D3

Three types of inclusions are observed in steel D3. The first type is a multiphase inclusion consisting of a Ce-O-S oxide core with MnS as an outer shell, as shown in Figure 15. The second type are pure MnS type inclusions, as shown in Figure 16, presumably originating from the grain refiner 14B. The third type of inclusion is rare. It is similar to the first type, but contains Al and Ti in the oxide core as well. Table III.2 lists the results from the EDS analyses of the oxide core in the first type. The oxysulphide core appears to be very similar to the inclusions observed in steel D1.

A possible explanation for the nucleation of acicular ferrite by inclusions containing MnS patches on the surface is the presence of a Mn depleted zone in the iron matrix adjacent to the inclusions. This zone could be caused by the precipitation of MnS on the surface of the inclusion in solid state. The lower Mn content in the matrix will increase the phase transformation temperature locally thereby promoting ferrite nucleation on the inclusions. Figure 17 shows an inclusion with a Ce-oxysulphide core and a patch of MnS on the surface. A linescan is performed from the inclusion into the matrix as indicated in Figure 17. The results are shown in Figure 18. The variation of Mn content in the matrix is not significant enough to confirm the presence of a Mn depleted zone.

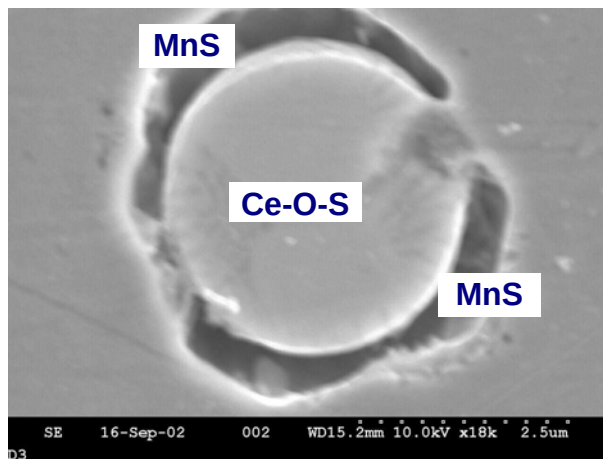


Figure 15. Multiphase inclusion in steel D3 consisting of an oxysulphide core with patches of MnS at the surface

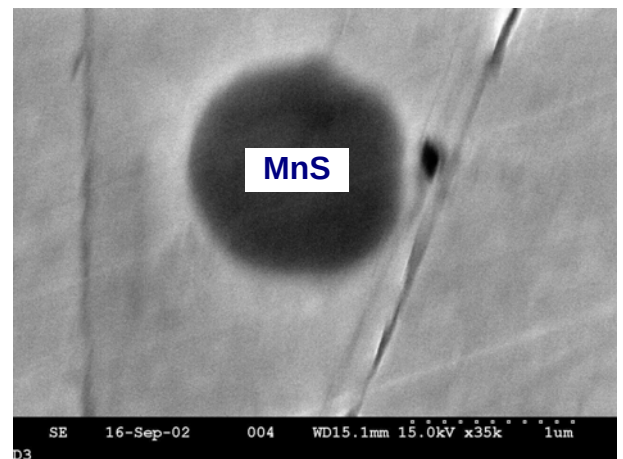


Figure 16. Pure MnS inclusion in steel D3 with a typical size of 1 μm

Table 9. Quantitative EDS analyses of the inclusions in steel D3.

At%	Ce	O	S
	36.5	43.7	19.9
	38.8	42.3	18.9
	34.1	47.2	18.7
	34.7	39.4	25.9
average	36.0	43.2	20.9
stand. dev.	2.1	3.2	3.4

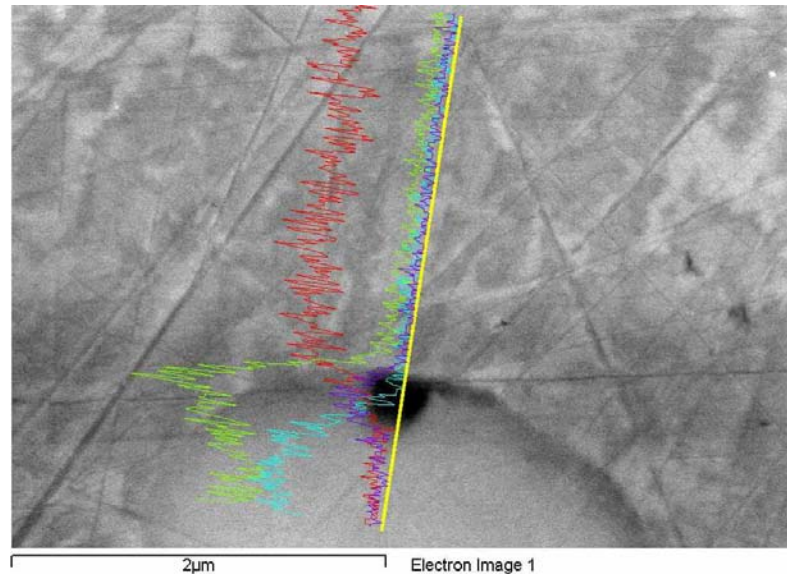


Figure 17. Inclusion in steel D3 consisting of a cerium-oxysulphide core with a patch of MnS at the surface. The straight line indicates the position where a linescan is taken. The other lines correspond with the EDS counts shown in Figure 18.

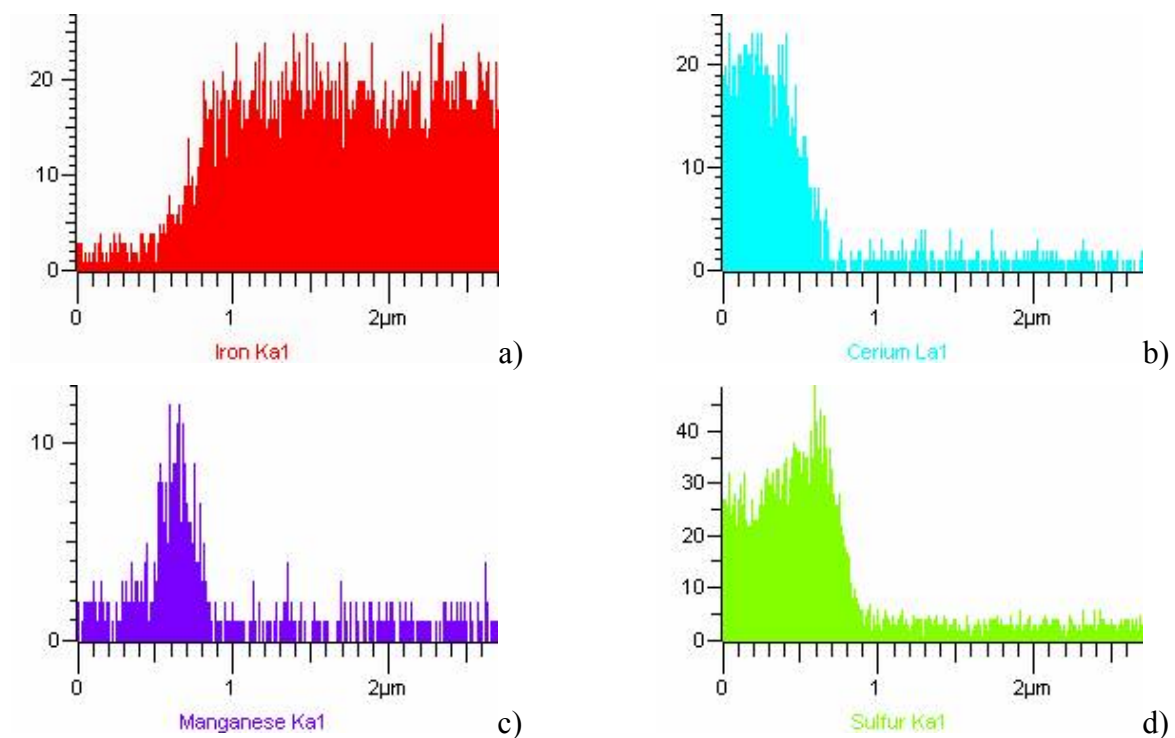


Figure 18. EDS counts along a linescan taken at the position indicated in Figure 17: a) Iron, b) Cerium, c) Manganese, d) Sulphur.

Steel D4

Three types of inclusions are observed in steel D4. The first type is a multiphase inclusion consisting of a Ce-O-S oxide core with MnS as an outer shell, as shown in Figure 19. In this case the core consists of two types of oxysulphides. The results from the EDS analyses of these two phases in the core are listed in Tables III.3 and III.4. The second type are pure MnS type inclusions similar to those observed in steel D3 and shown in Figure 16. These are presumably originating from the grain refiner 14B. The third type of inclusion in steel D4, shown in Figure 20, is a multiphase sulphide consisting of MnS and CeS. After addition of the preconditioner there is

still free Ce in the liquid steel, since there is enough Ce to tie up all oxygen and sulphur present. The MnS inclusions added through the grain refiner 14B will be “attacked” by the free Ce, since CeS is thermodynamically more stable than MnS. In order to investigate which type of inclusions is most potent as nucleation site for ferrite, SEM investigations were done on etched (nital) samples. The etching attacks however the inclusions, as shown in Figure 21 and Figure 22 which makes it impossible to do reliable analyses on these.

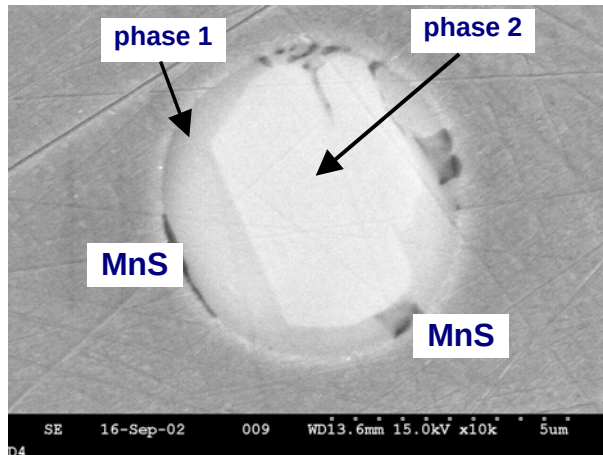


Figure 19. Multiphase inclusion in steel D4 consisting of an oxysulphide core with patches of MnS at the surface

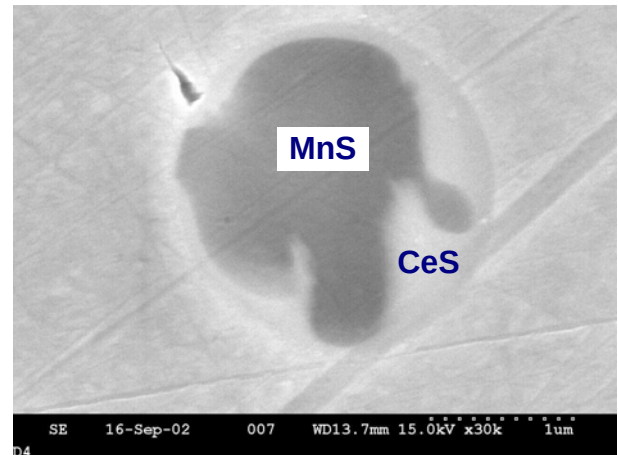


Figure 20. Mixed sulphide inclusion in steel D4 consisting of MnS and CeS

Table 10. Quantitative EDS analyses of “phase 1” in the inclusion core in steel D4.

At%	Ce	O	S
	38.2	44.6	17.2
	37.3	43.6	19.2
	37.2	40.9	22.0
	35.9	26.5	37.6
	38.8	42.8	18.4
	38.5	43.7	17.8
average	37.6	40.4	22.0

Table 11. Quantitative EDS analyses of “phase 2” in the inclusion core in steel D4.

At%	Ce	O	S
	40.7	15.6	43.6
	35.9	0.0	64.1
	43.8	0.0	56.2
	39.5	13.6	46.8



Figure 21. Inclusion in an etched sample of steel D4. The inclusion has nucleated acicular ferrite.

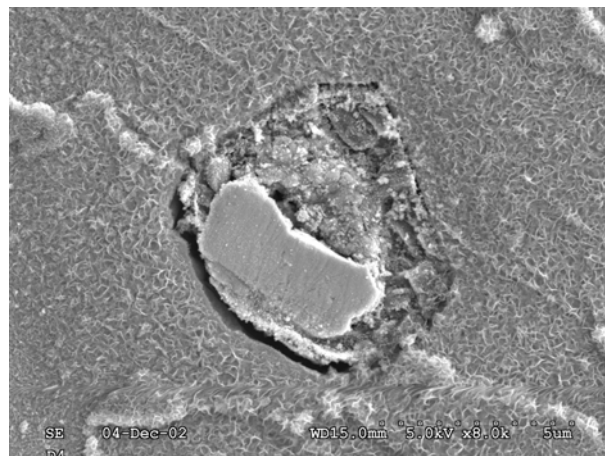


Figure 22. Close-up of the inclusion in Figure 21, showing clearly that the inclusion has been attacked by the etching procedure.

Steel 1D3, 2D4, 3D3, E1, E2 and E3

In all these steels, except E2 and E3, both Ce-containing inclusions and pure MnS inclusions are observed. The number density of the MnS inclusions is high in 1D3, 2D4 and E1. In steel 3D3, these MnS inclusions are, however, extremely rare. The composition of the Ce-containing inclusions in the steels, measured by SEM-EDS, is shown in Table 12. The higher O content in the steel in the third series (E1, E2 and E3) is reflected by a high O content in the inclusions.

Figure 23 shows the two types of inclusions present in 1D3. The single phase core of the inclusion shown in Figure 23a contains an oxysulphide of Ce, Al and Si along with MnS on the surface. Most of the MnS inclusions have a size below one micron, as shown in Figure 23b. Figure 24 shows a typical inclusion in steel 2D4 and contains the results of a line-scan across this inclusion in the direction of the arrow indicated in Figure 24a. The core contains Ce, O and S while MnS is clearly present on the surface. The inclusions in steel 3D3 are single phase Ce-oxysulphides, as shown in Figure 25.

The oxide inclusions in steel E1, shown in Figure 26a, are mixed oxides of Ce-Al-Si with MnS on the surface. Besides these oxysulphides, single phase MnS inclusions are present, as shown in Figure 26b. The inclusions in steel E2, shown in Figure 27, are single phase Ce-oxysulphides. Steel E3 contains similar Ce-oxysulphides, as shown in Figure 28a. Except for these, some Ce-oxide inclusions without sulphur, as shown in Figure 28b, are observed in this steel.

Table 12. Average analysed composition of the Ce-containing inclusions (at.%)

	Ce	O	S	Mn	Al	Si	Ti
1D3	16	53	9	7	8	6	1
2D4	23	23	33	19	1	1	0
3D3	38	22	39	1	0	0	0
E1	15	50	12	12	2	9	0
E2	37	46	17	0	0	0	0
E3	34	54	12	0	0	0	0

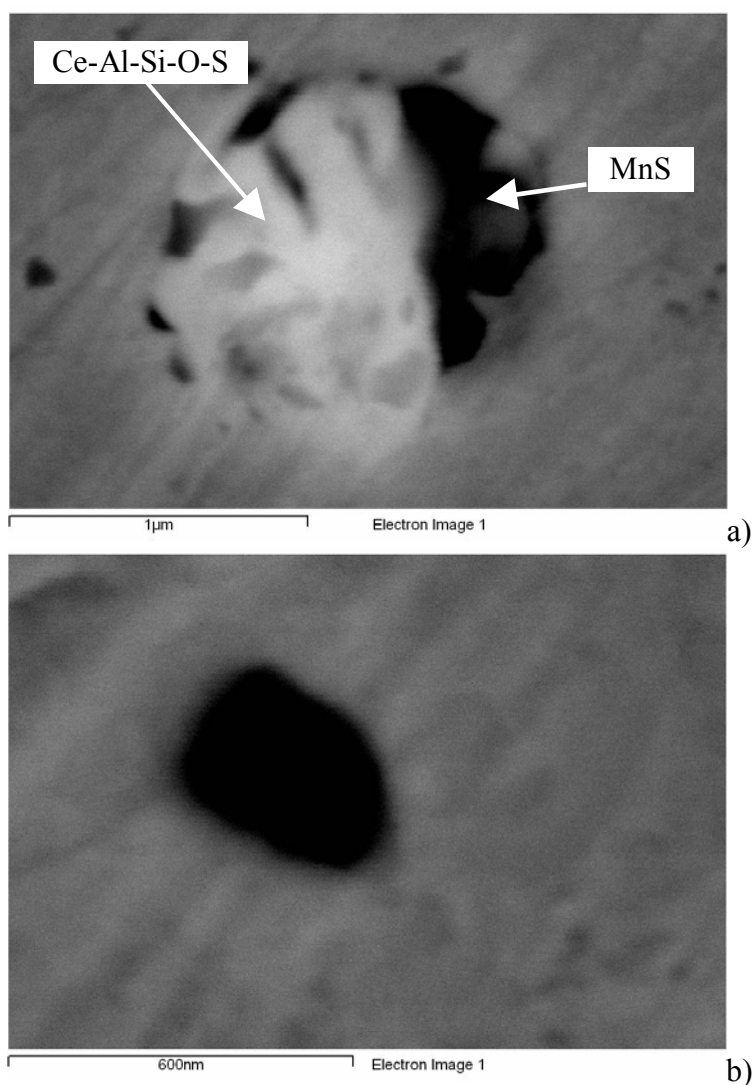


Figure 23. SEM Backscattered images of inclusions in steel 1D3, a) multiphase inclusion in which the bright phase is a Ce-Al-Si-oxysulphide and the dark phase MnS, b) single phase MnS inclusion.

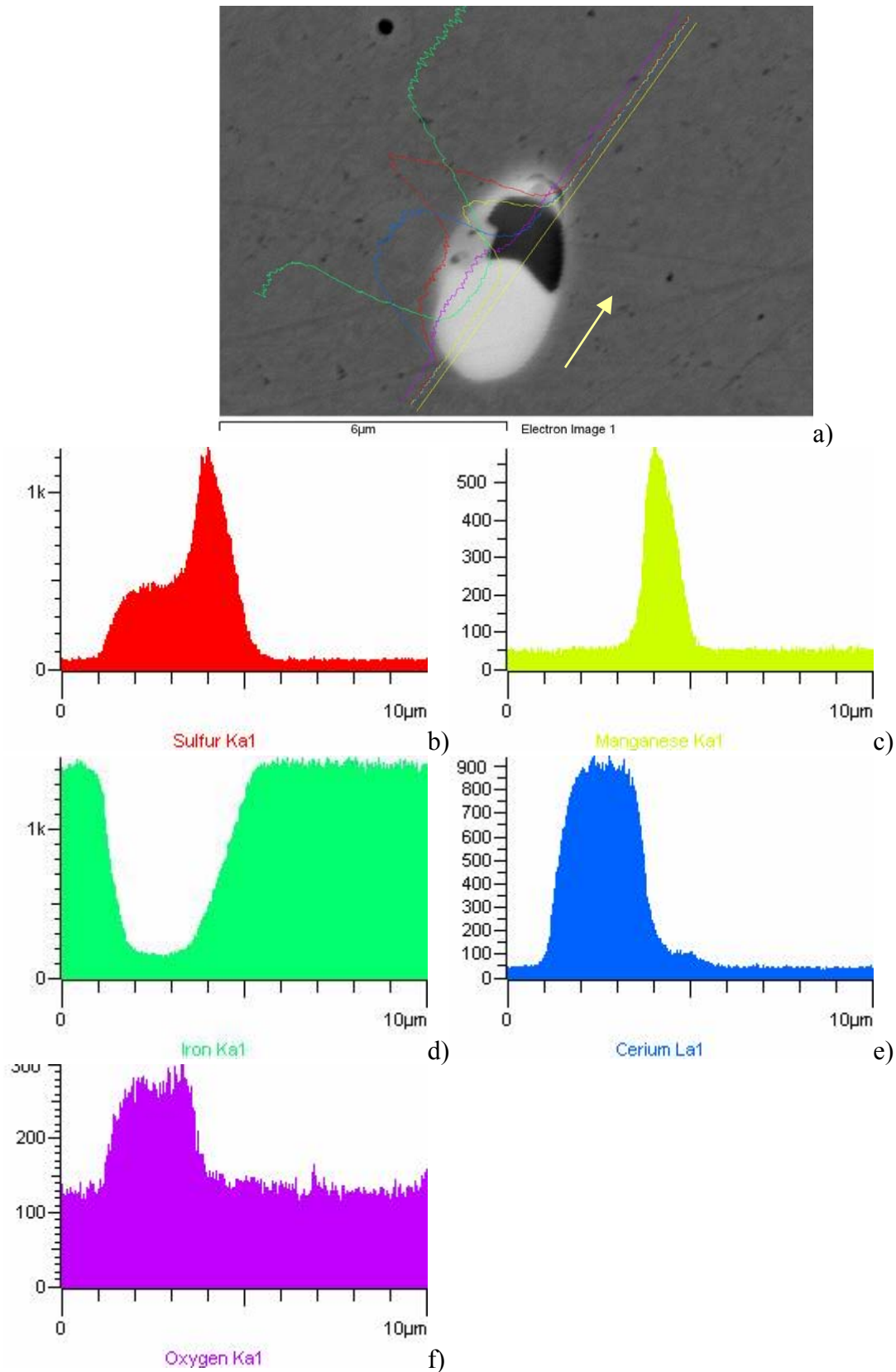


Figure 24. Linescan across a multiphase inclusion in steel 2D4, a) SEM backscattered image, b) Sulphur, c) Manganese, d) Iron, e) Cerium and f) Oxygen.

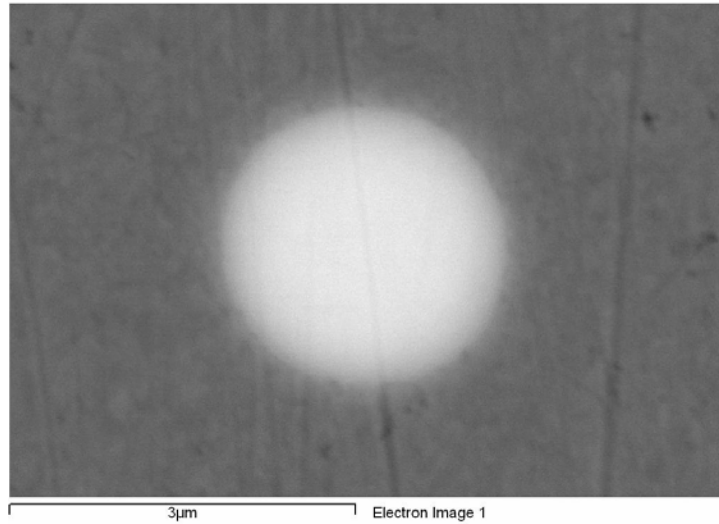


Figure 25. SEM Backscattered image of a single phase Ce-oxysulphide inclusion in steel 3D3.

