

## STUDY OF CERIUM SEGREGATION DURING SOLIDIFICATION OF LOW-CARBON 42CrMo4 STEEL

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### Abstract

The influence of cerium addition on solidification structure of the low-carbon 42CrMo4 steel was investigated. Alloys were prepared by means of a centrifugal casting. The addition of up to 0.05 wt. % of Ce in the steel produced greatly improved solidification structure with a suppressed columnar grain zone, finer grain size in the equiaxed grain zone, and zero area fraction of casting shrinkage cavity. The added cerium occurred in the steel both in the form of Ce oxide-sulphide inclusions and as dissolved atomic Ce segregated along with other elements at prior austenite grain boundaries and at interdendritic spacings. Microstructure (light optical microscope, SEM), X-ray EDX chemical microanalysis, and TOF-SIMS analysis (TESCAN ORSAY HOLDING) - mapping of elements in the structure of alloys were obtained. Rare-earth metals addition can be considered as a potential solution for grain structure refinement in heavy-weight castings of 42CrMo4 grade steel.

**Keywords:** 42CrMo4 steel, centrifugal casting, cerium addition, microstructure, inclusion, segregation

### 1. INTRODUCTION

Recently, cerium based particles have been tested as nucleation centers for heterogeneous nucleation of austenitic and duplex steels. The results have shown a mutual relationship between reduction of columnar grain zones and cerium addition [1]. Cerium particles have exhibited promising properties regarding to nucleation in steels, where mild overcooling is required for precipitation of cerium sulphides and oxides. Elkem company has in recent years, in cooperation with Sintef, developed grain refiners containing cerium. Elkem Grain Refiner (EGR) is an alloy containing ~10 wt. % of cerium along with elements present in the liquid. The grain refiner is added to the tapped stream before casting, making cerium react with impurities as sulphur and oxygen to precipitate particles.

There are two types of segregation distinguished in the solidified structures. There is macro-segregation, where composition changes to distances comparable to a sample size, and micro-segregation, occurring within a range of secondary dendrite arm spacing. Large differences in a composition can occur across dendrites as a result of formation of cores and non-equilibrium phases in the last proportions of the solidifying liquid metal. It has been found out through experiments that cooling rate affects the interdendritic spacing. However, the amplitude of the dissolved matter concentration is not changed significantly, providing that dendrite morphology does not change and diffusion in the solid matter is neglectable.

There are four factors, which can result in macro-segregations in ingots: shrinkage as a result of solidification and thermal contraction, density differences in interdendritic areas, density differences between a solid matter and liquid metal and conventional flows caused by temperature gradients and different densities in the liquid metal. All these factors can develop macro-segregations as a result of matter flowing to large distances during solidification. Thus, interdendritic flow of liquid metal can be caused by gravitational effects. Generally,

segregation is undesirable because it influences mechanical properties negatively. Micro-segregation effects can be reduced by subsequent homogenization heat treatment. However, diffusion in the solid matter is too slow for macro-segregations to be eliminated [2].

Cerium as a strong oxide- and sulphide-forming element can react with present oxygen and sulphur, when added to a liquid metal. Inclusions formed by cerium are useful for refinement. They affect actively the casting microstructure character, making inclusions become sites for heterogeneous nucleation. For an inclusion to become a suitable nucleation site, it must originate at mild overcooling. Cerium has been used as a grain refiner in many experiments. The experiments with low-alloyed steels with the cerium addition have shown shortening of secondary dendrite arm spacing and enlargement of the equiaxed crystal area proportion [3]. In austenitic manganese steels, the columnar grain zone has been reduced considerably, leading to an increase in notch toughness [1, 4, 5]. Stainless ferritic, austenitic and duplex steels have been tested in relation with grain refinement, whereas the microstructure has been refined, however, any significant improvement in mechanical properties has not occurred [6, 7]. There were problems with large cerium oxide clusters during industrial scale manufacturing.

Influence of cerium on formation of oxide-sulphide inclusions and segregation of elements in 42CrMo4 steel castings has been investigated in [8] and in this paper.

## 2. EXPERIMENT

The samples were prepared in the Regional Materials Science and Technology Centre (RMSTC) laboratory on the SuperCast equipment - an induction furnace with inert atmosphere and subsequent centrifugal casting. 42CrMo4 alloy delivered from VHM, a.s. and commercial steel in a form of a rod with 35 mm diameter from Ferona, a.s. were used as an input material. A thin foil of pure cerium (from Alfa Aesar, Germany - 3N purity) was used for microalloying. Heats were carried out in a medium-frequency casting equipment SuperCast, which was intended for induction melting of special alloys and intermetallic compounds in vacuum or Ar inert atmosphere. The samples were melted in a corundum crucible in an argon atmosphere at 35 kPa pressure and subsequently cast into a two-part graphite mould with an inner diameter of 20 mm. A cerium addition (0.05 wt. % Ce) in a form of a metal foil of 0.1 mm thickness, dimensions of 25x25mm and 0.42 g weight was put into a turned-out hole in one of the cylinders so that it could be completely melted and dissolved homogeneously in the melt before the subsequent rotary casting. An outlet opening of the crucible was positioned approximately 3 cm under the hub, where it