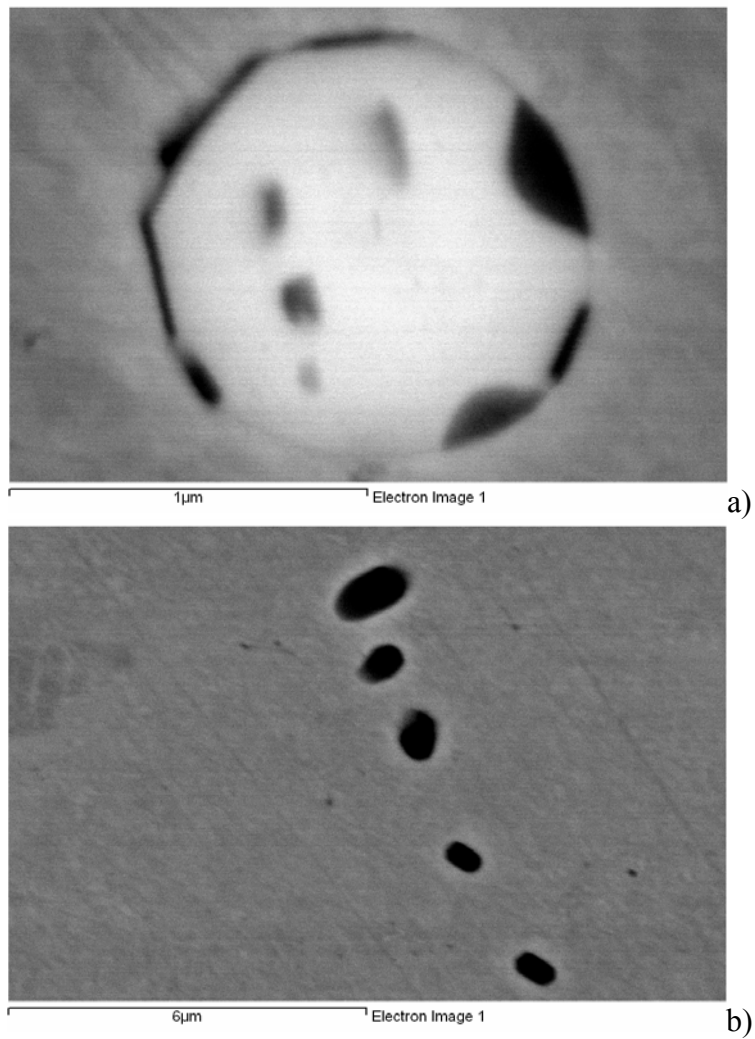


Figure 26. SEM Backscattered images of inclusions in steel E1, a) multiphase inclusion in which the bright phase is a Ce-oxysulphide and the dark phase MnS, b) single phase MnS inclusions.

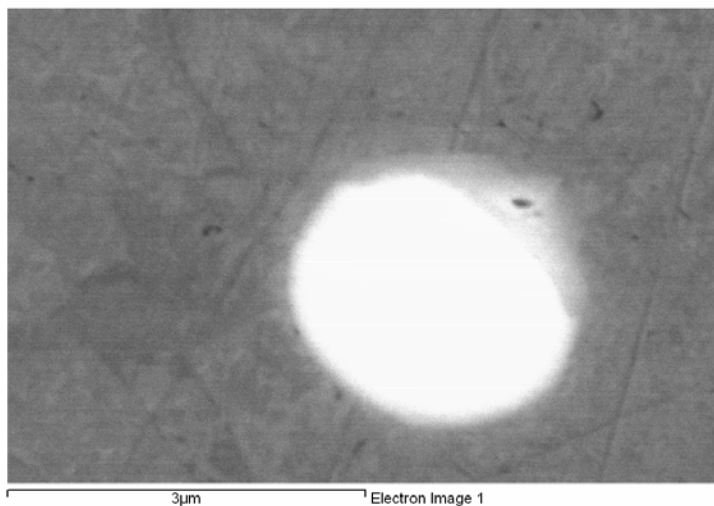


Figure 27. SEM Backscattered image of a single phase Ce-oxysulphide inclusion in steel E2.

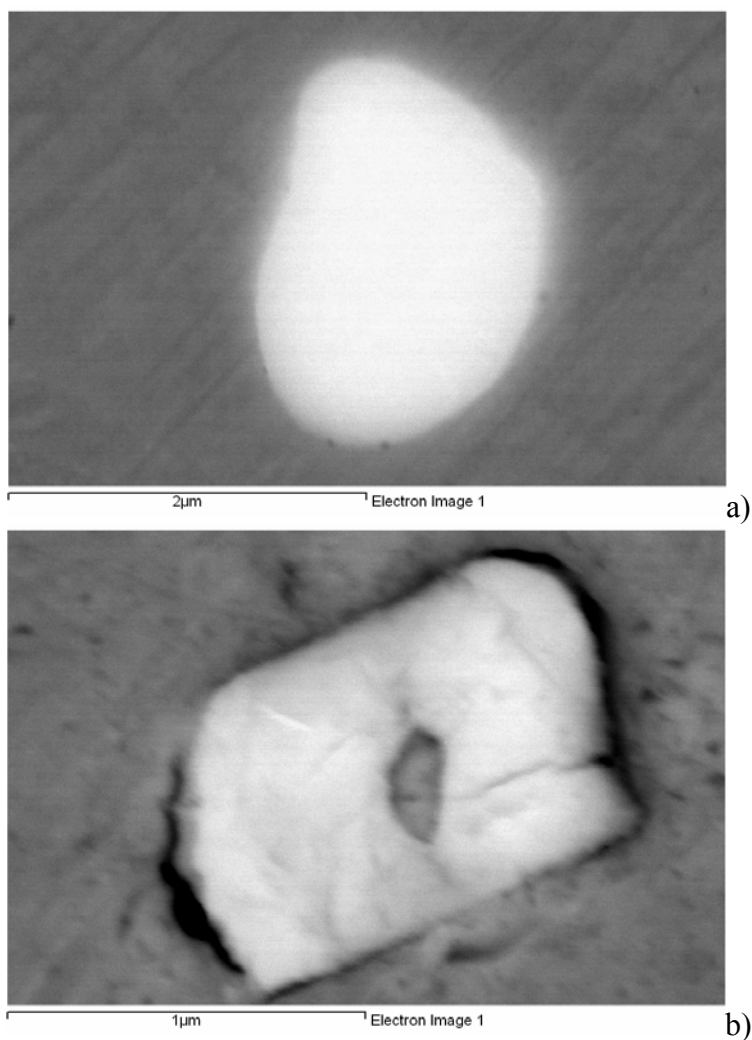


Figure 28. SEM Backscattered images of inclusions in steel E3, a) single phase Ce-oxysulphide inclusion, b) Ce-oxide inclusion.

4.3.4 Thermodynamic calculations

Qualitative prediction of the inclusion phases

Thermodynamic (FACTSAGE) calculations were performed on three different steel compositions in order to predict the expected inclusion phases in the solid state. The results are shown in Figure 29. Figure 29a shows the calculation for a steel with an oxygen content of around 36 ppm (D1, D2, D3, 1D3, 2D4 and 3D3), while Figure 29b shows the same for a steel with a higher O content, 47 ppm (E1, E2 and E3). Generally, the calculated phases agree well with the SEM analyses. An exception is steel E2, where MnS is expected to be stable on basis of the chemical analyses of the steel, but it is not observed in the SEM. A repetition of the chemical analysis of E2 shows that there is a large compositional difference in the Ce content in different parts of the casting. A difference in Ce content between the samples used for chemical analyses and the sample used for heat-treatment/SEM analysis might be an explanation for the inconsistency between the steel chemical composition and the SEM analyses.

Quantitative prediction of the inclusion composition

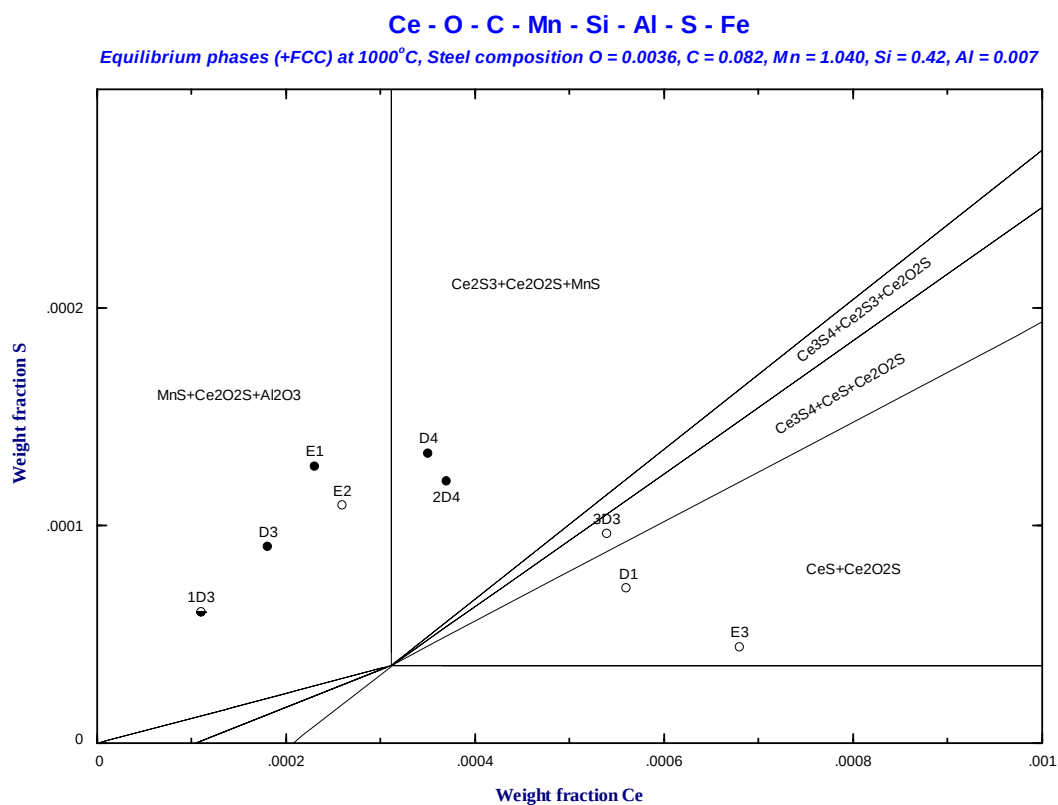
For the steels 1D3, 2D4 and 3D3, the expected inclusion composition was predicted quantitatively. The results, listed in Table 13, show that MnS is thermodynamically stable in steel 1D3 and 2D4, but not in steel 3D3. This is in good agreement with the SEM analyses. The expected inclusion composition, listed in Table 14, is calculated on basis of Table 13. There is good agreement between the analysed and the calculated inclusion composition for steels 2D4 and 3D3. This confirms that the oxysulphide phase present in steel 2D4 is, indeed, $\text{Ce}_2\text{O}_2\text{S}$. Thermodynamic data on the complex Ce-Al-Si-oxysulphide observed in steel 1D3 is not available in FACTSAGE. Therefore, the predicted inclusion composition does not correlate well with the analysed composition.

Table 13. Calculated weight fractions of different inclusion phases ($\times 10^{-4}$)

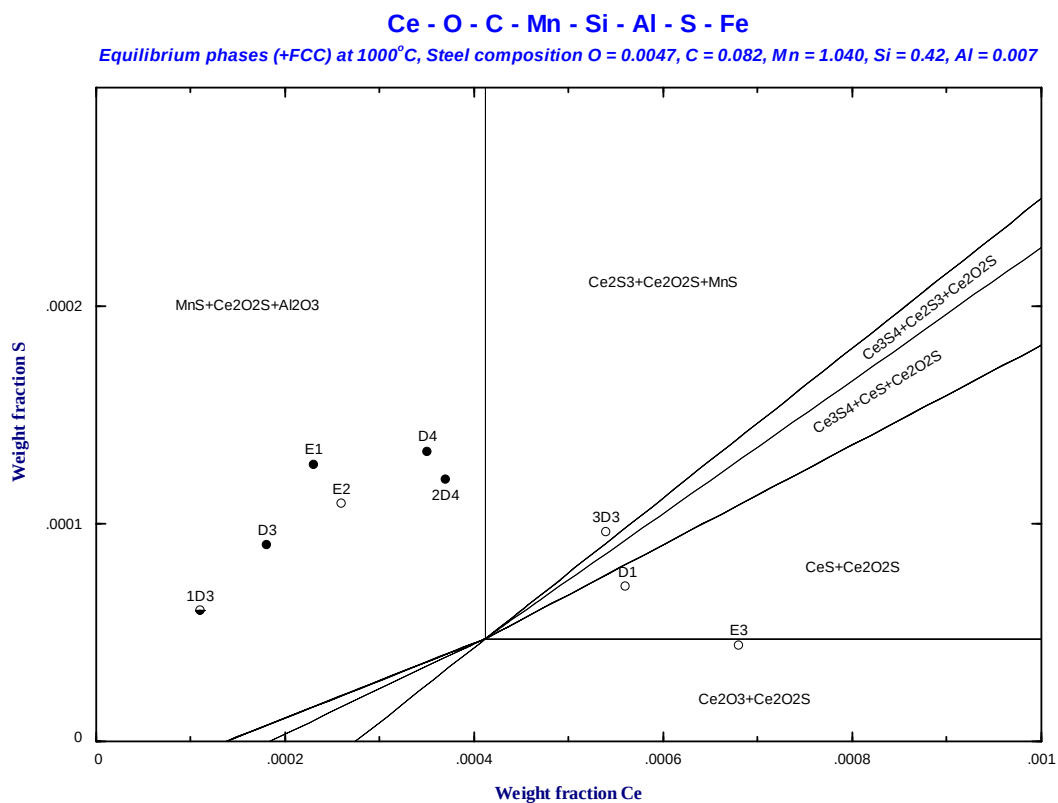
	$\text{Ce}_2\text{O}_2\text{S}$	Mns	Al_2MnO_4	Ces	Ce_3S_4
1D3	1.4	1.3	0.7	0	0
2D4	4.6	2.1	0	0	0
3D3	4.0	0	0	1.1	1.6

Table 14. Calculated inclusion compositions (at.%)

	Ce	O	S	Mn	Al
1D3	10.1	30.9	24.2	24.4	10.4
2D4	23.1	23.1	32.7	21.1	0.0
3D3	42.0	25.5	32.5	0.0	0.0



a)



b)

Figure 29. Predicted inclusion composition at 1000°C as a function of the Ce and S contents in the steels with a) 0.0036wt% O and b) 0.0047wt% O.

4.3.5 Ranking of inclusions with respect to ferrite nucleation potency

Table 15 summarises the results of all experiments. Figure 30 shows the Ce content versus the O content for all steels. The closed symbols indicate steels in which ferrite nucleation at inclusions is observed (active inclusions), the open symbols indicate steels with inactive inclusions. The open and closed symbols in Figure 29 have the same meaning. Note that Figure 30 does not imply that a high oxygen content is necessary to create active inclusions. The graph illustrates that, under the prevailing circumstances, an excess amount of Ce will prevent the formation of MnS, which seems to be a necessary inclusion constituent in the active inclusions.

From the results, it appears that the steels with inclusions having a Ce-oxysulphide core with MnS on the surface are most effective. Steel E2 is the only steel which lies in a compositional region where active inclusions are expected, but not observed. Local compositional heterogeneity in the casting might be an explanation for this. Because of the high O content in the steels, it has not been possible to form significant amounts pure Ce-sulphides, a type of inclusion which is believed to have good nucleation potency.

Table 15. Key results from all experiments.

Trial	Ce	O	S	Type of inclusions	Active inclusions
D1	0.056	0.0040	0.0071	☐ Ce-O-S	No
D2	0.006	-	0.0080	Not investigated	Not investigated
D3	0.018	0.0030	0.0090	☐ Ce-O-S with MnS ☐ MnS	Yes
D4	0.035	0.0033	0.0133	☐ Ce-O-S with MnS ☐ MnS ☐ CeS-MnS	Yes
1D3	0.011	0.0038	0.0060	☐ Ce-Al-Si-O-S with MnS ☐ MnS	Seldom
2D4	0.037	0.0044	0.0120	☐ Ce-O-S with MnS ☐ MnS	Yes
3D3	0.054	0.0037	0.0096	☐ Ce-O-S	No
E1	0.023	0.0092	0.0127	☐ Ce-O-S with MnS ☐ MnS	Yes
E2	0.026	0.0047	0.0109	☐ Ce-O-S	No
E3	0.068	0.0044	0.0044	☐ Ce-O-S ☐ Ce-O	No

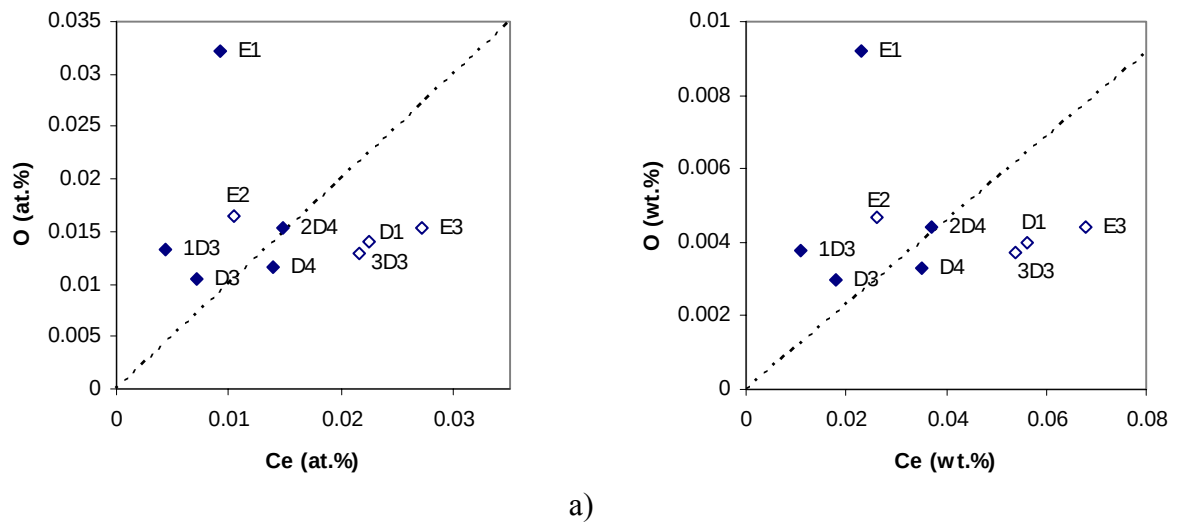


Figure 30. Ce vs. O content for all experimental steel, the dotted line indicates the stoichiometric ratio for $\text{Ce}_2\text{O}_2\text{S}$ formation, a) in at.%, b) in wt.%.

4.4 Conclusions

- A clear relationship between the type of inclusion and the microstructure which forms after heat treatment is observed. Ce-oxysulphides inclusions with MnS on the surface appear to be the most potent inclusions with respect to ferrite nucleation.
- The thermodynamic calculations, performed to predict the inclusion composition qualitatively, agree well with the analysed inclusion composition, an exception is steel E2.
- A problem is still the reproducibility of the experiments. Creating the right inclusion is a delicate balance between the Ce, O and S contents in the steel, requiring strict compositional control. This is difficult to obtain in lab-scale experiments, but should be easier in full scale production.

5 Grain refining of stainless steel AISI329 using grain refiner No. 2 and 7

5.1 Introduction

As-cast steels are examples of materials where the material properties depend on the solidification structure. Generally, a coarse columnar grain structure will evolve upon solidification if potent heterogeneous nucleation sites are absent. In the presence of potent nucleation sites, equiaxed grains form directly in the melt and grow from these sites. If the conditions are favourable, this equiaxed zone may even entirely override the formation of columnar grains. This results in an improved castability through a smaller grain size which reduces the problems with hot cracking and centreline segregation. Furthermore, through smaller grain sizes, other material properties may be improved. There are four different mechanisms for increasing the strength of steel. These are grain refining, work hardening, solid-solution hardening and precipitation hardening. Of these, only grain refining has a positive effect on both yield strength and toughness of the material. The yield strength of steel is governed by the Petch-Hall relationship in which yield and fracture strength is related to the grain size. Grain refining can be achieved by increasing the number of nucleation sites. Non-metallic inclusions that are solid in the steel melt prior to solidification can quite possibly act as the necessary potent heterogeneous nucleation sites for equiaxed grains. Examples of such inclusions are sulphides and oxides with high melting points, for example Ce or Ca sulphides and oxides. Other possible catalyst particles would be carbides and/or nitrides with Ti, V and Nb.

The present investigation intends to evaluate the possibility of adding inclusions to the steel to act as nucleation sites, thus creating favourable conditions for nucleation and growth. For the purpose of this evaluation, two such grain refining ferroalloys containing inoculant inclusions have been developed. These are produced from ferronickel chromium base alloys. The presented results include metallographic characterisation of samples from two sets of experiments with these alloys.

There have been several problems during the course of this work that has severely limited the number of successful heats. As a result of this, two different types of experimental setups have been used. Both these are described in further detail below. It should be noted that included in this report are only the experiments that have resulted in ingots that are worthwhile evaluating. Several other experiments were done where failures of different kinds stopped the experiment before casting. Some examples of this is water cooling system breakage, breakthrough in the crucible, failure of the vacuum pump unit and also failure of the induction furnace power supply. All these factors have slowed down the process of making all the wanted heats and to make them in due time. However, the presented results are heats that have been produced in the best of ways using all the knowledge gathered during the unsuccessful experiments.

5.2 Experimental work

5.2.1 First experimental setup

Two different grain refiners have been studied. These were both developed from low-carbon FeCrNi alloys. Grain refiner no. 2 was produced from an oxygen rich melt by adding a Ce-rich melt and cast on either a steel plate or in a graphite crucible. Grain refiner no. 7 was produced by having high oxygen content and then adding a molten Ce-Si alloy prior to casting. In addition to these two grain refiners, a pre-conditioner containing Fe-Ce-Si has also been used. The composition of these materials can be found in Table 16. An experimental plan was set to explore the possibilities of using either of the two grain refiners alone or in combination with the pre-conditioner. In addition to this, a reference heat was also produced. The experimental plan is listed in Table 17. This plan was chosen with the aim of producing oxidic (Ce_xO_y) inclusions in the melt which are believed to have a grain refining effect during casting. Amounts of the different additions were calculated so that a high enough number density of inclusions should be attained after completed melting and dissolution of the pre-conditioner and grain refiner.

Experiments no. 1 to 6 were carried out in a Balzer VSG50 vacuum induction furnace, as shown in Figure 31. An alumina crucible with an inside height of 220 mm and inside diameter of 120 mm was used. These crucibles are made of high density alumina and each experiment used a brand new crucible to make certain that there was no contamination from the previous heat. The temperature was monitored by a thermocouple of type B attached to the inside of the crucible at about 5 mm above the bottom. A PID regulator was connected to the thermocouple to control the temperature within $\pm 1^\circ\text{C}$. At the start of each experiment, 6 kg of stainless steel AISI 329 was placed in the crucible and thereafter the vacuum chamber was sealed and evacuated down to about 0.05 torr ($\sim 7 \cdot 10^{-5}$ atm). The composition of the used AISI 329 stainless steel is presented in Table 18.

Table 16. Chemical analyses of used additions.

	Cr	Fe	Ni	Si	Ce	Mg	Al	P	S	C	O
No.2	33.0	20.0	27.1	12.0	7.03	0.049	0.045	0.01	0.007	0.067	0.082
No.7	46.1	23.3	28.1	1.96	0.026	0	0	0.02	0.02	0.34	0.13
PC		51.7	0	35.2	12.8	0	0	0.009	0.001	0.028	0.251

Table 17. Experimental plan.

Exp. no.	Target Ce (wt %)	AISI 329	Pre-Cond	Refiner no. 2	Refiner no. 7
1	0	6 kg			
2	0.10	6 kg	46 g		
3	0.23	6 kg		200 g	
4	0	6 kg			50 g
5	0.06	6 kg		50 g	
6	0.15	6 kg	46 g	50 g	
7	0.23	10 kg		333 g	
8	0.10	10 kg	77 g		83 g
9	0.10	10 kg	77 g		
10	0.15	10 kg	77 g	83 g	
11	0	10 kg			

Table 18. Chemical analyses of used AISI 329 stainless steel.

Al	B	C	Ca	Ce	Co	Cr	Cu	Mg
0.004	0.0028	0.042	0.0019	<0.01	0.11	26.00	0.022	0.0115
Mn	Mo	N	Ni	O	P	S	Si	Ti
1.54	1.39	0.064	4.72	89	0.018	0.016	0.70	<0.005

The vacuum chamber was then purged with pure argon (< 5 ppm O_2 and < 5 ppm H_2O) and the induction heating was started. When the temperature in the crucible reached approximately 1000°C , the vacuum chamber was evacuated a second time to about 0.1 torr ($\sim 1 \cdot 10^{-4}$ atm) to further reduce the oxygen content in the atmosphere surrounding the crucible. After completed purging, argon was continuously introduced to the vacuum chamber at a rate of about 30 Nl/min to maintain an inert atmosphere during the experiment. After melting was completed, the melt was heated to 1520°C and kept at this temperature.

Since the additions container is directly connected to the vacuum chamber, it was also evacuated and purged at the same time. Consequently, the additions were made without disturbing the inert atmosphere surrounding the steel melt. Liquid steel samplings were made through a valve to ensure as little disturbance to the atmosphere as possible. Pressure in the vacuum chamber and temperature in the crucible were monitored throughout the whole experiments.

Figure 32 presents the time schedule for additions and sampling for a typical experiment. Stainless steel of type AISI 329 was melted and heated to 1520°C before any additions were made or samples taken. After the melting was completed, the first addition was made followed by the second addition 3 minutes later. Yet another 3 minutes later, the steel melt was cast into a crucible. If no additions were made, casting was performed at the time for the first addition. If only one addition was made during the experiment, casting was done at the time for the second addition.

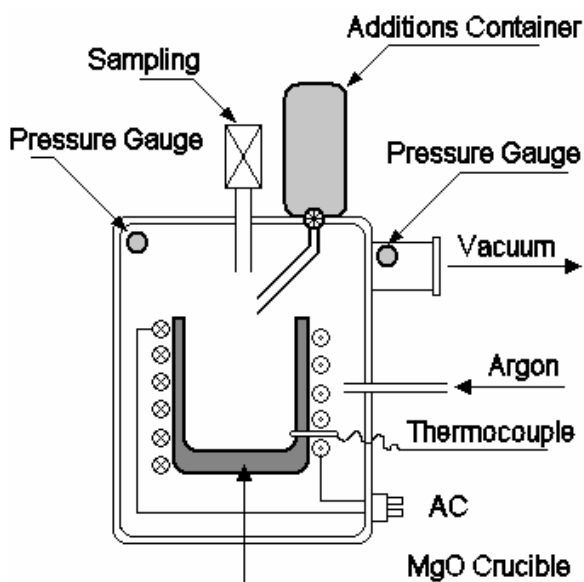


Figure 31. Experimental setup for experiments no. 1 to 6.

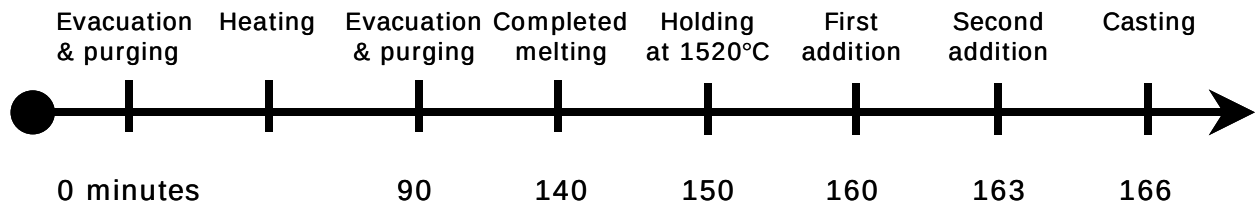


Figure 32. Time schedule for experiments in vacuum induction furnace.

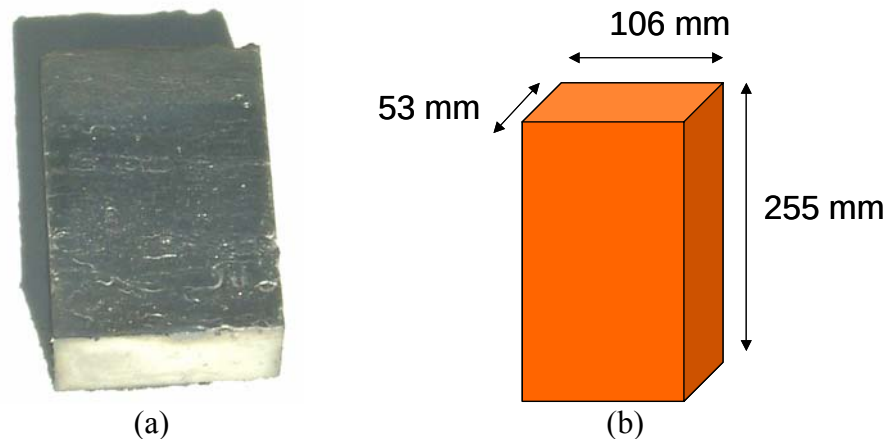


Figure 33. Ingot from grain refining experiments at KTH. (a) Actual ingot (b) Ingot dimensions.

Any liquid steel samples that were taken, were extracted from the melt by suction into quartz tubes with an inner diameter of 5.8 mm. These samples were usually taken immediately before addition or casting. After sampling, these were cooled in water to ensure a quick solidification and cooling rate of the sample. Before any evaluation was made on the sample, measures were taken to make certain that no quartz was left on the surface of the sample. Since the samples have pipes in both ends, both of these were cut away before sending sample to chemical analysis or using it for metallographic examinations.

To ensure that all experimental heats were cast in a similar manner, the same mould was used for all the experiments. The measurements of the ingot and an image of an actual ingot are shown in Figure 33a and b. The mould was designed to be of similar size to the one used at HUT with the experiments on low-alloyed steel. Inner measures of the mould are 53 mm thick, 106 mm wide and 255 mm high, giving a maximum weight of the ingot of about 12 kg.

5.2.2 Second experimental setup

The described setup was used in the first 6 successful experiments. Most unfortunately, the vacuum induction furnace suffered several severe breakdowns during the course of the first set of experiments. In the beginning of the second set of experiments, the evacuation system of the vacuum induction furnace suffered a fatal breakdown of the roots pump. As a consequence it was decided that the second set of experiments should be performed in another furnace. In the following, this setup will be described.

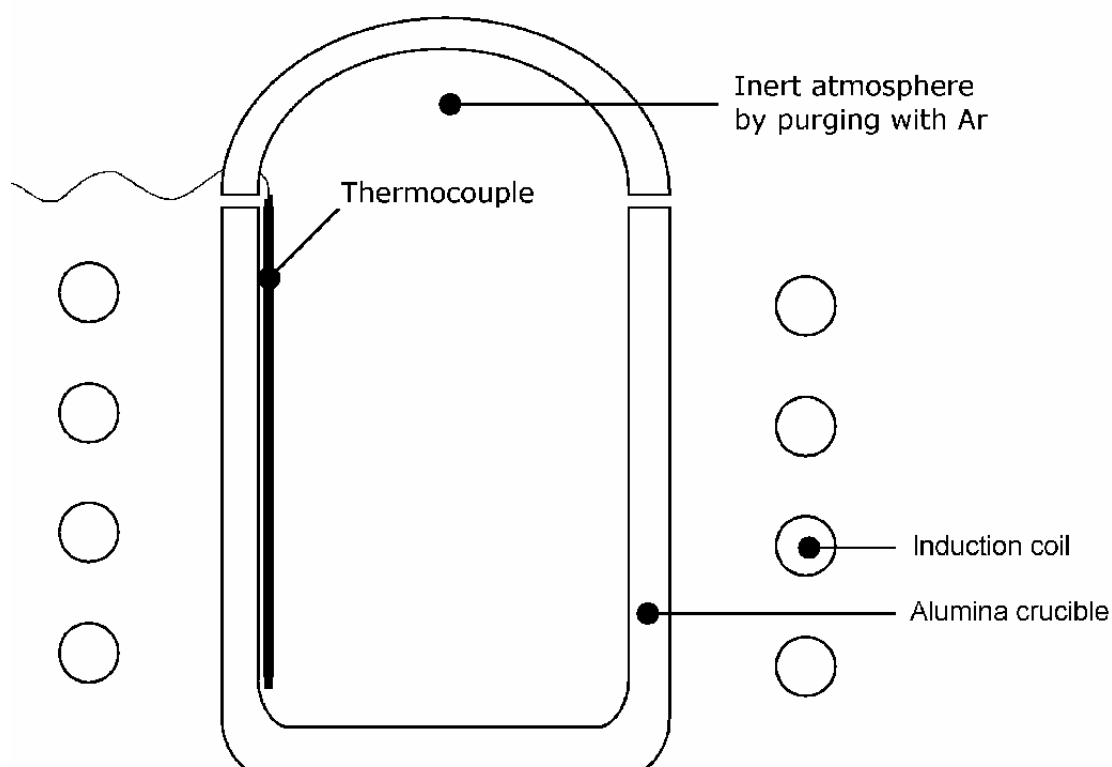


Figure 34. Experimental setup for experiments no. 7 to 11.

Experiments no. 7 to 11 were carried out in a medium frequency induction furnace, shown in Figure 34. An alumina crucible with an inside height of 220 mm and inside diameter of 110 mm was used. The temperature was monitored by a thermocouple of type B attached to the inside of the crucible at about 5 mm above the bottom. A PID regulator was connected to the thermocouple to control the temperature within $\pm 1^\circ\text{C}$. At the start of each experiment, 10 kg of stainless steel AISI 329 was placed in the alumina crucible. Each experiment was performed using a new crucible to avoid any contamination from previous heats. An alumina lid was placed over the top of the crucible. Argon was continuously introduced at a rate of approximately 5 Nl/min to maintain an inert atmosphere. After a few minutes of purging, the induction heating was started. After about 2 hours the steel was completely melted, it was then heated to and kept at a temperature of 1520°C .

Additions and sampling followed the same timeline as in the first experimental setup. Casting was made into the same mould with the difference that these castings were made in air and not in an argon atmosphere.

5.2.3 Chemical analyses

Analyses of stainless steel samples were handled by Sandvik Materials Technology AB, while analyses of the different ferroalloys and pre-conditioner were provided by Elkem ASA.

5.2.4 Metallography

Steel samples from all experiments were taken for metallographic evaluation. Methods used include optical microscopy for inclusion assessment and grain size determination, scanning electron microscopy (SEM) for inclusion composition determination and element mapping analysis. Finally, a combined electron microprobe unit was used for qualitative and quantitative micro area analyses.

Grain size determination was performed according to the ASTM standard E112 "*Standard Test Methods for Determining Average Grain Size*". Etchant used for this purpose was V2A.

Scanning electron microscopes were used for inclusion composition determination and element mapping analysis. At NTNU, Trondheim, Norway a so-called field emission gun scanning electron microscope (FEG-SEM) was used. At KTH, Stockholm, Sweden a JEOL JSM840 was used. The FEG-SEM allows for a much finer resolution than an ordinary SEM does which is why it is very valuable for these studies where most of the interesting inclusions are at around 1 μm . The analyses at KTH with the JEOL JSM840 with EDS were performed using an acceleration voltage set to 20 kV with a working distance of 15 mm. The live time for each analysis was set to 60 seconds with 6 recurrent calculations. Calibration against a cobalt reference was performed at about two hour's interval. Only elements that were matching an energy peak were considered during quantification of the analyses which were calculated using the ZAF method with two or three iterations. The software used was LINK ISIS© quantification software from Oxford Instruments.

Combined electron microprobe was used for analysing inclusions qualitatively and quantitatively. For this purpose, a JEOL JXA-8900M WD/ED was used at NTNU. This unit has a combined Wavelength and Energy Dispersive analytical technique.

5.3 Results

5.3.1 Chemical analyses

The chemical analyses of the different sets of experiments have been divided for clarity. The first table, Table 19, presents the analyses from the experiments in the vacuum induction furnace. The second table, Table 20, shows the analyses from the experiments in the medium frequency induction furnace. The information in the header of the table shows which and how much of grain refiner and/or preconditioner that was used.

One item for concern regarding the analyses is the oxygen content in all of the experiments. In each case, except for experiment no. 3, it is far higher than anticipated. The average total oxygen content is about 100 ppm, which is far too high to give the pre-conditioner and/or grain refining ferroalloy a good chance of success as a grain refining addition.

Table 19. Chemical analyses of experiments 1 to 6.

Heat No.			1	2	3	4	5	6
	Unmelte	Just	Cast	PC	GF 2	GF 7	GF 2	PC
	d	melted						
	AISI329	AISI329	AISI329	7.7 g/kg	33.3 g/kg	8.3 g/kg	8.3 g/kg	7.7 g/kg
								GF 2
								8.3 g/kg
C	0.042		0.041	0.057	0.046	0.040	0.058	0.051
Si	0.70	0.70	0.62	0.80	1.33	0.70	0.74	0.89
Mn	1.54	1.50	1.51	1.49	1.52	1.56	1.53	1.57
P	0.018		0.104	0.149	0.026	0.031	0.017	0.017
S	0.016		0.016	0.015	0.010	0.017	0.017	0.015
Cr	26.00	25.98	25.91	25.80	26.41	26.17	26.02	25.76
Ni	4.72	4.74	4.69	4.68	5.87	4.92	4.88	4.73
Mo	1.39	1.40	1.38	1.38	1.32	1.37	1.38	1.38
Co	0.11		0.11	0.11	0.10	0.11	0.11	0.11
Ti	<0.005		<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cu	0.022		0.022	0.023	0.020	0.022	0.020	0.020
Al	0.004	0.004	<0.003	<0.003	0.004	<0.003	<0.003	<0.003
B	0.0028		0.0023	0.0024	0.0026	0.0027	0.0028	0.0028
O	89	186	163	172	35	127	186	189
N	0.064		0.064	0.035	0.060	0.057	0.053	0.062
Ce	<0.01		<0.01	0.04	0.11	<0.01	0.01	0.02
Mg	0.0115		0.0134	0.0118	0.0134	0.0138	0.0116	0.0113
Ca	0.0019		<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	0.0006

Another element that is crucial to the experiments is cerium. In this case, the contents in the different samples are low to very low. Unfortunately, the cerium yield is low in most of these experiments. The exception again is experiment no. 3 where the cerium content is at about 0.11 wt-%, which is by far the highest in the group. The aluminium level is low in all cases due to that no pre-deoxidation was carried out with aluminium or any other element.

The variation in total oxygen content in the ingots from experiments 7 to 10 have been illustrated in Figure 35. Samples were taken from the bottom, middle and top part of the ingot and analysed by combustion for total oxygen content. The value in shown in the figure is the average between two analyses for each sample. It should be noted that the variation between the experiments is well above the analytical accuracy.

The figure shows a clear relationship that the oxygen content increases from bottom to the top of the ingot. This relationship indicates that the oxygen content increases in the steel during the casting procedure.

To better analyse the contents of some key elements, the yield for each of these elements were calculated. These yields are presented in Table 21. From these results it can be seen that the Cerium contents in the samples from experiments where cerium was added are far too low to be acceptable. The yield varies between 13 to 49 percent, which is low to very low. Only experiments 2 and 3 have a close to acceptable yield at 40 to 49 percent. This result lowers the possibilities for a good grain refining effect from cerium oxides on the steel.

Table 20. Chemical analyses of experiments 7 to 11.

Heat No.	7 GF 33.3 g/kg	8 2PC, 7.7 g/kg GF 7, 8.3 g/kg	9 PC, 7.7 g/kg	10 PC, 7.7 g/kg GF 2, 8.3 g/kg	11 Pure AISI 329
C	0.047	0.043	0.025	0.025	0.025
Si	1.00	0.91	0.71	0.78	0.78
Mn	1.46	1.53	1.73	1.69	1.68
P	0.017	0.017	0.023	0.023	0.023
S	0.011	0.013	0.012	0.007	0.007
Cr	26.15	25.97	24.52	24.68	24.63
Ni	5.39	4.85	5.05	5.24	5.25
Mo	1.35	1.37	1.42	1.42	1.41
Co	0.10	0.11	0.07	0.07	0.07
Ti	<0.005	<0.005	<0.005	<0.005	<0.005
Cu	0.019	0.020	0.150	0.150	0.150
Al	<0.003	<0.003	<0.003	<0.003	<0.003
B	0.0028	0.0028	0.0005	0.0005	0.0005
N	0.074	0.066	0.032	0.031	0.031
Ce	<0.01	<0.01	<0.01	0.01	0.01
Mg	<0.001	<0.001	<0.001	<0.001	<0.001
Ca	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
O	135	96	120	86	87

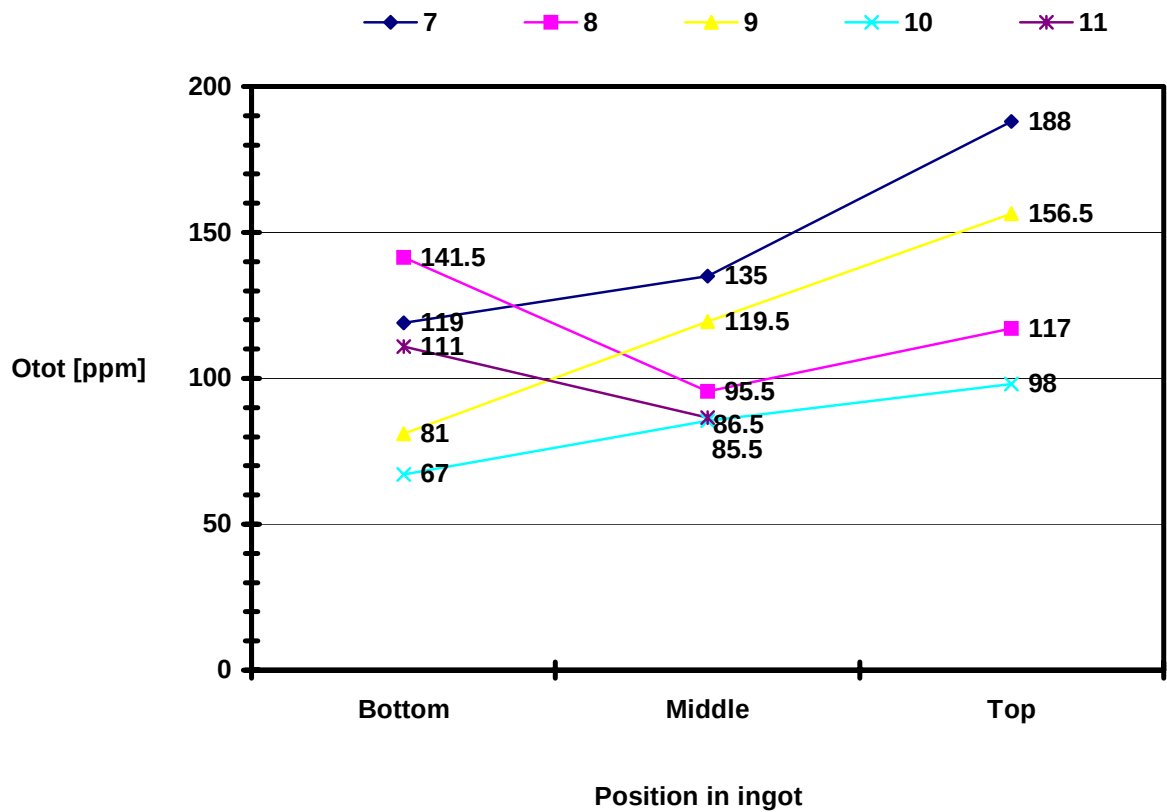


Figure 35. Total oxygen content in ingot samples from experiments 7 to 11.

In some cases in Table 21, the yield numbers are over 100%. This may have many reasons. The two most important contributions to this are probably errors in the chemical analysis as well as segregation within the ingot. Regarding the very high yield of silicon in experiment 3, this might also be the result of differences in the composition of the added grain refiner. There is also a small uncertainty regarding the chemical analysis of the charged stainless steel. The analysis used for calculating the yield, presented in Table 18, is from one of the heats. To have 100% accuracy on the analysis, each heat would have to be represented by one base steel analysis.

It is believed that the low cerium contents are coupled with the high oxygen levels in such a way that cerium has in fact acted as a deoxidizer instead of as a grain refiner. After that cerium has reacted with oxygen to form cerium oxides, these have floated up to the surface or to the walls of the crucible.

To facilitate better conditions for grain refining additions it is therefore considered necessary that a pre-deoxidation is performed to create the given conditions in the melt. It is further believed that if the coming experiments are performed with a deoxidation addition prior to the grain refiner addition, the improved conditions will probably give much better results concerning cerium yield and grain size refinement.

Table 21. Cerium, Silicon, Chrome and Nickel yield for experiments 1 to 6.

Cerium + Silicon

Exp. no.	Additions	Ce(in)	Ce(out)	Yield	Si(in)	Si(out)	Yield
1	AISI329	0	< 0.01	-	0.70	0.62	0.89
2	AISI329+PC (7.77 g/kg)	0.10	0.04	0.41	0.96	0.80	0.83
3	AISI329+2 (33.3 g/kg)	0.23	0.11	0.49	1.06	1.33	1.25
4	AISI329+7 (8.33 g/kg)	0	< 0.01	-	0.71	0.70	0.99
5	AISI329+2 (8.33 g/kg)	0.06	0.01	0.17	0.79	0.74	0.93
6	AISI329+PC+2	0.15	0.02	0.13	1.05	0.89	0.85
7	AISI329+2 (33.3 g/kg)	0.23	<0.01	-	1.06	1.00	0.94
8	AISI329+7 (8.33 g/kg)	0.10	<0.01	-	0.97	0.91	0.94
9	AISI329+PC (7.77 g/kg)	0.10	<0.01	-	0.96	0.71	0.74
10	AISI329+PC+2	0.15	0.01	0.06	1.05	0.78	0.74
11	AISI329	0.00	0.01	-	0.70	0.78	1.11

Chrome + Nickel

Exp. no.	Additions	Cr(in)	Cr(out)	Yield	Ni(in)	Ni(out)	Yield
1	AISI329	26.00	25.91	1.00	4.72	4.69	0.99
2	AISI329+PC (7.77 g/kg)	25.79	25.80	1.00	4.68	4.68	1.00
3	AISI329+2 (33.3 g/kg)	26.23	26.41	1.01	5.44	5.87	1.08
4	AISI329+7 (8.33 g/kg)	26.17	26.17	1.00	4.91	4.92	1.00
5	AISI329+2 (8.33 g/kg)	26.06	26.02	1.00	4.90	4.88	0.99
6	AISI329+PC+2	25.86	25.76	1.00	4.87	4.73	0.97
7	AISI329+2 (33.3 g/kg)	26.23	26.15	1.00	5.44	5.39	0.99
8	AISI329+7 (8.33 g/kg)	25.97	25.97	1.00	4.88	4.85	0.99
9	AISI329+PC (7.77 g/kg)	25.80	24.52	0.95	4.68	5.05	1.08
10	AISI329+PC+2	25.89	24.68	0.95	4.87	5.24	1.08
11	AISI329	26.00	24.63	0.95	4.72	5.25	1.11

5.3.2 Metallography

Grain size determination has been performed for the following samples; 1M, 2M, 3M, 4B, 4M, 4T, 5B, 5M, 5T, 6B, 6M, 6T, 7M, 8M, 9M, 10M and 11M. B is taken from the bottom of the ingot in the centre part of the cross-section, M is from the middle and T from the top. The results from these determinations are presented in Figure 36 and Figure 37.

According to ASTM E112 the grain size is determined by examining a number of viewing fields where each is examined with respect to the number grains per square inch. It is common to express grain sizes in terms of a simple exponential equation:

$$n = 2^{G-1} \quad (1)$$

where n is the number of grains per square inch at 100X magnification, and G is the ASTM grain size number. The ASTM grain size number can be converted to average grain size by equation 2 as follows:

$$\bar{x} = \frac{1000}{\sqrt{2^{3+G}}} \quad (2)$$

Figure 36 shows the results from determining the average grain size in samples from experiments 1 to 11. Here, all the values of the different examined samples are plotted in a diagram and given in a table. Evidently, this type of casting method and casting temperature (1520°C) gives large grains, from 200 μm up to about 800 μm . It can also be seen that the experiments that have been most successful are those where the casting was made under inert atmosphere. This is especially true for the experiments done with grain refiner no. 2. A reasonable explanation for this is that there was, in these cases, no oxidation during the casting procedure.

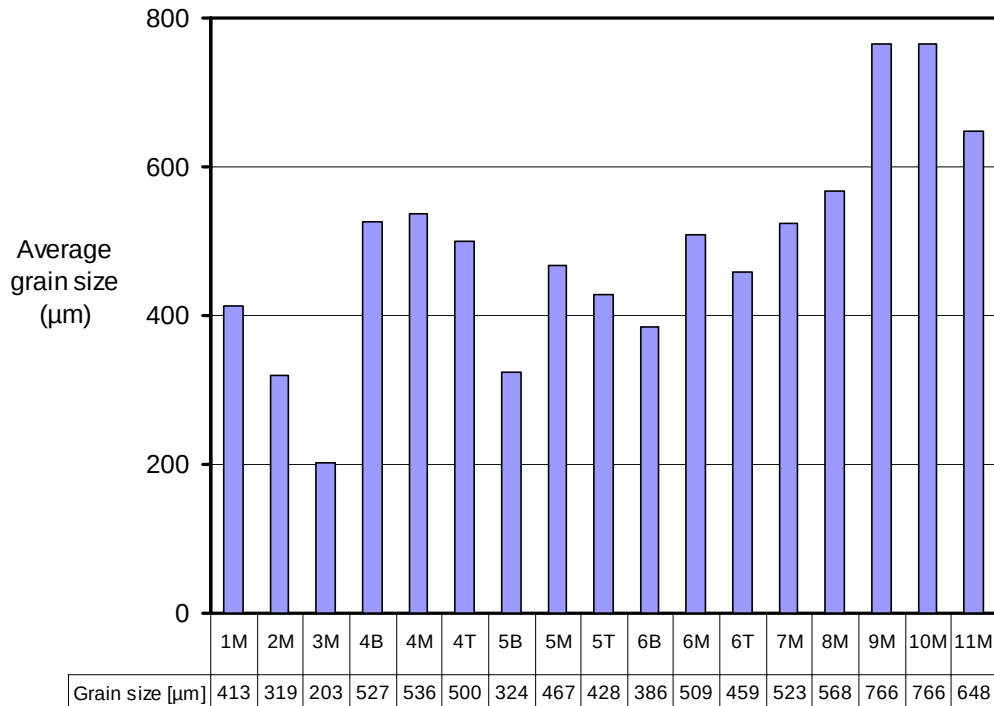


Figure 36. Measured grain sizes in ingots. (B) stands for bottom sample, (M) for middle and (T) for top.

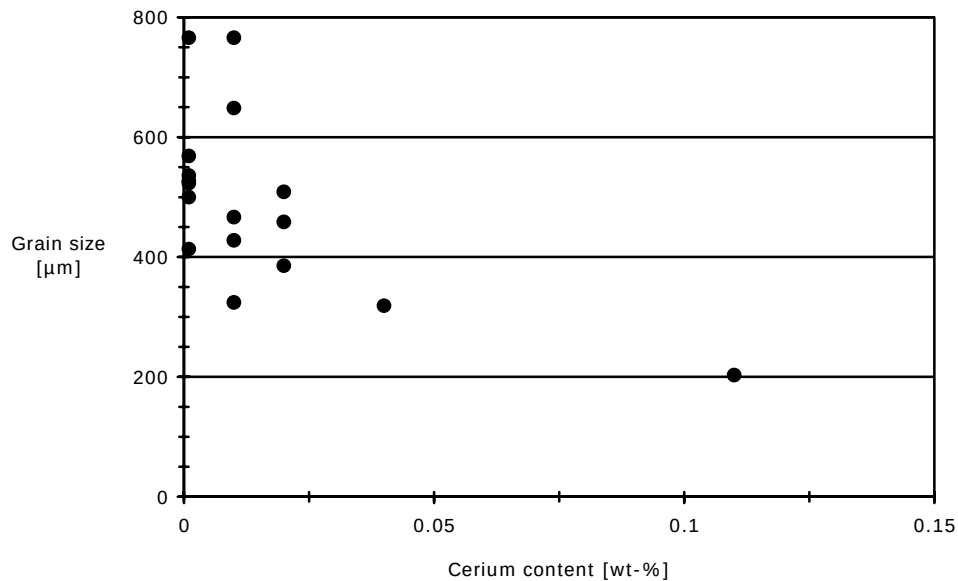


Figure 37. Cerium content vs. grain size in ingot samples.

Figure 37 shows the grain sizes plotted against the cerium content in the sample. For samples with a cerium content below 0.01wt%, which is the analytical limit, the value 0.001wt% was used. It is evident that in those few cases where the cerium content is very high, the grain refining effect is also good. This implies that there still is a very good possibility to attain a respectable grain refining effect if the correct conditions are met.

During the course of evaluating the grain sizes in the different samples, several images of grain structures were produced. In the following pages some of these will be presented. These figures show the grain size variation from top to bottom in the ingots from three different experiments. The results from experiment no. 1, 4 and 5 and are presented in Figure 38a-c, Figure 39a-c and Figure 40a-c, respectively.

Figure 38 shows the grain structure of the middle part of the as-cast ingot. In this experiment, the base metal used in all experiments, a duplex stainless steel AISI329, was subjected only to re-melting and subsequently casting in mould. The images 8a, 8b and 8c are from different positions on the same sample. Clearly, the size and shape of the grains do not vary much over the sample. The average grain size of this sample is about 413 μm .

In Figure 39 the corresponding images for an experiment with grain refiner no. 7 are presented. In this case there is a considerable amount of columnar grains which are not present in the similar positions in the experiment with grain refiner no. 2. The resulting grain sizes in this experiment varied between 500 and 536 μm .

Figure 40 presents the images that have been taken from the surface of each sample from an experiment with grain refiner no. 2. These pictures show that there is only a small variation in shape and size between the different positions in the as-cast ingot. The average grain sizes in this case are between 324 and 467 μm .

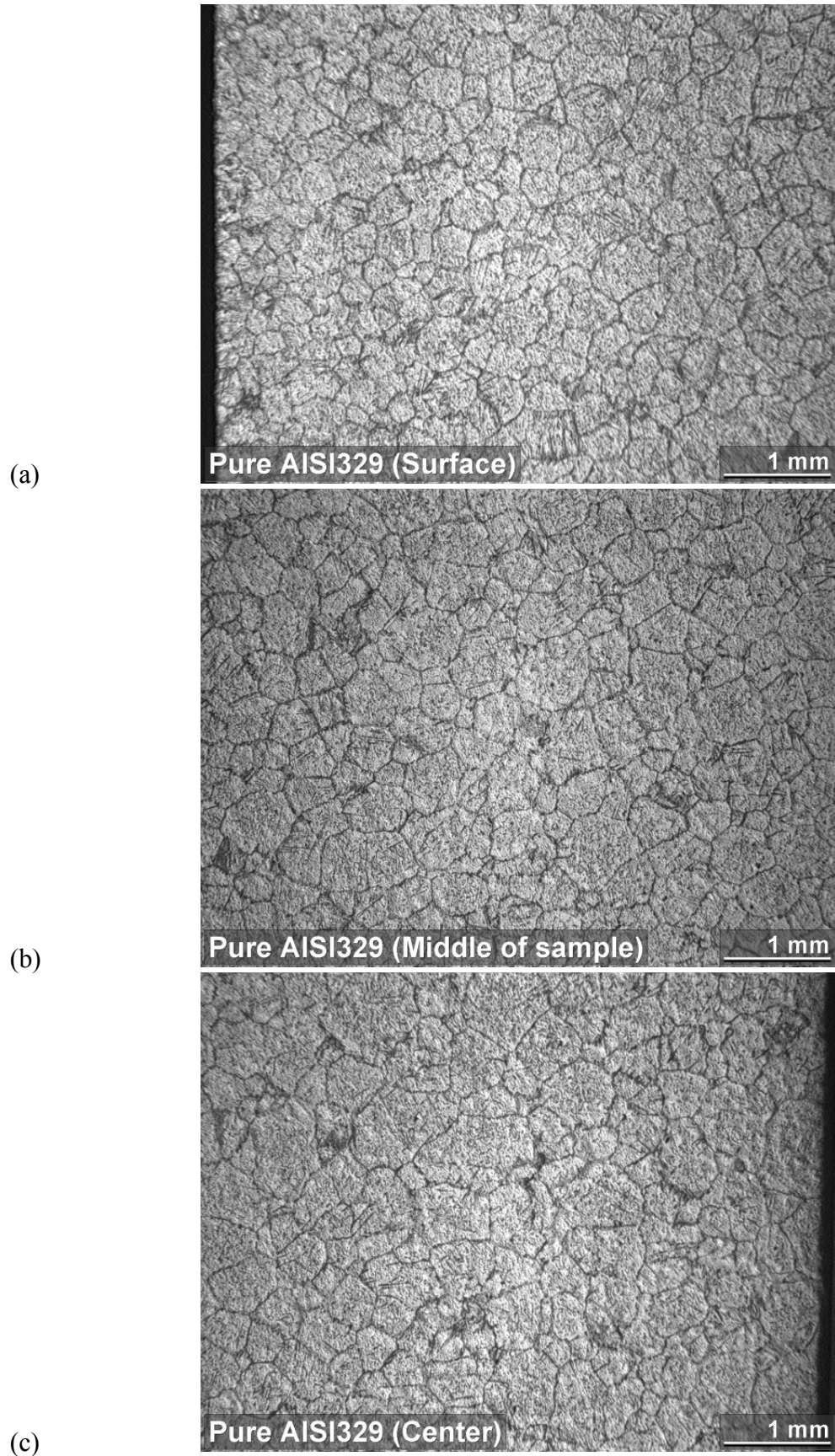


Figure 38a-c. Illustration of grain size variation over the middle cross-section in experiment no. 1.

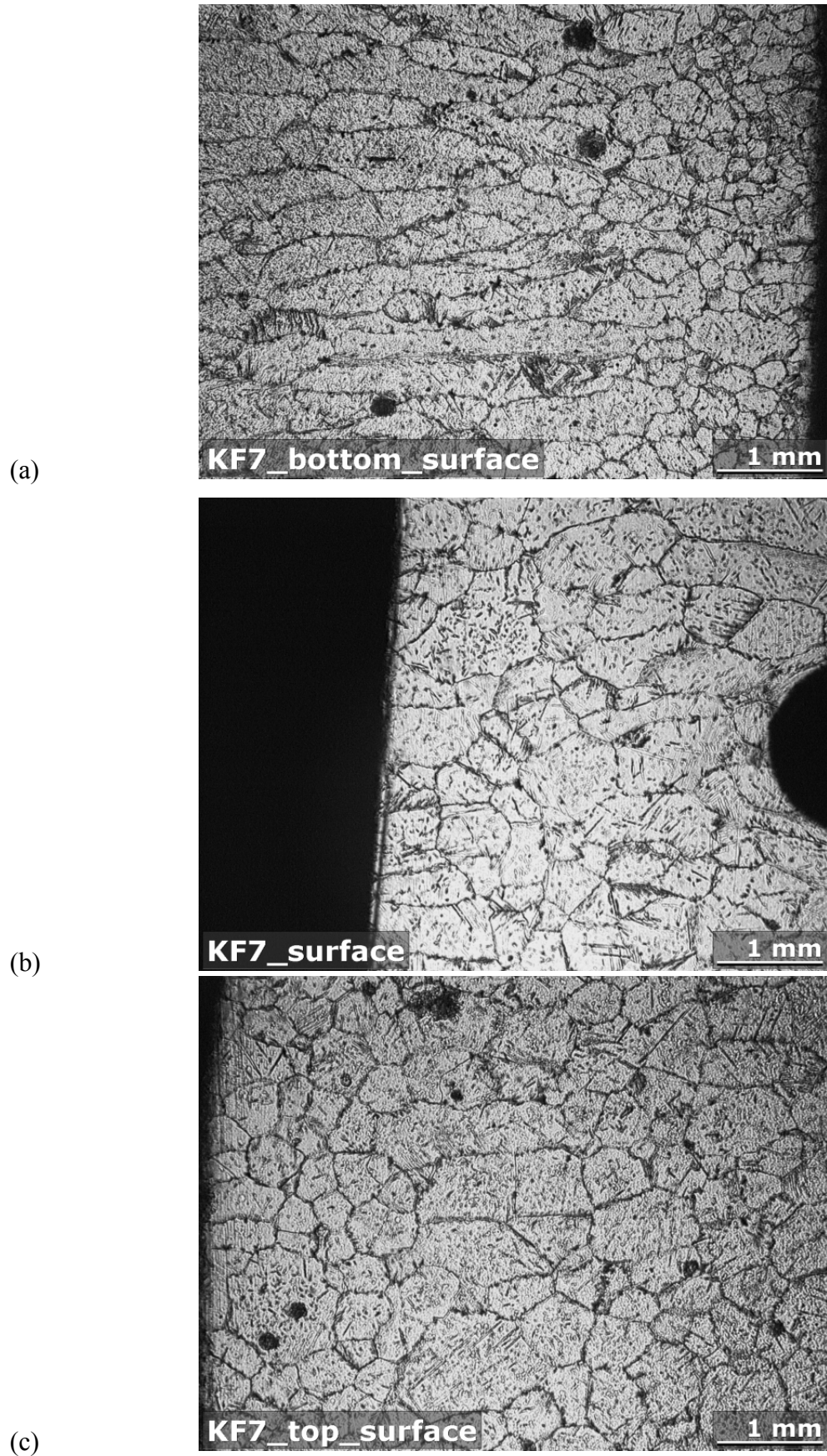


Figure 39a-c. Illustration of grain size variation on the ingot surface in experiment no. 4.

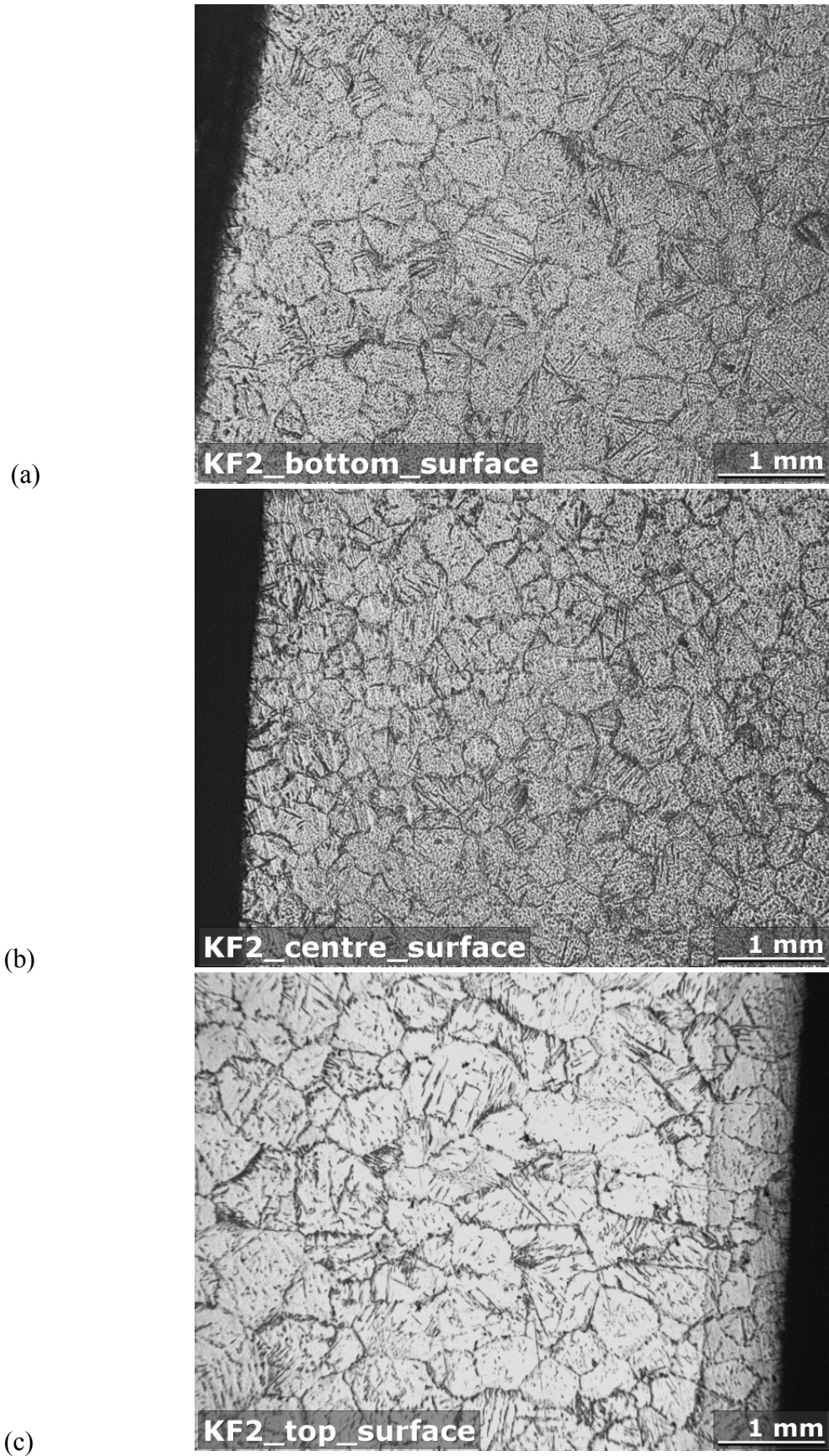


Figure 40a-c. Illustration of grain size variation on the ingot surface in experiment no. 5.

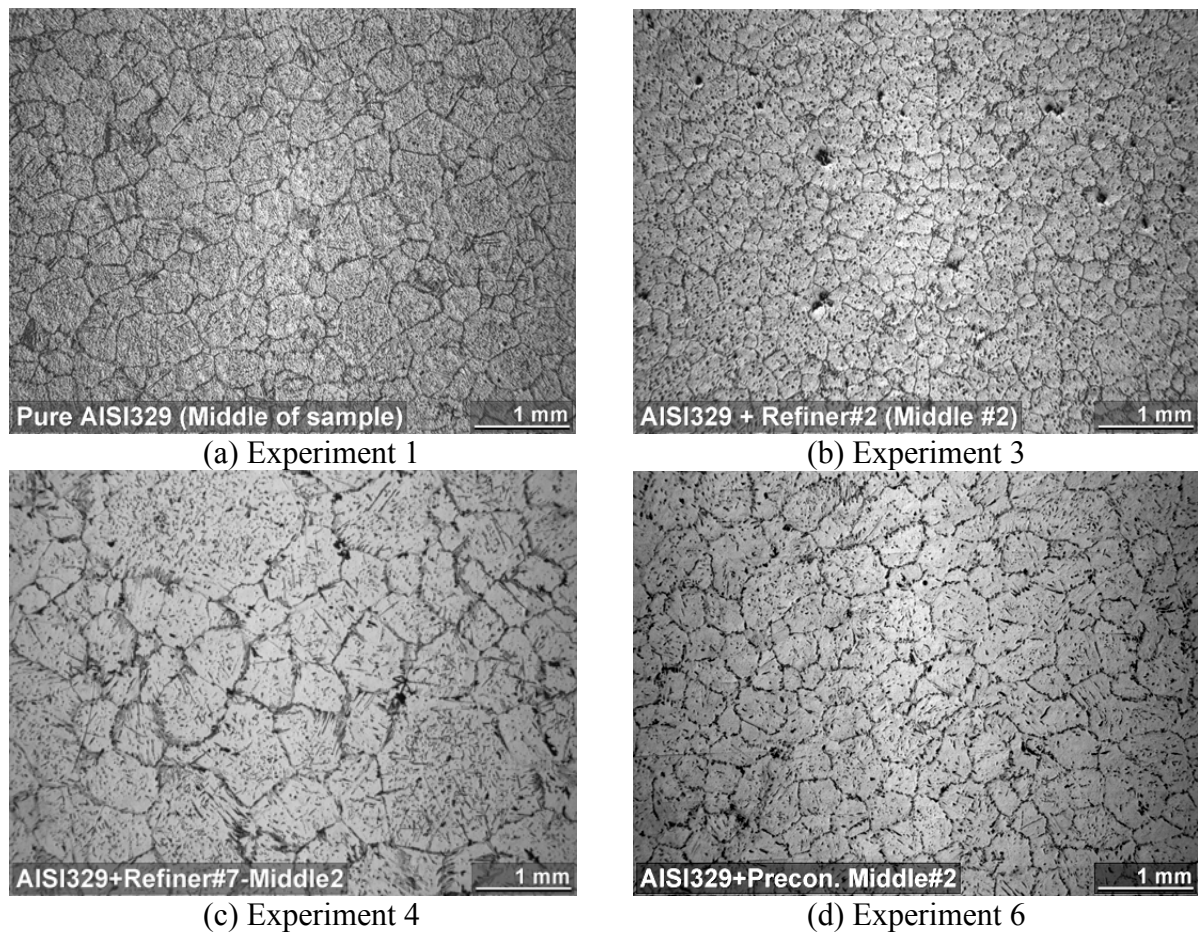


Figure 41a-d. Comparison between different grain refiners.

Figure 41 presents comparative pictures of etchings from the middle part of the ingot in four different experiments. It is evident that experiment no. 3 with grain refiner no. 2 yielded the best results from the experimental series. This is further supported from the grain size assessment present in Figure 36.

5.3.3 SEM

SEM analyses showed that a number of different elements were present in the inclusions. Before any comparison was made, all analyses with a high Fe-content were excluded. This resulted in 18 inclusions with a cerium content higher than 15 at%. The highest Cerium content was 42 at%. Many other inclusions consisted of compounds containing silicon, manganese and/or aluminium. However, the majority of the found inclusions contained either SiO_2 or Ce_2O_3 . It should furthermore be noted that manganese sulphides are present in all the analysed samples.

Table 22 shows a representation of the different groups of inclusions that were found in these samples. The analysed experiments were taken from experiments 3 to 6. The value indicated for each inclusion group is the number of occasions that this type was found in the respective sample. Figure 42 shows an example inclusion where 3 analyses have been made. The results are shown in Table 23. It is apparent that the white rectangle in the middle has a high cerium and oxygen content. Also, the black spots lining the edge of the particle have an increased content of manganese and sulphur strongly indicating the formation of a manganese sulphide ring.

Table 22. SEM analysis of inclusions in one sample from each of experiments 3 to 6.

Experiment No.	SiO ₂ -MnS	SiO ₂ -Ce ₂ O ₃	SiO ₂	MnS	Cr ₂ O ₃ -SiO ₂	Al ₂ O ₃ -SiO ₂ -Cr ₂ O ₃	Al ₂ O ₃ -SiO ₂ -Ce ₂ O ₃
3		4		1			
4			4	2	3	3	
5	7	4	5	6	1		
6		7		1			8

Table 23. SEM analyses of an inclusion from experiment no. 3, at%.

	O	Al	Si	S	Ti	Cr	Mn	Fe*	Ce
Spectrum 1	66	1	12	1			6	2	13
Spectrum 2	58	3	8	1	1	5	11	7	6
Spectrum 3	28	1	4	15		10	21	18	3

*Fe signal coming from the matrix and not from the inclusion.

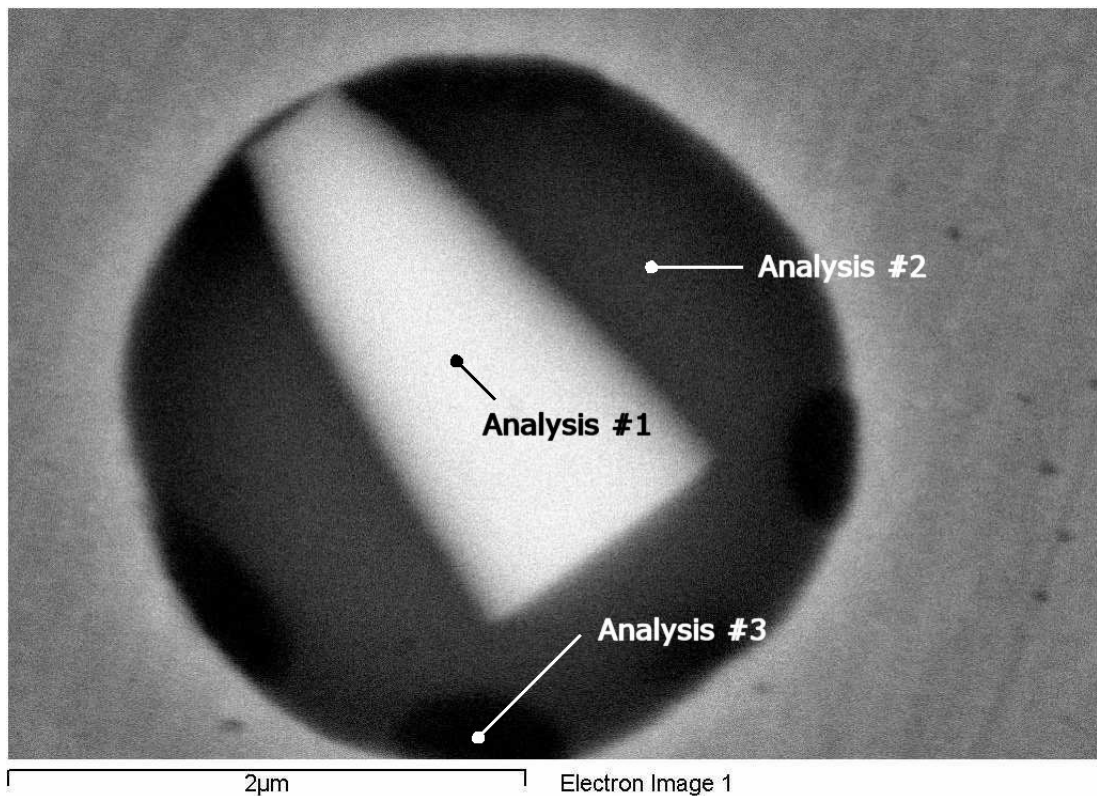


Figure 42. Example of inclusion analysed in FEG-SEM from experiment No. 3.

5.3.4 Microprobe

Figure 43 shows an Al-Ce inclusion with a high content of Mn and Si. The inclusion seems to be divided into two parts, one of which is essentially free of aluminium and manganese. The other is, on the other hand, richer on cerium and silicon. This would essentially mean that the lower part is a Ce-Si-O and that the upper part consists of Al-Ce-Mn-Si-O. As a border around this complex inclusion there is supposedly MnS.

Another type of cerium inclusion is shown in Figure 44. Here the inclusion contains the same elements in a reasonably even distribution. There is, however, one similarity between these. There is a manganese sulphur band around the edge of these inclusions. This sulphide has most likely formed during the later stages of solidification or cooling in the course of casting.

This would mean that the inclusion in Figure 44 consist of Al, Ce, Mn, Si and O. Information from SEM analyses of a similar inclusion suggests that the composition is approximately 4 at% Al, 7 at% Ce, 7 at% Mn, 11 at% Si and the balance is oxygen. Re-calculating this into oxides gives the approximate composition of 7 at% Al_2O_3 , 26 at% Ce_2O_3 , 26 at% MnO and 41 at% SiO_2 .

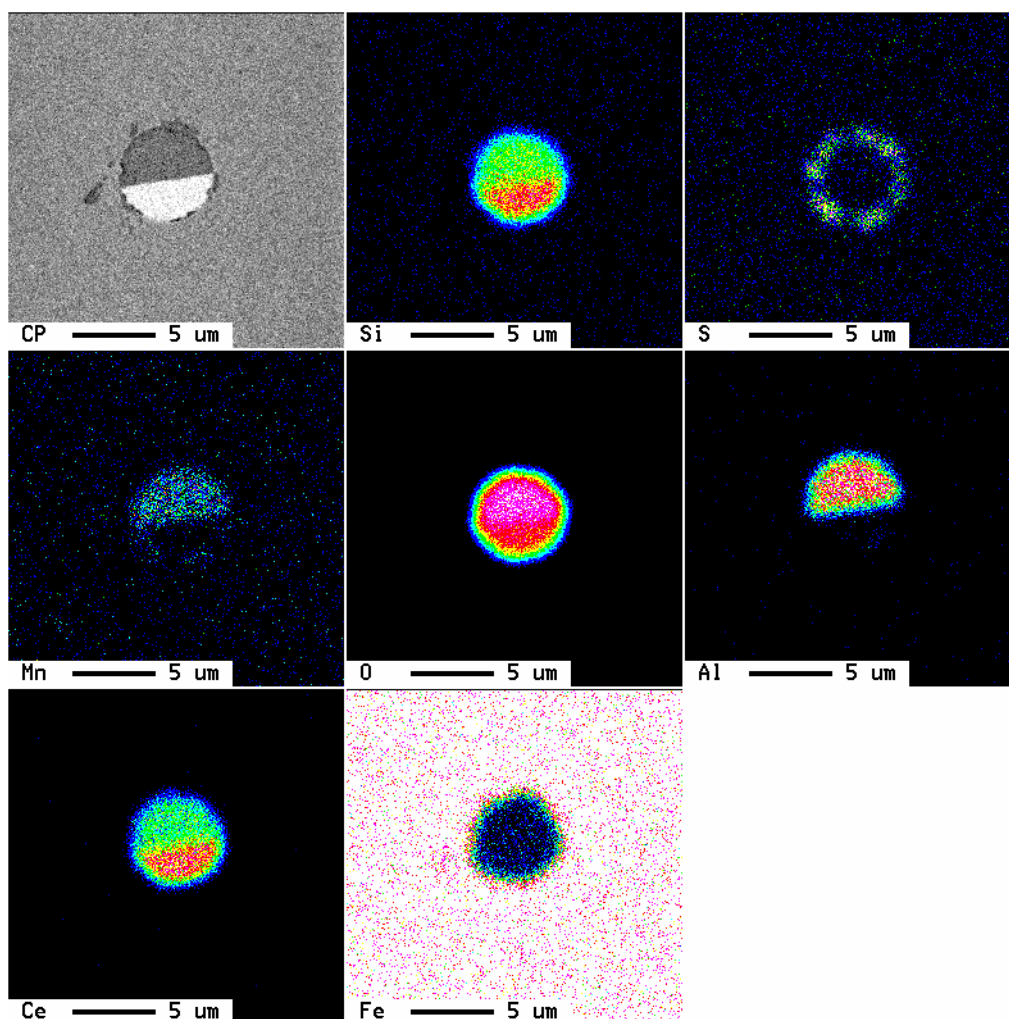


Figure 43. Microprobe element mapping of Cerium inclusion from sample of experiment 3.

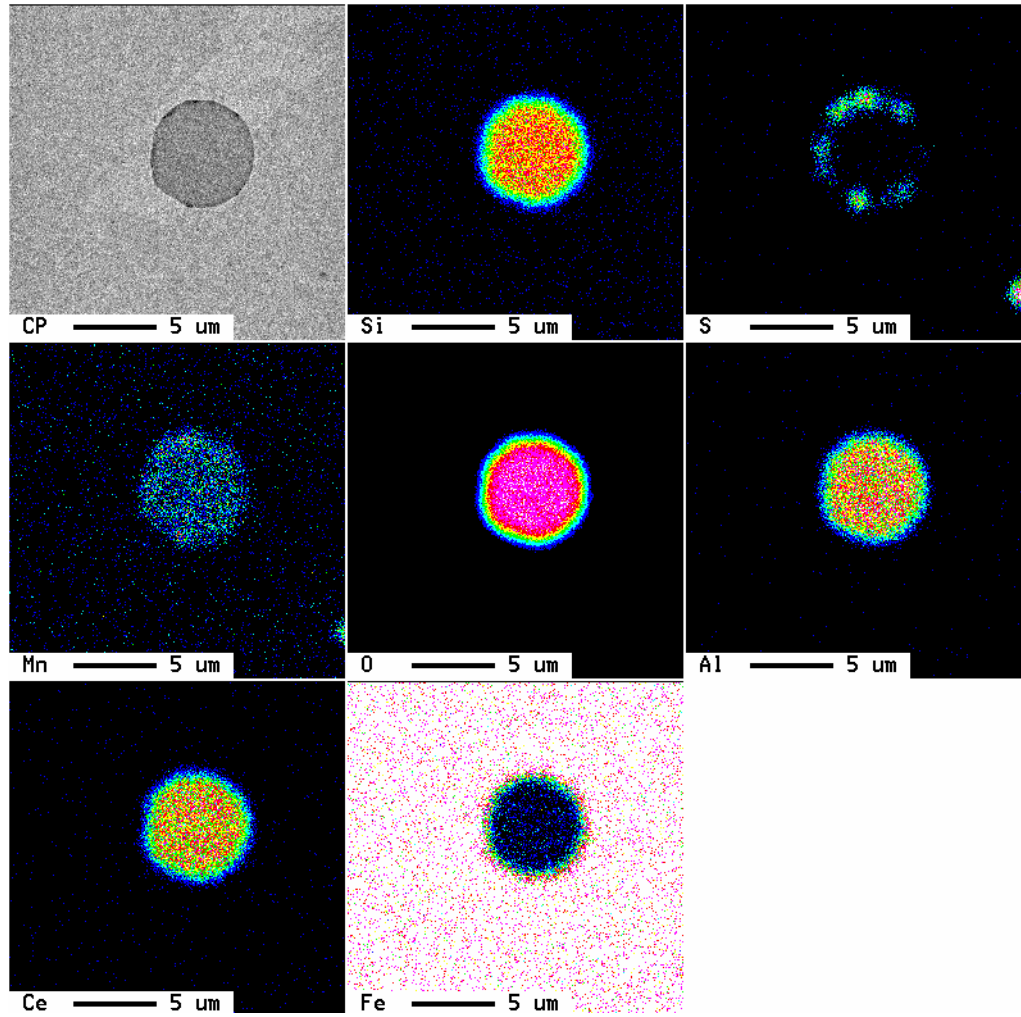


Figure 44. Microprobe element mapping of Cerium inclusion from sample of experiment 5.

5.4 Conclusions

The performed experiments have shown that it is possible to get a grain refining effect when using a cerium/oxygen based addition. It can be concluded that it is necessary to maintain low levels of oxygen in the melt prior to the addition of cerium.

In these experiments however, it is believed that the high oxygen levels have negated the effect of the cerium additions in such a way that cerium has in fact acted as a deoxidizer instead of as a grain refiner.

In order to facilitate correct conditions for grain refining additions it is therefore considered necessary that a pre-deoxidation is performed to ensure the proper conditions in the melt. It is further believed that if the coming experiments are performed with a deoxidation addition prior to the grain refiner addition, the improved conditions will probably give much better results concerning both cerium yield and grain size refinement. The more specific conclusions are as follows:

- Chemical analyses show very high oxygen content indicating a leakage of oxygen to the system. The main source is probably the surrounding atmosphere.
- Chemical analyses show a very low content of cerium indicating a strong removal of cerium oxides from the system.
- Very few cerium oxides have been located in the different samples.
- The impact on grain refining has been limited and in some cases even absent. This is concluded to be coupled with a very low cerium content in the steel.
- Grain refiner no. 2 gives a good result regarding grain size; best result was obtained using 33 g per kg of steel. It has unfortunately proven difficult to validate these results.

It is recommended that a new short series of experiments to be performed including pre-deoxidation with aluminium prior to the addition of pre-conditioner in order to create the necessary conditions for grain refinement.

6 Grain refining of stainless steel AISI329 using grain refiner No. 14

6.1 Introduction

Grain size control is one of many important aspects in steelmaking, due to the fact that many of the material properties are influenced by the grain size. Examples of such properties are yield strength and toughness which both benefits in a high degree from smaller grain sizes. In as-cast steel this is mainly due to the fact that centreline and interdendritic segregation is reduced which, in turn, reduces problems with for example high temperature cracking.

The solidification grain size of steel can be decreased by increasing the number of potential nucleation sites. This study investigates the possibility of adding such potential nuclei to the steel, thus creating favourable conditions for smaller grains. This is believed to be achieved by adding a grain refining agent to the steel directly prior to casting.

During this project a number of previously reported experiments have been performed using different grain refiners with varying results. Only a few of these experiments resulted in a good grain refining effect. The conclusions of these previous experiments are that it is difficult to obtain a high enough cerium yield throughout the experiment. Also that the high oxygen content most probably attributes to the low grain refining effect in the remaining experiments. Therefore it was decided that a series of experiment should be performed to conclude what levels of deoxidation that was needed in order to ful-fill the believed requirements for a good refining experiment.

For the experiments presented in this report, a duplex stainless steel, AISI 329, was chosen. This duplex stainless steel solidifies ferritic. Experiments were performed with only deoxidiser, with deoxidiser and pre-conditioner and also with deoxidiser, pre-conditioner and the grain refining agent. The experiments were performed in a medium frequency induction furnace under argon atmosphere. All heats were cast into the same mould to ensure similar casting conditions. Samples from the as-cast material were acquired and then examined metallographically, including grain size and inclusion assessment, chemical analysis, and scanning electron microscopy.

6.2 Experimental work

6.2.1 Experimental set-up

All experiments have been carried out in a medium frequency (5 kHz) induction furnace. One grain refiner and one preconditioner have been studied. The grain refiner is called GR14C. The preconditioner is the same as have been used in earlier experiments. Both pre-conditioner and grain refiner were provided by Elkem ASA. The present experiments have been performed using a regular stainless steel, AISI 329, as the base metal. The melt size for the experiments has been 10 kg. Table 24 and Table 25 show the chemical compositions of the used materials.

Table 24. Chemical analyses of used AISI 329 stainless steel.

C	Si	Mn	P	S	Cr	Ni	Mo	Co
0,026	0,46	1,75	0,024	0,025	24,71	5,15	1,44	0,072
Ti	Cu	Al	B	N	Ce	O	Mg	Ca
<0,005	0,15	<0,003	0,0004	0,029	<0,005	N/A	<0,001	0,0038

Table 25. Chemical composition of pre-conditioner and grain refiner.

Element	C	Si	Mn	P	S	Ce	O	Fe
Preconditioner	0.028	35.2		0.009	0.001	12.8	0.251	balance
Grain refiner 14C			1.61		0.9			balance

Quartz tubes were used to take samples. The tubes had an inner diameter of about 6 mm and an outer diameter of 8 mm. A thermocouple of type B was attached on the inside of the inner crucible, see Figure 45. This thermocouple was then connected to a PID regulator to measure and control the temperature within $\pm 1^\circ\text{C}$.

In Figure 45, it can be seen how the furnace is constructed and how the experimental equipment was set up. The furnace consists of a steel shell protecting the water-cooled induction coil. A safety crucible protects the induction coil from the inside, in case of a break-through of molten metal from the inner crucible. The inner crucible contains the molten steel. Between the shell and the safety crucible is a filling made of magnetite. This filling also surrounds the induction coil. A lid protects the melt from surrounding air from above. The lid has two holes, one for argon gas and one for sampling. The latter has a diameter of about 63 millimetres to let a sampler through. This hole is covered with a ceramic plug at all times except during sampling.

The safety crucible and the lid were made of aluminium oxide casting material (Victor Korund ES QF) with 94% Al_2O_3 which was provided by Lafarge Svenska Högånäs, see Table 26. The inner crucible was a pre-fabricated hard sintered aluminate (99.7 wt-% Al_2O_3) crucible with an inside height of 220 mm and inside diameter of 120 mm.

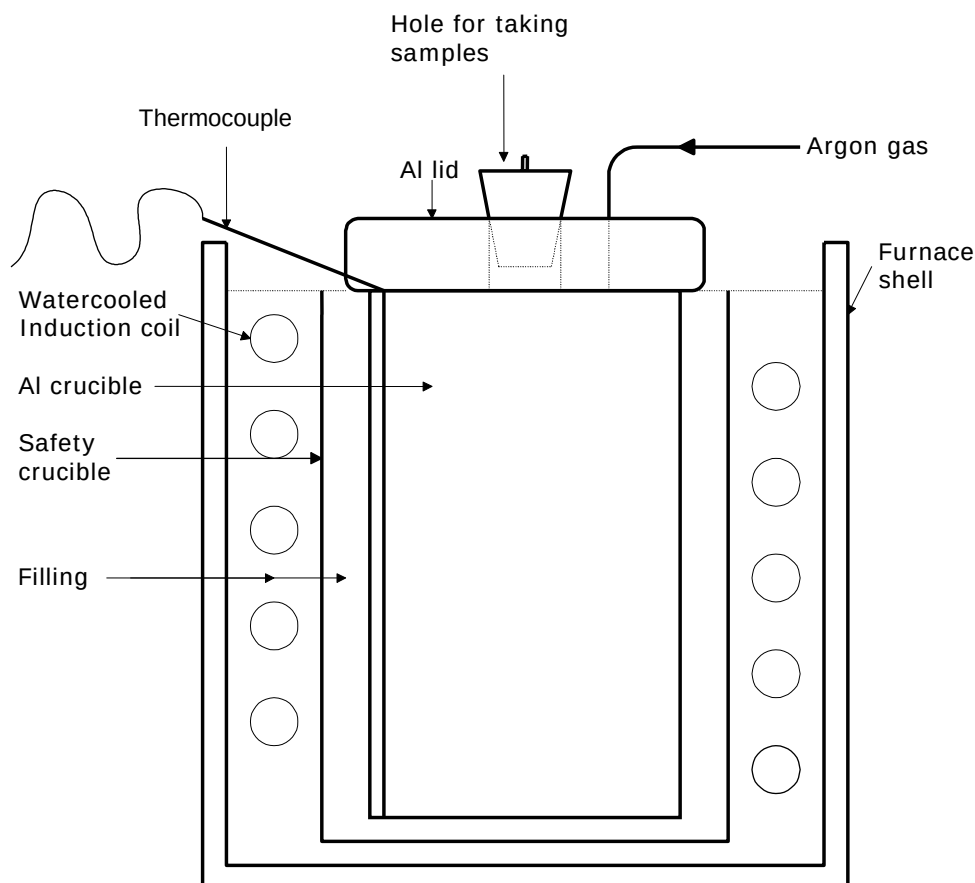


Figure 45. Furnace construction and experimental setup

Table 26. Chemical composition of the used aluminium oxide casting material.

Element	Al ₂ O ₃	CaO	Na ₂ O+K ₂ O	SiO ₂	TiO ₂	Fe ₂ O ₃
Casting material	94	5,8	0,5	0,2	0,01	0,1

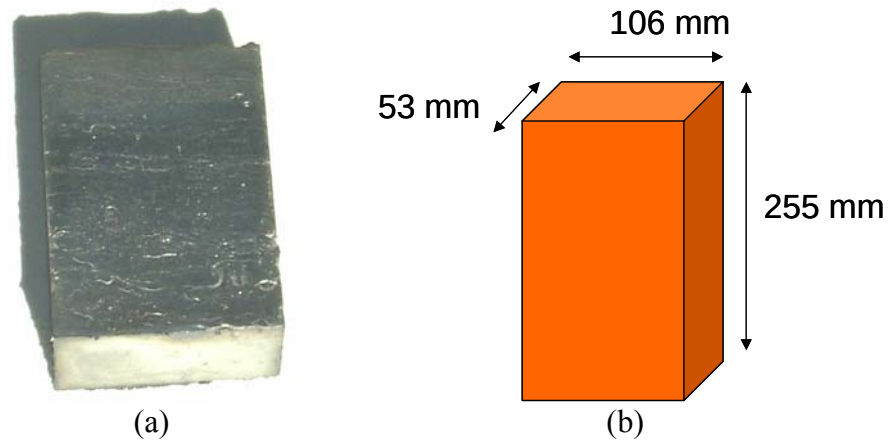


Figure 46. Ingot from grain refining experiments at KTH. (a) Actual ingot (b) Ingot dimensions.

The experiments were finished with a casting procedure, where the melt was cast into a steel mould. The dimensions of the ingot and an ingot can be seen in Figure 46a and b. The size of the ingot is 53 x 106 x 255 mm.

6.2.2 Implementation of experiments

An experimental plan was set up as listed in Table 27. The first three experiments were aimed at determining the amount of aluminium needed to have a controlled deoxidation. The latter four experiments were set to determine the effect of preconditioner and grain refiner #14C on the grain size of the ingot. Experiments with PC and GR 14C were set to two different experiments, 4 and 5. Two more experiments were performed, no. 6 and 7, in order to verify the results of experiments 4 and 5.

Table 27. Details of experimental plan

Experiment #	AISI 329 (kg)	Aluminium (g)	Preconditioner (g / kg steel)	Grain refiner 14C (g / kg steel)
1	10	10		
2	10	20		
3	10	30		
4	10	10	5,8	
5	10	30	5,8	9,0
6	10	10	5,8	
7	10	10	5,8	9,0

During the experiments the small hole in the lid was covered by a plug at all times except when being used. Argon gas with a flow rate of about 8 litres per minute was continuously fed through the inner crucible to ensure an inert atmosphere. The gas is lead through a small hole in the lid.

All additions were pushed into the melt to achieve a high yield. Aluminium rods were put on the top of a short stick and then pushed into the melt, but to achieve the same for the pre-conditioner and grain refiner these were put into a container that was strapped onto a short stick and then

pushed into the melt. The container was constructed from a thin-walled stainless steel tube. Once the weighed material was inserted in the tube it was sealed carefully to avoid any losses of material before insertion into the melt. The tube material was a stainless steel AISI329 with the same composition as the base melt.

The casting temperature was 1520°C. Samples from the as-cast material were obtained from the ingots. About 1 centimetre thick slices of each ingot were cut at three heights of the ingot; top, middle and bottom. In order to avoid any influences from the pipe formation, this area was cut away before the top sample was acquired. Also, the bottom sample was acquired at about 1 centimetre from the absolute bottom. Three sets of samples were cut from each slice. One for chemical composition determination, one for SEM analyses and one for inclusion distribution and grain size evaluation.

6.2.3 Chemical Analyses

Chemical analyses of stainless steel samples were performed at Sandvik Materials Technology in Sandviken, Sweden.

6.2.4 Metallography

The average grain size of the stainless steel samples was determined according to the ASTM standard E112 "Standard Test Methods for Determining Average Grain Size".[1] Etchant used for this purpose was V2A.

Inclusion size distribution for inclusions larger than 4.7 μm was determined according to the Swedish standard SS111116-"Steel - Method for estimation of the content of non-metallic inclusions-Microscopic methods-Jernkontoret's inclusion chart II for the assessment of non-metallic inclusions".[2] This method was originally developed for assessment of inclusions in wrought or rolled steel but the method may also be used in as-cast steel. However, this means that a limitation is set towards the results. The specific limitation in this case is that the connection between form and composition of the inclusion cannot be used. However, all information that is acquired regarding inclusions size, density and form is still valid.

Scanning electron microscopes were used for inclusion composition determination and element mapping analysis. At NTNU, Trondheim, Norway a so-called Field Emission Gun Scanning Electron Microscope (FEG-SEM) was used, and at KTH, Stockholm, Sweden another SEM (JEOL JSM840) was used. The main reason for using the FEG SEM is that it allows for a much finer resolution than an ordinary SEM.

6.3 Deoxidation experiments

The aim of the three first experiments was to find out how much aluminium was needed as a deoxidizer in order to keep the oxygen levels low. A low oxygen level is considered to be below 100 ppm. Thermodynamic calculations showed that 10 to 30 g of aluminium should be sufficient to keep the oxygen levels low. It should be duly noted that these thermodynamic calculations were based on Wagner's first order interaction parameters only. Hence, these calculations should only be used as an indication for determining what level of aluminium additions that were needed.

The experimental plan for the deoxidizing experiment was set to three experiments. The results from these three experiments were used to set the timelines for the experiments with pre-conditioner (PC) and grain refiner no. 14C.

The timeline for the aluminium deoxidizing experiments was arranged so that as many samples as possible could be acquired during the first ten minutes. Figure 47 presents the timeline for the deoxidisation experiments. Aluminium was added at 0 min and then samples were taken every minute until 10 minutes had passed. After ten minutes a sample was taken at 15 minutes and 20 minutes and then the steel was cast into a mould.

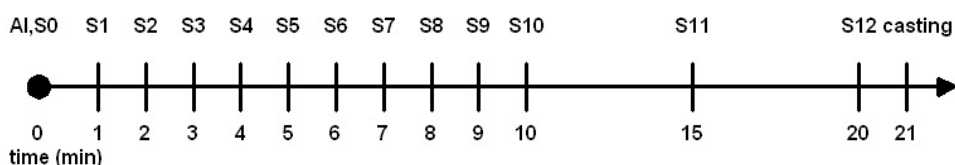


Figure 47. Timeline for deoxidation experiments.

6.3.1 Results from deoxidation experiments

The aluminium deoxidation experiments were carried out with three different amounts of aluminium, 10, 20 and 30 g. The conditions have been the same for all three experiments

The experiment with 10g aluminium showed a trend to re-oxidize after approximately 10 minutes. During the first ten minutes the oxygen level was low, approximately 25 to 50 ppm as shown in Figure 48. Experiment #2, in which the addition was 20 g aluminium, the oxygen level showed to be low throughout the whole experiment. Except after 7 to 9 minutes after the aluminium addition when reoxidation occurs. After about 7 minutes, there was an increase in oxygen level which after 9 minutes declined again to lower levels.

In experiment 3, 30 g aluminium was used. The results, as shown in Figure 48, show a very low oxygen level throughout the whole experiment, except for the sample taken 4 minutes after the addition. The level varies at about 20 ppm.

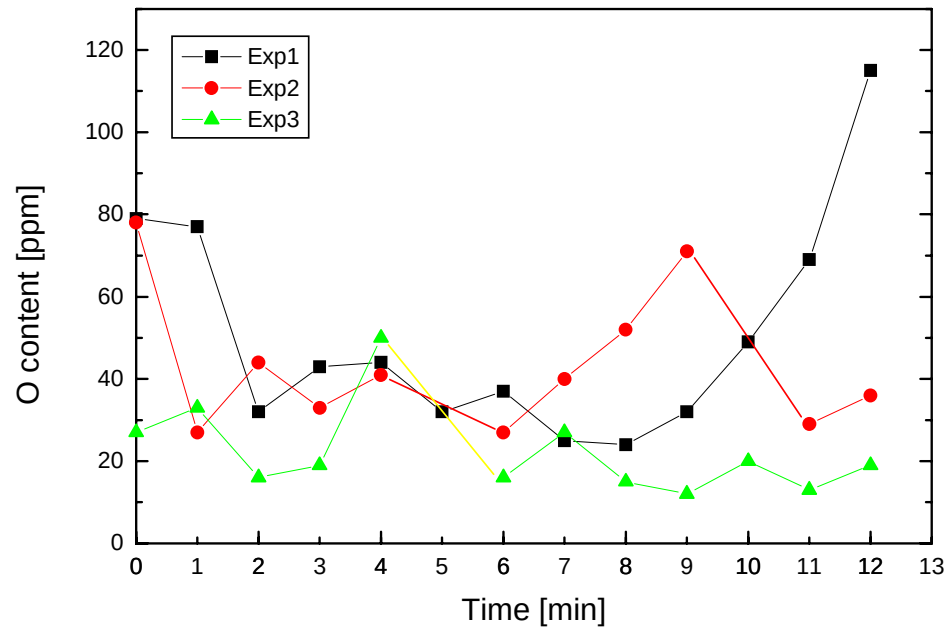


Figure 48. Oxygen content during experiments 1, 2 and 3.

The aluminium content in the steels during experiments 1, 2 and 3 is shown in Figure 49. The aluminium content peaks when Al is added. After the peak the aluminium content is constant throughout the experiments. It should be noted that some points are unfortunately missing due to bad samples. These samples were acquired but in such a bad condition that these were impossible to analyse. The samples that are missing include sample 6 from experiment 2 and 3, as well as sample 11 from experiment 2. These samples basically contained too many cavities and pores to give a correct chemical analysis.

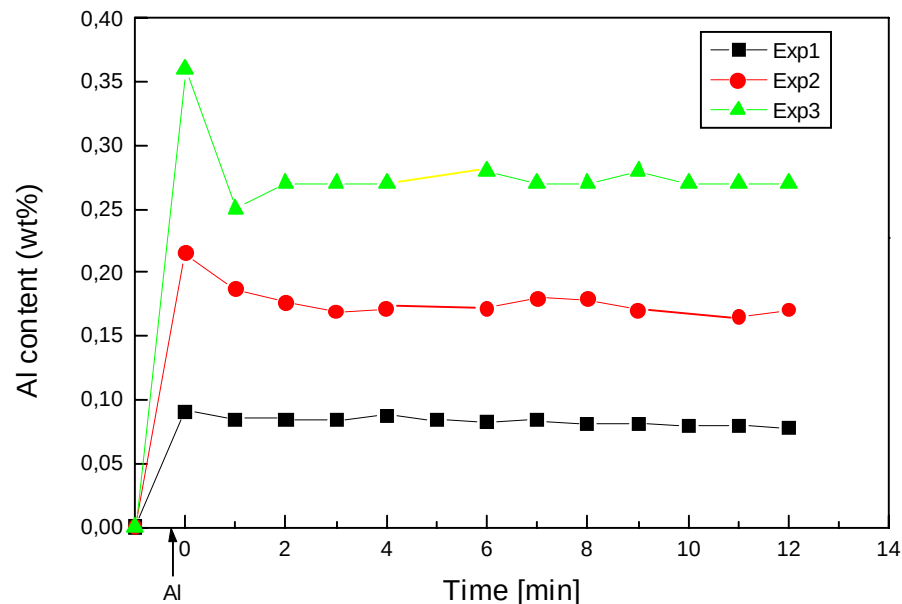


Figure 49. Aluminium content during experiments 1, 2 and 3.

6.3.2 Resulting timelines for experiments with preconditioner and grain refiner

The deoxidation experiments gave results that have been used to set up timelines for the experiments with preconditioner and grain refiner. It was shown in Figure 48, that 30 g of aluminium was sufficient to deoxidize the steel. Also 20 g of aluminium showed tendencies towards totally Al- killed steel. The experiment with 10 g of aluminium had a reoxidation after 10 minutes. To avoid too much aluminium, that might effect the results in the following experiments, it was considered that 10 g of aluminium should be used. This only if the casting was done before within 10 minutes from adding aluminium.

In Figure 50 and Figure 51 the resulting timelines from the deoxidation experiments are showed. Figure 50 describes experiment 4 and 6 while Figure 51 describes experiment 5 and 7.

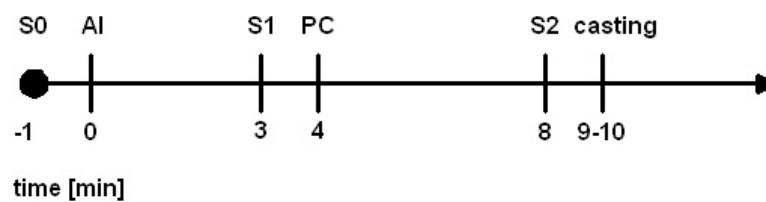


Figure 50. Timeline for experiments 4 and 6.

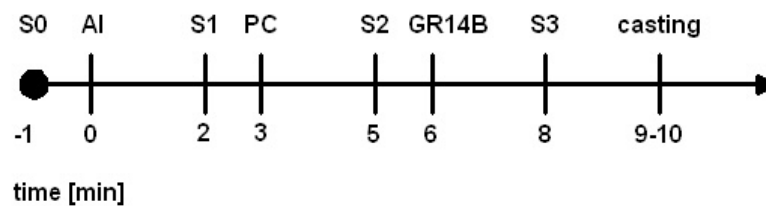


Figure 51. Timeline for experiments 5 and 7.

6.4 Results from experiments with preconditioner and grain refiner

In this chapter and onwards, preconditioner will be addressed as PC and grain refiner as GR14C. As mentioned in chapter 2.2, two experiments with PC and two experiments with PC + GR14C have been carried out. The results are divided into chemical analysis and graphs showing the major elements.

6.4.1 Chemical analyses

Table 28 presents the chemical analyses of the ingots resulting from experiments 4 to 7 as well as the analyses of unmelted AISI 329. In experiments 4 and 6 when only PC is used, the amount of cerium is hardly detectable while the amount of sulphur is high. For experiments 5 and 7 where PC and GR14C was used the amounts of cerium is higher and the amount of sulphur is lower. The amount of aluminium is high in experiment 5 in contrast to experiments 4, 6 and 7. This is due to the increased amount of aluminium used for deoxidation in this experiment.

Table 28. Chemical analysis of experiment 4, 5, 6 and 7 plus unmelted AISI 329, wt%.

Element	Unmelted AISI329	Exp [4]	Exp [5]	Exp [6]	Exp [7]
C	0,026	0,026	0,035	0,028	0,035
Si	0,46	0,64	0,80	0,64	0,79
Mn	1,75	1,68	1,68	1,69	1,68
P	0,024	0,024	0,025	0,025	0,024
S	0,025	0,022	0,001	0,022	0,002
Cr	24,71	24,45	24,38	24,09	24,20
Ni	5,15	5,14	5,19	5,02	4,93
Mo	1,44	1,41	1,41	1,41	1,38
Co	0,072	0,070	0,070	0,071	0,069
Ti	<0,005	<0,005	<0,005	<0,005	<0,005
Cu	0,15	0,15	0,15	0,15	0,15
Al	<0,003	0,059	0,18	0,094	0,094
B	0,0004	0,0005	0,0006	0,0005	0,0005
N	0,029	0,034	0,036	0,033	0,031
Ce	<0,005	0,007	0,009	0,04	0,05
O	48 ppm	89 ppm	17 ppm	41 ppm	69 ppm
Mg	<0,001	0,007	0,009	<0,001	<0,001
Ca	0,0038	<0,0005	<0,0005	<0,0005	<0,0005

With the exception of aluminium and cerium, the contents of other strong oxydeformers, such as calcium, titanium and magnesium is very low. The typical content is below 0.005 wt-% which suggests that the deoxidation reaction equilibrium in this experimental series is only governed by the content of aluminium and cerium, and the reactions between these elements and oxygen.

It should be duly noted that the content of nitrogen has increased slightly between the base metal, at 0.029 wt-%, and the average of the ingot samples at 0.034 wt-%.

6.4.1.1 Aluminium content during experiments 4, 5, 6 and 7

Experiments 4-7 were carried out using 10-30 g aluminium for deoxidation purposes. Despite what has been said in chapter 3.2 experiment 5 has a larger aluminium addition. Figure 52 shows that the aluminium content increases very rapidly after that aluminium has been added to the steel. The content rises to approximately 0.08 to 0.10 wt-% for experiments 4, 6 and 7. Experiment 5 shows higher aluminium content of about 0.2 wt-% which is probably due to an unintended faulty addition of extra aluminium.

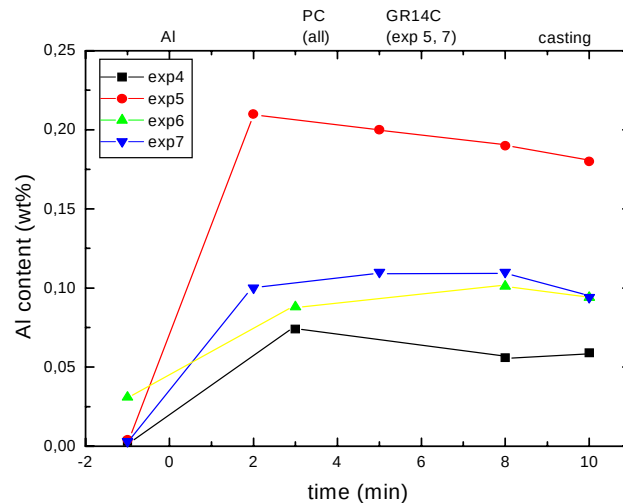


Figure 52. Aluminium content during experiments 4, 5, 6 and 7.

6.4.1.2 Oxygen content during experiments 4, 5, 6 and 7

Aluminium addition shall serve as a deoxidiser when added to the melt. In Figure 53 it shows that the oxygen content during the experiments is decreasing and the content is low in the ingots as well. It should be noted that the oxygen content is relatively high during experiment 6. This means that the oxygen content does not decrease when aluminium is added but decreases when PC (cerium) is added. In experiment 7 there is also a small reoxidation before casting.

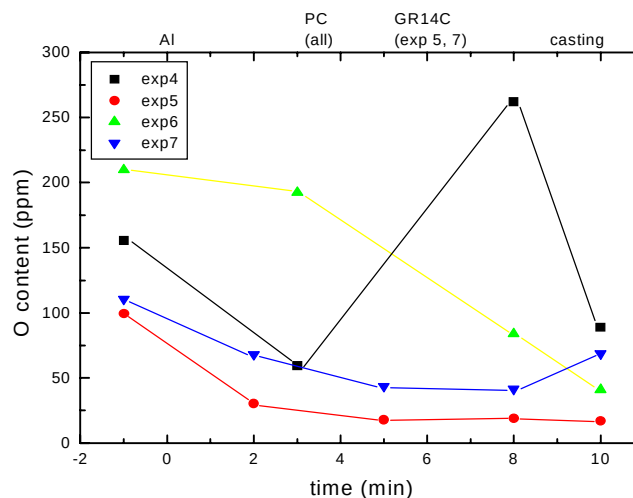


Figure 53. Oxygen content during experiments 4, 5, 6 and 7.

6.4.1.3 Cerium content during experiments 4, 5, 6 and 7

Cerium is added to the melt in the form of a preconditioner. The cerium content during experiments can be seen in Figure 54. The amount of cerium is increasing when PC is added, especially in experiment 7. When casting in the mould the amount of cerium is drastically decreasing, in experiments 5 and 7. Sample 3 (S3) taken just before casting (8 minutes) gives a much higher cerium content compared to the resulting content in the ingot, especially in experiments 5 and 7.

In experiments 4 and 6 only preconditioner (PC) is used to establish the effect of the PC. An interesting fact is the increase of cerium in experiment 6, when all the other experiments have a cerium decrease.

The preconditioner contains 13 wt% Ce, as listed in Table 25. The amount of added PC is 58g (see Table 27 above). This results in a cerium yield in each experiment listed in Table 29. From Table 29, it is evident that the Ce yield is very low with a little increase for experiments 6 and 7.

Table 29. Cerium yield in experiments 4, 5, 6 and 7.

Experiment #	Ce, added [wt- %]	Ce, out [wt- %]	Ce ingot yield (%)
4	0.075	0.007	9 %
5	0.075	0.009	12 %
6	0.075	0.040	54 %
7	0.075	0.050	67 %

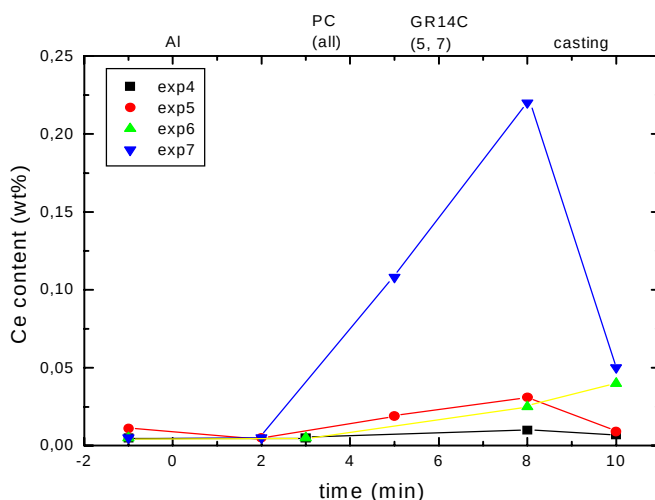


Figure 54. Cerium content during experiments 4, 5, 6 and 7.

6.4.1.4 Sulphur content during experiments 4, 5, 6 and 7

Sulphur is added to the melt using the grain refiner. The initial sulphur content in the steel before melting is 0,025wt-%. In Figure 55 the sulphur content during experiments is displayed. It shows that the sulphur content has decreased below initial level for all experiments. In experiments 5 and 7 it is clearly shown that the sulphur content is dramatically decreased, although sulphur is added to the melt in the form of a grain refiner after 6 minutes. A strong desulphurisation reaction has occurred when the sulphur level has decreased to lower levels than the initial steel composition. The grain refiner 14C contains 0,9 wt% S and 9 g of GR14C has been added per kilo of steel, aiming for a content in the steel of about 50 ppm with an assumed yield of about 60%.

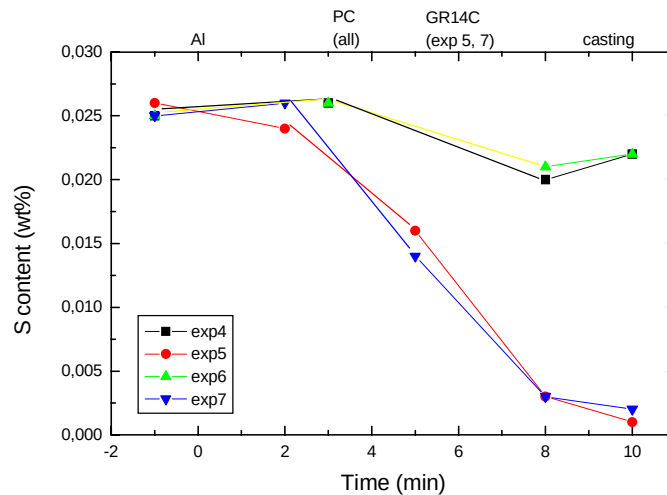


Figure 55. Sulphur content during experiments 4, 5, 6 and 7.

6.4.2 Metallography

Samples from the as-cast materials were obtained from the ingots at three positions; top, middle and bottom. The dimensions of the acquired samples were about 3 x 3 centimetres for the grain size and inclusion assessments. At first, these samples were used to assess the size distribution and number density of inclusions. An area of about 160 mm² was assessed according to the standard method SS111116.

Each of these samples was then etched with standard etchant V2A before the grain size measurements were performed. Both of these measurements were performed at the metallographical laboratory of the Department of Materials Science and Engineering at Kungl Tekniska Högskolan, Stockholm, Sweden.

6.4.2.1 Grain size

Since experiment 1 was selected to be the guiding experiment for the used deoxidation practise, experiment 1 is the only experiment from the deoxidation experiments that has been evaluated regarding grain size. The result of all the assessments is presented in Table 30. It should be noted that the average standard deviation for this kind of assessment is about ± 0.10 mm.

Table 30 shows that the average grain size for experiment 4, 5 and 6 is larger compared to experiment 1. Furthermore, the middle sample from experiment 7 shows the smallest grain sizes of all the samples. In this experiment, both pre-conditioner and grain refiner was used, resulting in an average grain size in the middle sample of about 0.65 mm.

Table 30. Average grain sizes and standard deviations for experiments 1 and 4 to 7.

Average grain size [mm]	Exp 1		Exp 4		Exp 5		Exp 6		Exp 7	
	Av	StD	Av	StD	Av	StD	Av	StD	Av	StD
Top of ingot	0.72	0.10	0.77	0.14	1.0	0.22	1,26	0,52	0,65	0,2
Middle of ingot	0.82	0.22	0.93	0.31	1.2	0.24	0.84	0.12	0.65	0.10
Bottom of ingot	0.80	0.40	1.0	0.32	0.95	0.28	1,42	0,56	0,64	0,09
Average	0.78		0.90		1.06		1,17		0.65	

It should be noted that the largest grain sizes is in the middle of the ingots for all experiments. The difference between the top, middle and bottom of the ingots is varying between the experiments. In experiment 1, this difference is small.

Figure 56 to Figure 59 presents micrographs of ingot samples from experiments 4 to 7 showing the different typical grain sizes. The pictures is taken from the samples cut out from the middle of the ingots

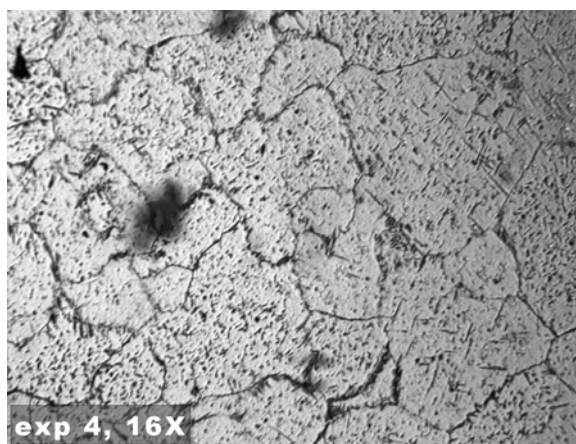


Figure 56. Micrograph of grain distribution in ingot sample from experiment 4.

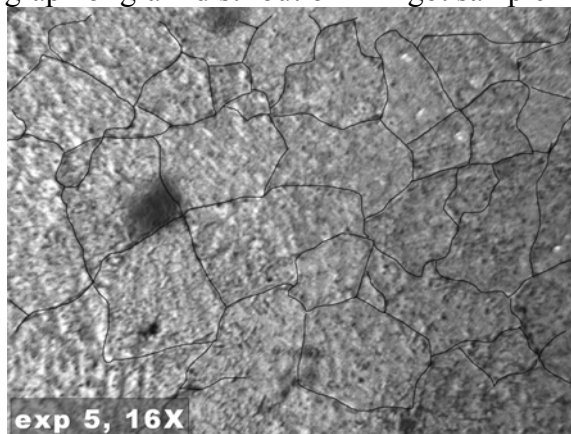


Figure 57. Micrograph of grain distribution in ingot sample from experiment 5.

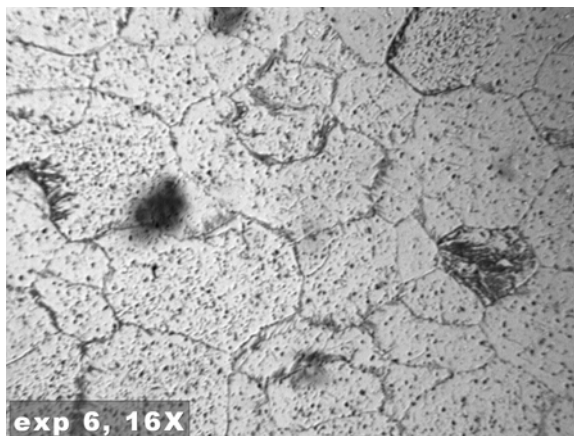


Figure 58. Micrograph of grain distribution in ingot sample from experiment 6.

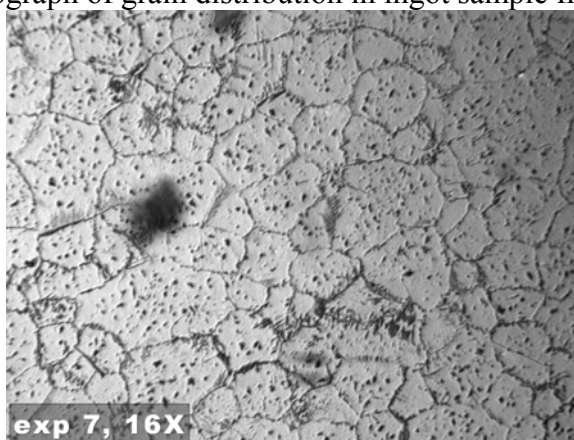


Figure 59. Micrograph of grain distribution in ingot sample from experiment 7

6.4.3 Inclusion size distribution

The size distribution and number density of inclusions has been investigated according to the Swedish Standard method for inclusion assessment SS111116. In accordance with the standard, an area of at least 160 mm² has to be assessed for each sample. The samples in this study were as-cast steel taken from the middle of the ingots in each experiments. In this case, the correlation between shape and inherent composition cannot be used.

The results from these assessments have been summarized in Table 31 and Table 32, showing the area-percentage of inclusions and the inclusion size distribution, respectively.

Table 31. Inclusion size distribution (number per mm²) in experiments 1 and 4 to 7.

Experiment	DT (4.7-9.2 μm)	DM (9.3-18.6 μm)	DH (18.7-37.2 μm)
1	1.7	1.8	0.75
4	1.1	2.1	0.59
5	2.3	1.7	0.53
6	1.5	0.90	0.17
7	1.5	1.1	0.41

Table 32. Area-% inclusions in experiments 1 and 4 to 7.

Experiment	DT (4.7-9.2 μm)	DM (9.3-18.6 μm)	DH (18.7-37.2 μm)
1	0.0059	0.025	0.041
4	0.0039	0.029	0.033
5	0.0080	0.023	0.029
6	0.0051	0.012	0.0095
7	0.0053	0.015	0.023

Figure 60 shows the results of the different assessments. Clearly the different experiments have resulted in different levels of inclusion density. The figure shows the area-% of inclusions of different sizes in the samples. In this figure, by looking at the combined level for all the inclusions it is also possible to observe the total area-% of inclusions in each experiment.

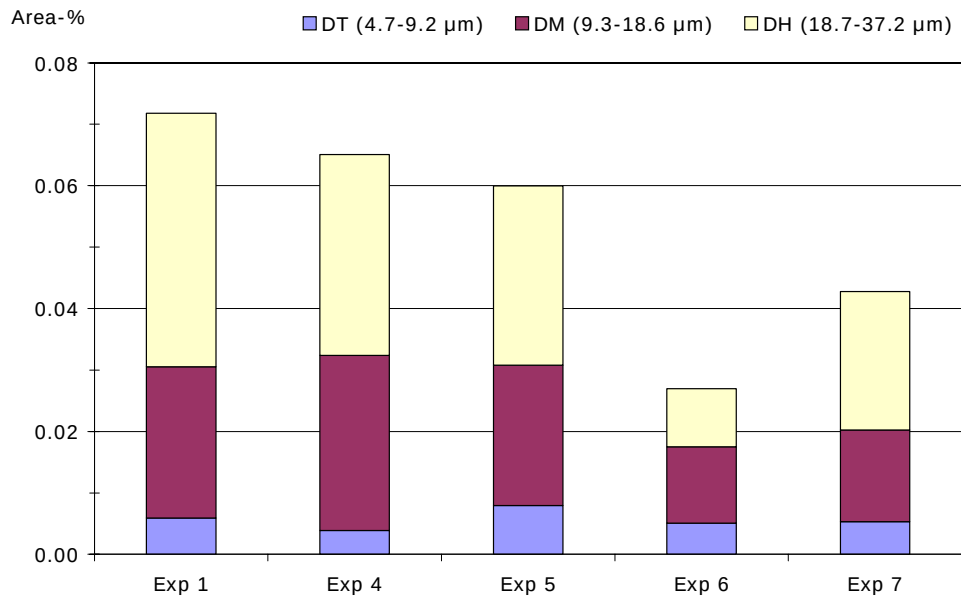


Figure 60. Area-% of inclusions in ingot samples from experiments 1 and 4 to 7.

Of major importance with the experiments was to obtain a large number of smaller inclusions in order to facilitate grain nucleation. The highest number of small inclusions has been accomplished in experiment 5 as can be seen in Figure 61. As could be expected, the highest number of large inclusions present could be found in experiment 1. The highest density of smaller sized inclusions was found in experiment 5 followed by a slightly lower density in experiments 6 and 7. In the larger size groups, experiments 4 and 5 had the highest densities.

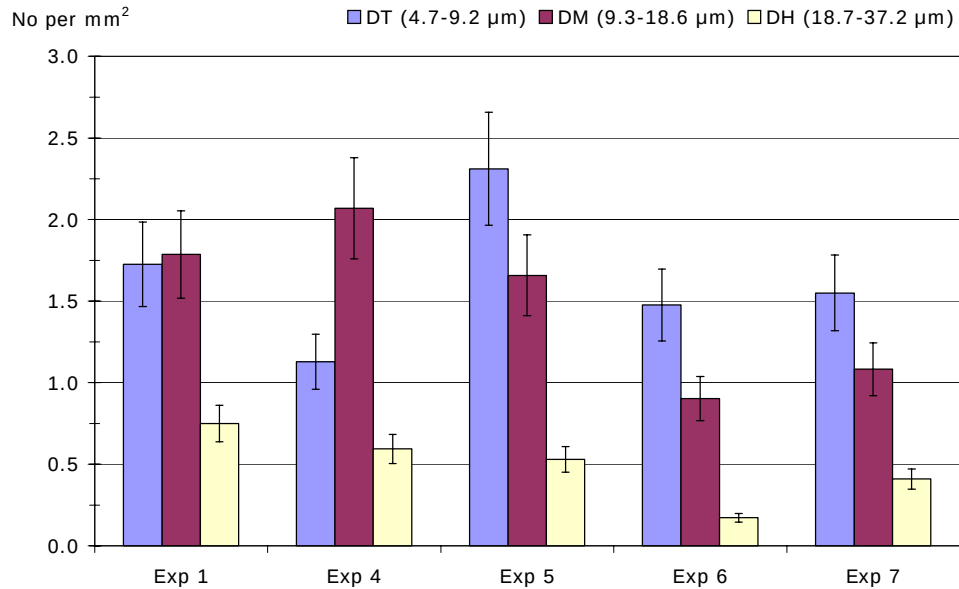


Figure 61. Number of inclusions per mm² present in ingot samples from experiments 1 and 4 to 7.

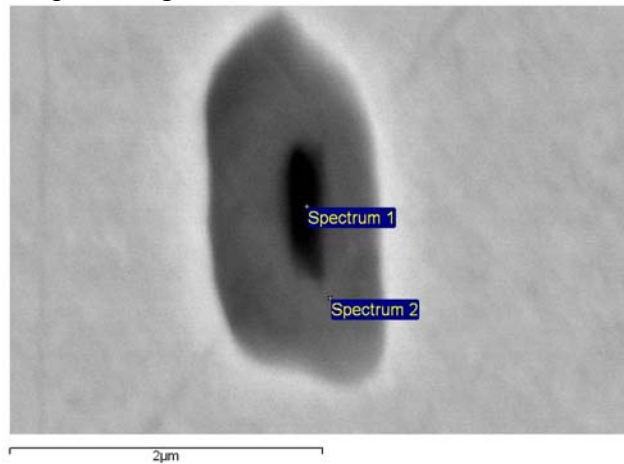
Please note that only one assessment has been made on each of the ingot samples from each of the experiments. Consequently, there is no standard deviation or average data for these samples. However, from experience this type of assessment has an inherent error level independent of the operator carrying out the assessment. According to a study in which 35 operators assessed the same samples, the standard deviation was reported to be about 15%.[3] This value has been used to indicate the inherent error in the inclusion assessments.

6.4.4 SEM

All quantitative data has been normalised for iron (Fe) and nickel (Ni) signals from the steel matrix. The resulting data are presented in at%.

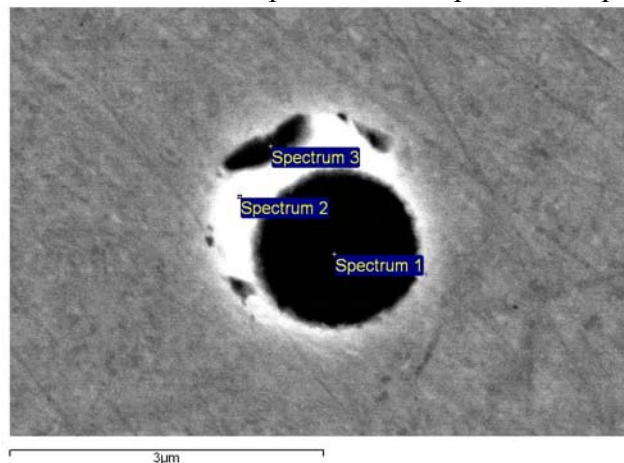
6.4.4.1 Experiment 4

The main type of inclusion observed in this steel is Al-oxide with MnS on the surface. An example of such an inclusion is shown in Figure 62. Single phase MnS inclusions are also observed. Ce containing inclusions are rare. Ce-oxides are only observed in combination with another oxide, like the example in Figure 63.



Spectrum	O	Al	Si	S	Cr	Mn
Spectrum 1	43	18	0	19	2,1	18
Spectrum 2	0	1,9	1,4	46	5,7	46

Figure 62. Al₂O₃-MnS inclusion present in sample from experiment no. 4.



Spectrum	O	Al	S	Cr	Mn	Ce
Spectrum 1	61	31	2,6	1,9	0,9	2,6
Spectrum 2	30	14	30	4,4	2,4	20
Spectrum 3	22	9,4	34	6,4	18	11

Figure 63. Al₂O₃, Ce-oxysulphide, MnS inclusion present in sample from experiment no. 4.

6.4.4.2 Experiment 5

In the SEM/EDS analyses of experiment 5, two types of inclusions were found. The first is a single phase cerium oxysulphide as shown in Figure 64. The composition of this type is close to the stoichiometric composition of $\text{Ce}_2\text{O}_2\text{S}$. The second is a multiphase inclusion with a core of AlCe-oxysulphide and a needle shape Al-nitride phase growing from this core.

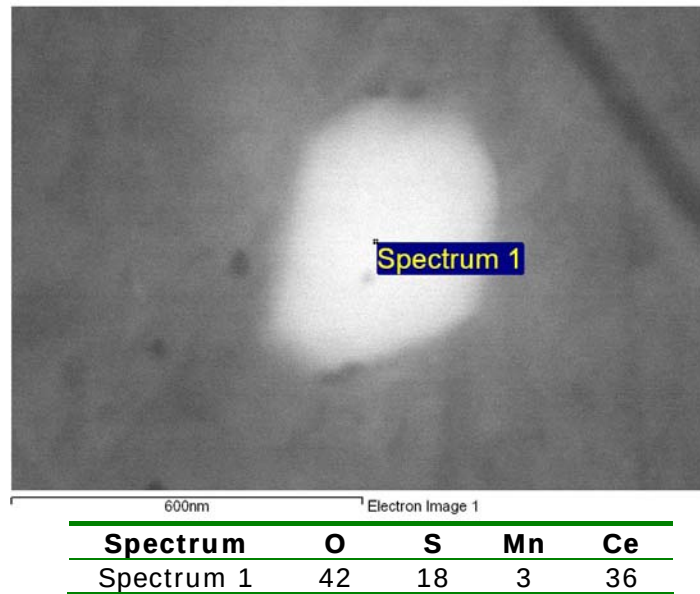


Figure 64. cerium oxysulphide inclusion present in sample from experiment no. 5

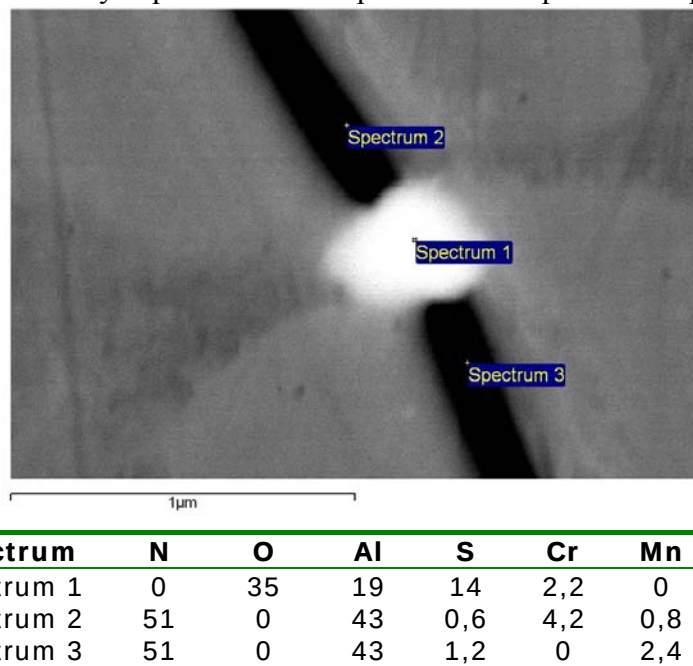


Figure 65. AlN and AlCe-oxysulphide inclusions present in sample from experiment no. 5

6.4.4.3 Experiment 6

Figure 66 shows a low magnification backscattered image of the steel from experiment no. 6. The majority of the inclusions in this steel are MnS inclusions like the ones shown in Figure 67. There is a significant amount of Ce (0.04 wt%) present in this steel. This Ce is however only observed in large CeS-MnS inclusions like the one shown in Figure 68 and in Ce-oxysulphide clusters like the cluster shown in Figure 69.

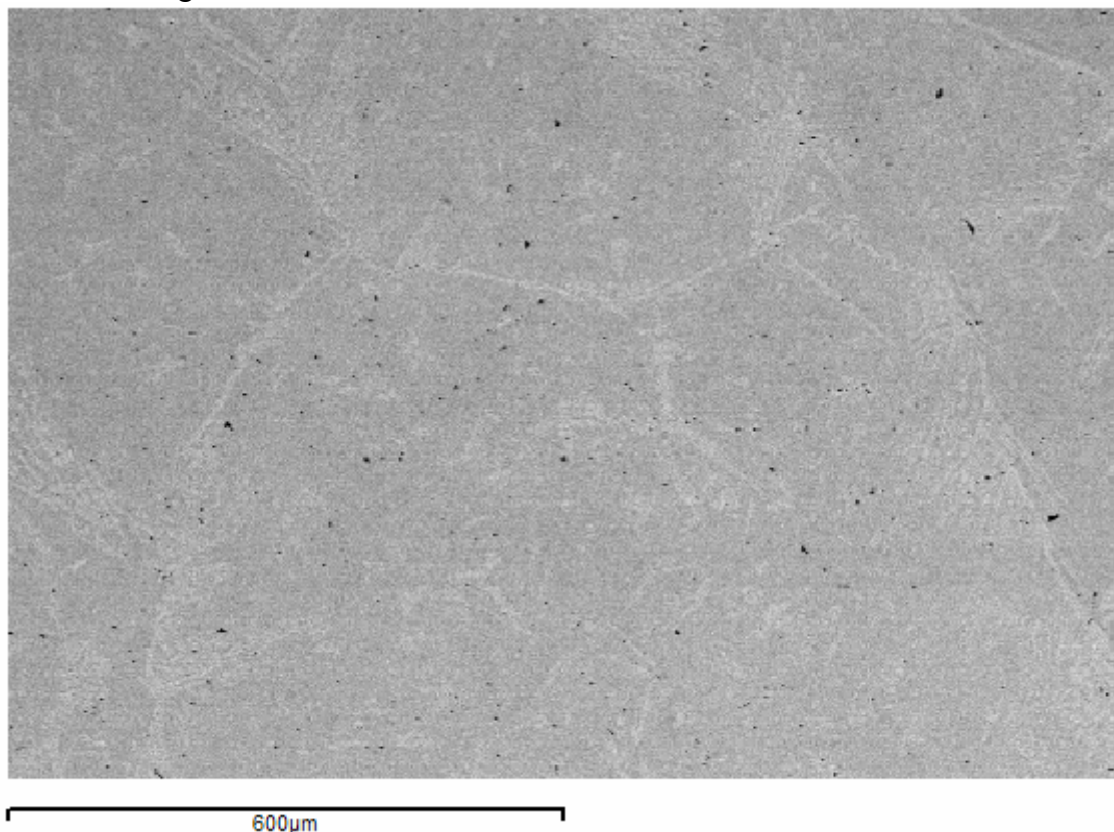


Figure 66. Low magnification backscattered image of the steel of experiment no. 6

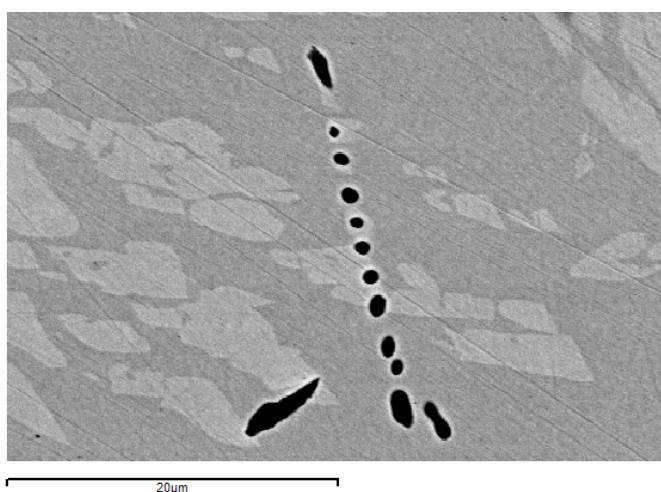


Figure 67. MnS inclusions in sample from experiment no. 6

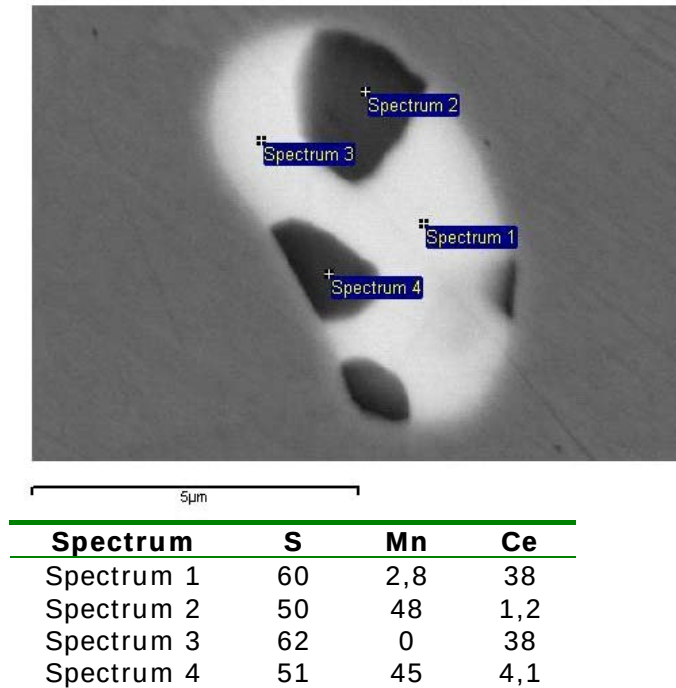


Figure 68. CeS-MnS complex inclusion present in sample from experiment no.6

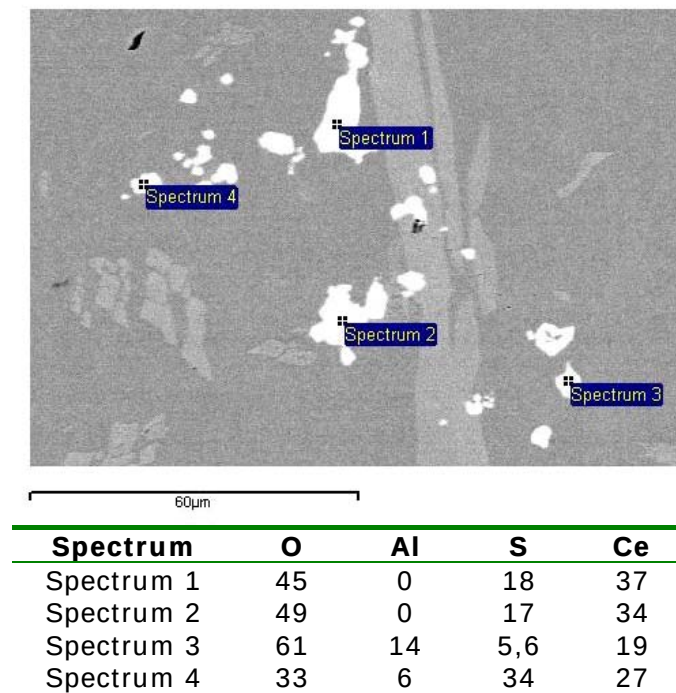


Figure 69. Ce-oxysulphide inclusions with some Al₂O₃ present in sample of experiment no.6

6.4.4.4 Experiment 7

The low magnification backscattered images shown in Figure 70 and Figure 71 show that there is a fine distribution of bright spots in contrast to the image shown in Figure 66. The bright spots indicate the presence of inclusions containing heavy elements, like Ce. The majority of the inclusions are cerium-oxysulphides like the one shown in Figure 72. The composition of these is close to the $\text{Ce}_2\text{O}_2\text{S}$ stoichiometry. Some of these have Al-nitride on the surface, as shown in Figure 73.

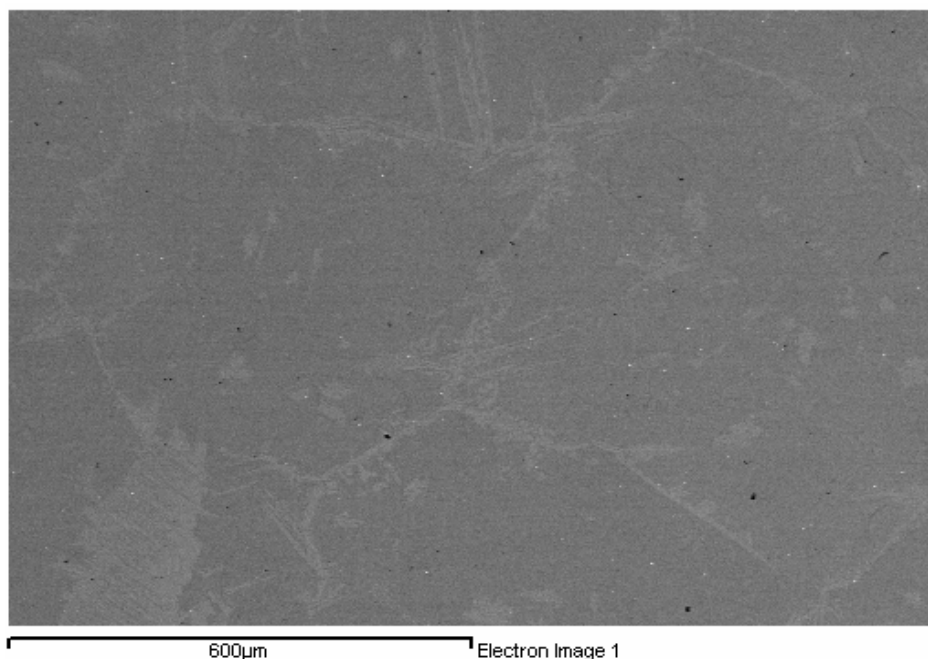


Figure 70. Low magnification backscattered image of the steel of experiment no. 7

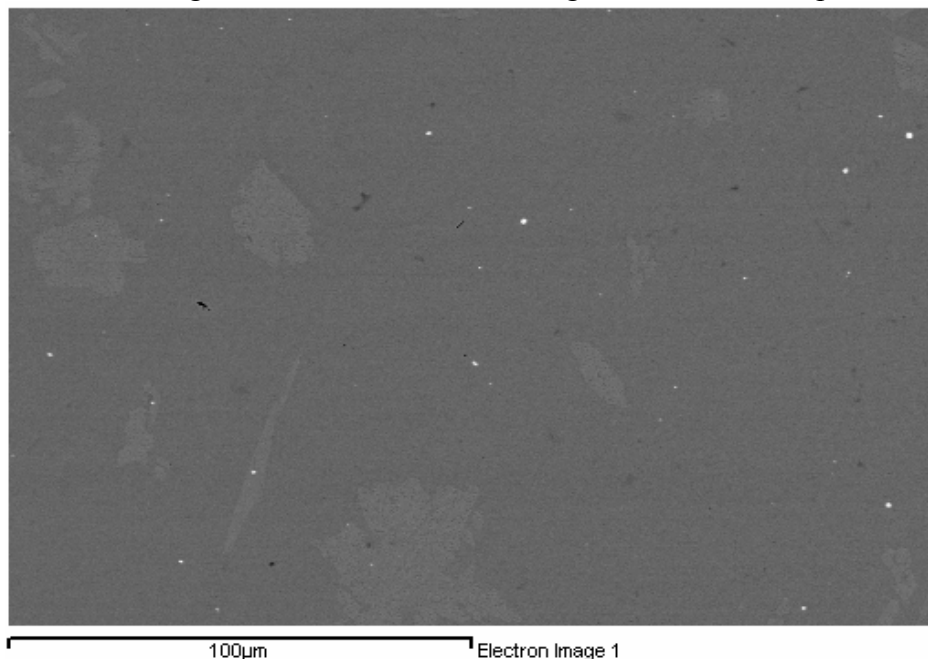
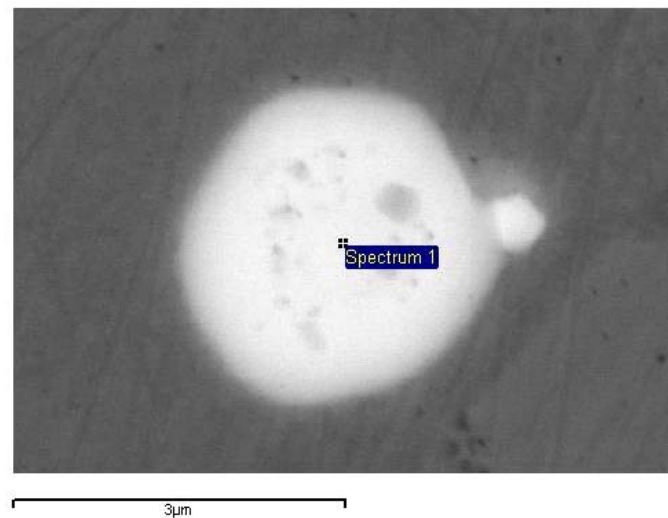
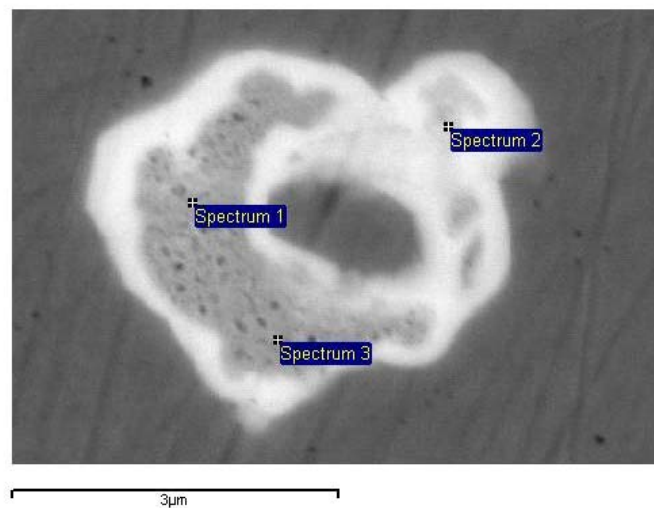


Figure 71. Low magnification backscattered image of the steel of experiment no. 7



Spectrum	O	S	Ce
Spectrum 1	44	18	39

Figure 72. Ce-oxysulphide inclusion present in sample from experiment no. 7



Spectrum	N	O	Al	Ce
Spectrum 1	20	38	21	21
Spectrum 2	0	63	4,4	33
Spectrum 3	15	43	21	22

Figure 73. AlN on Ce-oxysulphide inclusions present in sample from experiment no. 7

6.5 Discussion

In the following certain aspects concerning the chemical analysis of the acquired samples will be discussed. At first some general points will be discussed and then aspects concerning aluminium, sulphur and cerium will be investigated. Finally, the results pertaining to grain size and inclusion examinations will be discussed.

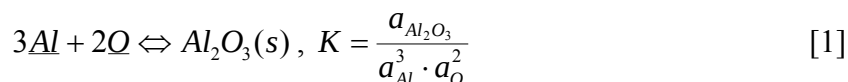
6.5.1 Chemical analysis

Among the results of the chemical analyses some aspects deserve to be thoroughly scrutinized. For instance, the nitrogen content in the unmelted material is at 0.029 wt% while the average of the nitrogen content in the as-cast material is at about 0.034 wt%. This indicates that there has been a certain amount of interaction between the melt and the atmosphere during the experiment. Since the melt during melting, deoxidation and alloying is protected by argon, which is an inert gas, it is most probable that this increase has occurred during the casting process. Having an increase of nitrogen, it is probable that also oxygen has leaked into the melt during casting causing a so called re-oxidation where oxygen dissolves into the melt. This has implications on the results of the inclusion assessment, which will be discussed later.

There is also an increase in carbon and silicon content in experiments 5 and 7 which cannot be neglected. The increase in content of silicon is about 0.15 wt% and the increase of carbon is about 0.009 wt%. Results from experiment 4 and 6 do not show the same tendency. Most unfortunately, having scrutinized the analyses of the base metal, the various addition materials, and the used aluminium, no explanation for this increase can be given at this time.

6.5.1.1 Aluminium and oxygen

The first three experiments aimed at determining how much aluminium that was needed as a deoxidiser in order to keep low levels of dissolved oxygen. Aluminium was chosen since it has a high oxygen affinity. As a result of this a slag is formed on top of the melted steel. Dissolved aluminium reacts with dissolved according to Reaction [1].



Where $a_{\text{Al}_2\text{O}_3}$ is the activity of solid aluminium oxide, a_{O} is the activity of dissolved oxygen, a_{Al} is the activity of dissolved aluminium, and K is the equilibrium coefficient for the reaction.

The dissolved oxygen content in the melt following deoxidation, shown in Figure 48 above, follows the expected and wanted results. Oxygen levels are generally low and steady even for the smallest tested addition of 10 gram. The results show that it takes about 10 minutes before re-oxidation becomes a problem. It was therefore concluded that 10 g of Al is sufficient if casting will take place within 10 minutes.

The experiment with 20 g of Al addition for deoxidation shows an anomaly for the samples acquired at 7, 8 and 9 minutes. With the exception of these three samples, the oxygen level is at about 40 ppm. Most probably atmospheric reoxidation has occurred which temporarily increases the dissolved oxygen content in the melt. Since the aluminium content is fairly high, about 0.1wt%, aluminium subsequently reacts with oxygen again and deoxidises the steel. This can be seen Figure 49 as a slight decrease in aluminium content.

In experiment 3, an addition of 30 g aluminium was used. The analysis shows a very low oxygen level throughout the whole experiment, at a level of about 20 ppm with the exception of the sample taken 4 minutes after deoxidation. At this point the oxygen content is as high as 50 ppm which is almost three times as high as the normal level for this experiment.

A probable explanation to this is that this particular sample had a high degree of pores, air entrapment. These pores add to the analysed oxygen by the surface oxidation that occurs during sampling. Traces of surface oxidation are normally removed by grinding, but this is impossible for pores inside samples, hence the much higher oxygen content.

After reviewing the results of the deoxidation series of experiments it was concluded that a low and steady level of oxygen can be obtained by using 10 g to 10 kg of steel, i.e. 0.1 wt% Al. In order to ensure that the oxygen level is kept low, inert gas should be used at all times during the experiment and it is imperative that it is used until the very last minute before casting commences. The results from the deoxidation practise in experiments 4 to 7 were mostly as expected. The aluminium and oxygen content is varying in a similar way as in the deoxidation experiments. There is one point in experiment 4 which is significantly higher than what the other analyses indicate is a reasonable level. A possible explanation of what happens is a similar behaviour as in the deoxidation experiment with 20 g of aluminium. In that experiment a reoxidation occurred during 3-4 minutes and then the steel was deoxidised again.

The oxygen content in experiment 6 does not decrease as rapidly in the beginning as it does in experiments 4, 5 and 7. The oxygen content then drops sharply after that cerium containing PC has been added. Most probably, the cerium contributes to the deoxidation process by forming cerium oxide inclusions which are then subsequently removed to the slag or to the crucible walls. Experiment 5 was performed with a higher addition of aluminium. At this time 30 g of aluminium was used. This fully explains the higher aluminium contents in these analyses. In addition, the high aluminium content also results in a lower oxygen content compared to the other experiments. The conclusion is that the deoxidation has worked fairly well with a fairly low oxygen level as a result. However, there is certainly room for improvement. One additional way of making sure that no oxygen is allowed to the melt, besides using inert gas purging, can be adding liquid argon or nitrogen to the surface of the melt and thereby making sure that the atmosphere in the immediate vicinity of the melt is inert.

6.5.1.2 Cerium

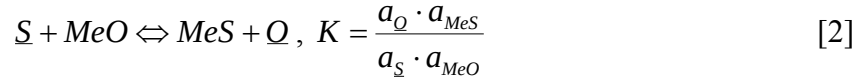
As mentioned above, cerium is added as a pre-conditioner. In the results it was shown that the cerium content was higher during ongoing experiments in experiments 5 and 7, compared to experiments 4 and 6. This is probably the result of higher oxygen content in experiments 4 and 6. When cerium is added to these melts, the oxygen content is high. In these cases the aluminium deoxidation has not been satisfying, which results in that cerium most certainly work as a deoxidizer and, thereby, forming cerium oxide inclusions.

In the ingot, the analyses show that experiments 6 and 7 have a much higher cerium content compared to experiments 4 and 5. This is probably due to more stability in the casting procedure. A stable casting procedure is equal to accurate casting with short exposure time to surrounding atmosphere. Accurate casting is equal to no spilling which results in a more intact tapping jet. In experiment 7, which has the highest cerium yield, the amount of cerium is very high immediately before casting. The same pattern can be seen for experiment 5 but at lower levels. A lot of cerium is obviously removed from the melt during casting.

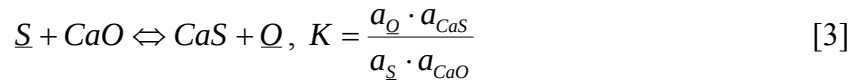
During casting, which is made in normal atmosphere, the melt is exposed to the surrounding air for a period of about 1 minute. Casting requires the lid to be lifted from the crucible, thereby removing the feeding of inert gas. Subsequently the melt is poured from the furnace into the mould in open air. The amount of time this procedure takes can differ from experiment to experiment with an average casting period of about 1 to 2 minutes. In that period, the melt suffers heavy stirring conditions due to the casting stream and it is also exposed to the surrounding atmosphere. This will accelerate the removal process where the inclusions, mostly cerium oxide inclusions, are removed by flotation to the surface according to Stokes law.

6.5.1.3 Sulphur

Sulphur has a tendency to be removed as the experiment is going on. This behaviour is most probably due to the low oxygen content that is achieved with deoxidation. The steel ASISI 329 also contains small amounts of calcium that most probably come from calcium oxide inclusions which are then lifted to the top of the melt to form slag. This type of basic slag combined with a low dissolved oxygen content and a well stirred melt provides very good conditions for sulphur refining of the melt. During refining, sulphur reacts with a metal oxide forming a metal sulphide, which is subsequently removed from the melt. The sulphur refining reaction is shown as reaction 2 below.



Where $a_{\underline{O}}$ is the activity of dissolved oxygen, a_{MeS} is the activity of metal sulphide, $a_{\underline{S}}$ is the activity of dissolved sulphur, a_{MeO} is the activity of metal oxide, and K is the equilibrium coefficient for the reaction. One typical example of this reaction that might well have occurred in the present experiments is the following between calcium oxide and sulphur:



Where $a_{\underline{O}}$ is the activity of dissolved oxygen, a_{CaS} is the activity of calcium sulphide, $a_{\underline{S}}$ is the activity of dissolved sulphur, a_{CaO} is the activity of calcium oxide, and K is the equilibrium coefficient for the reaction.

The desulphurisation process can also be described by the following expression that takes into account the kinetic aspects of slag/metal-reactions.[4]

$$\frac{d[\%O]_{st}}{dt} = ([\%O]_{int} - [\%O]_{eq}) \beta_O A \quad [4]$$

Where $[\%O]_{st}$ is the dissolved oxygen content in the steel, $[\%O]_{int}$ is the dissolved oxygen content at the slag/steel interface, $[\%O]_{eq}$ is the dissolved oxygen content at equilibrium, β_O is the oxygen mass transfer coefficient, and A is the interfacial area between the slag and the metal.

With these equations, the most important parameters of desulphurisation can be described. An effective desulphurisation is likely to occur when the dissolved oxygen content is low, the activity of CaO in the slag is high, the reaction area is large, and the melt is well stirred. When all these conditions have been met, the desulphurisation will be very efficient.

It was seen in Figure 55 that the sulphur content in experiments 4 and 6 decreases very slowly, while the desulphurisation rate is much higher in experiments 5 and 7. A probable explanation to this behaviour is that in experiments 4 and 6 the aluminium and cerium contents are lower compared to experiments 5 and 7. In addition, the dissolved oxygen content is also lower in the latter experiments. This is, probably as a result of the higher aluminium and cerium contents.

As opposed to this, both aluminium and cerium contents are quite high in experiments 5 and 7, resulting in a low dissolved oxygen content. Expectedly this results in the steel being refined in a much more efficient way. Thus, as the oxygen level decreases in the course of the experiment, the sulphur content decreases rapidly. It can be concluded that, quite the contrary to the intent, the conditions in experiments 5 and 7 are such that an efficient desulphurisation has taken place and that it leaves a very low sulphur level. But, as the SEM/EDS analyses show, this small amount of sulphur is still enough for cerium oxysulphides to form.

6.5.2 Inclusion size distribution

The difference in inclusion densities of the inclusions with a size larger than 4.7 μm is fairly small. However, the difference in inclusion density between the experiments is larger than the standard deviation of the assessment indicating that the differences are, at least to some extent, relevant for making conclusions. Overall, the results show that there are most of small sized (4.7 to 9.2 μm) inclusions in the samples, followed by medium sized (9.2 to 18.6 μm) and finally large (18.7 to 37.2 μm) inclusions.

It is evident that although the small sized inclusions are present to the highest amount, the contribution to the total surface fraction of inclusion is not so large. The volume fraction of larger sized inclusions is high considering the cleanliness of the steel. An explanation to this behaviour is that clustering of cerium oxysulphides has occurred so that smaller sized inclusions have combined into larger sized. In this way, the small inclusions that were intended to be used as nucleation sites for new grains have instead transformed into larger sized and thus, in that sense, inactive inclusions. It should be noted that the experiment with the highest combined oxygen and sulphur level, experiment 4, also show the highest volume fraction of inclusions.

Unfortunately there is no obvious correlation between inclusion density and grain sizes in the samples. This short-coming in results may very well be the result of the inability to acquire the inclusion density of smaller sized inclusions by using optical microscopy. However it should be duly noted that the cerium oxy sulphides found in the SEM were of the smaller sizes, approximately 0,5-3 μm . It is therefore most probable that the major part of the cerium oxysulphides has not been accounted in the analysis.

There are, however, other possibilities available for determining the inclusion size distribution and chemistry. For instance, modified OES could be used for assessment of inclusions with sizes up to about 8 μm . Nevertheless, if this kind of assessment could be performed, a more accurate relationship between inclusion density and grain refining effect could be revealed.

6.5.3 SEM

In experiment 4, Ce does not play a significant role in the inclusion formation since the content is not high enough in relation to the O and S content. Most of the inclusions in this steel are MnS and Al-oxides. In experiment 5, the O and S contents are so low that, although there is just 0.009 wt% Ce, the Ce is dominating the inclusion formation. After the formation of the oxide, there is still free Al available. This Al precipitates as AlN, presumably in the solid state. Because of the low O and S contents, the total inclusion volume fraction is however low.

In experiment 6 and 7, a significant amount of Ce is present in the steel. The inclusion size distribution differs however strongly in this case. Large inclusions (>5 μm) are observed in experiment 6 while a fine distribution is observed in experiment 7. In experiment 6, a high number of MnS inclusion is present.

6.5.4 Grain Size

In Table 30 the average grain size for experiments 1, 4-7 is displayed. It is clear that experiment 7 has a decrease in grain size while the others have an increase compared to the standard case, experiment 1. There is a significant difference regarding grain size effect between exp. 7 and exp. 5 although they have the same additions. In the chemical analysis, Table 28, it is evident that experiment 7 has a higher level of cerium in the ingot than experiment 4 and 5. The oxygen level in experiment 7 is rather high, compared to experiments 5 and 6 while the sulphur content is noticeable very low compared to experiment 4 and 6.

It is of course too few experiments to draw final conclusions but there are indications from the chemical analysis. These are, no single element could be correlated to a grain refining effect. High sulphur is not enough to create grain refining.

The results also indicates that the number and size distribution of the inclusions is of more importance than the composition of the inclusion since the inclusions found in experiment 5 and 7 are quite similar to each other. Despite experiment 5 higher inclusion content experiment 7 had a better grain refining effect. However has inclusions smaller then 4,7 microns not been included, so it is most possible that experiment 7 might have a larger number of smaller inclusions. The inclusions found consisted mostly of cerium-oxysulphides. In both experiments, 5 and 7, the inclusions investigated were of the type cerium-oxysulphides. They were often in co-existence with other types of inclusions suck as aluminium-nitrides. Hence a deeper investigation of these two experiments should be conducted in order to quantify the number of smaller inclusions.

The difference in grain size from top to middle to bottom of the ingot can be explained by the experimental technique. This has to be considered when the experimental technique is further developed.

6.5.5 Summary

In order to summarize the various results in this study a table has been drafted.

Experiment #	Al (wt%)	O (ppm)	Ce (wt%)	S (wt%)	Inclusion type	Grain Size effect, compared to grain size exp 1 (%)
4 (PC)	0,059	89	0,007	0,022	Al ₂ O ₃ _MnS MnS Al ₂ O ₃ _Ce-oxysulphide_MnS	+ 11,8
5 (PC+ GR14C)	0,18	17	0,009	0,001	Ce ₂ O ₂ S AlCe-oxysulphide_AIN	+ 46
6 (PC)	0,094	41	0,04	0,022	MnS CeS_MnS AlCe-oxysulphide	+ 2
7 (PC + GR14C)	0,094	69	0,05	0,002	Ce ₂ O ₂ S Ce ₂ O ₂ S_AIN	-21

6.6 Conclusions

The present experimental set-up and used deoxidation practise has resulted in a high aluminium yield and reasonably low oxygen levels. Combining a hard sintered high alumina crucible with inert gas purging and deoxidation with aluminium gives a good result. A review of the results from the deoxidation series show that it sufficient to use an addition equivalent to 0.1 wt% Al. As a precaution, inert gas should be used from the start of the heating cycle and until the casting commences.

SEM analyses of ingot samples show that Ce-oxysulphides inclusions were present in all the samples from experiments 4 to 7. In addition, in samples with low sulphur contents AlN inclusions were present. High sulphur contents resulted in MnS inclusions being present.

6.6.1 Experimental technique and metallurgical results.

The more specific conclusions are as follows:

- Re-oxidation occurs during casting which probably is detrimental to the final cerium content.
- Cerium oxysulphides are present in all the ingot samples from experiments using pre-conditioner.
- Aluminium nitrides are present in samples where the sulphur content is low.
- A too high addition of Al and Ce can lead to low sulphur amounts in the cast ingot.
- In lab scale too much oxidation occurs during casting to really control the experiment. Therefore it is necessary to develop an improved sampling technique.

6.6.2 Grain refining effects.

The number of experiments is too low to draw final conclusions but there are rather large differences in grain sizes between the different experiments indicating that non-metallic inclusions really affect the grain size. It is of course very encouraging and positive that a clear effect on the grain size has been achieved. It is reasonable to draw the conclusion that more information and knowledge can lead to an industrial practice for grain size control by steering the oxide and sulphuric inclusions.

After having demonstrated a sizable grain size effect, it is of course important to identify the factors controlling this effect. We cannot say if it basically is a question of effect from the levels of different elements like oxygen, sulphur or cerium or if it is solely a question of effect from the non-metallic inclusions. Results seem to support the idea that it is an inclusion effect since the experiment (No. 7) with the lowest grain size is the only experiment where a fine distribution of a large number of Ce-oxysulphides was accomplished. It is to recommend that a deepened analysis of the inclusion picture is being done. It is especially two things, which ought to be measured, and that is:

- The number densities for sizes below 4,9 microns
- Quantification of dominant types of inclusions at different sizes in the different samples.

We believe that there is a reasonable chance that these measurements will give a correlation to the grain size effect and a final explanation of the mechanism.

6.7 Future experimental work

It is evident that the experimental technique must be improved. The experiments must be more cost-effective leading to more experiments and faster throughput for the same cost. At the same time, a better control of oxygen and sulphur levels must be established. During the course of this work, there were several ideas discussed for improvement of experimental methods. Some of these ideas have been summarised below.

6.7.1 New sampling devise

Since the cerium content was very hard to trace to a specific reason, a better casting procedure is needed. A better method would be to use larger quartz tubes, which can suck a certain part of the melt and bring it to solidification. This would also be a better way to copy the solidification in the continuous casting procedure. The tubes would be lowered into the melt without letting the melt come in contact with the surrounding atmosphere. The tubes should be large enough to take a sample that could be evaluated of its grain size and inclusion distribution.

Successful experiments have been performed using this improved sampling technique. The samples are currently being evaluated.

6.7.2 Adding pre-conditioner and grain refiner simultaneously

It is believed that experiments where pre-conditioner and grain refiner is added to a melt together should be performed. Since results in the present and previous study indicate that the removal and/or agglomeration rate is high, simultaneous addition should be tested in order to allow a faster casting or sampling after the addition, thereby minimising the removal or agglomeration.

By combining this with larger liquid samples taken during the period just after addition, the dissolution rate of the pre-conditioner and/or grain refiner could be measured.

6.7.3 Improved inert gas purging

The deoxidation practise used in the present study has resulted in a fairly low oxygen level. However, there is certainly room for improvement. One additional way of making sure that no oxygen is allowed to the melt, besides using inert gas purging, can be adding liquid argon to the surface of the melt and thereby making sure that the atmosphere in the immediate vicinity of the melt is inert.

6.8 References

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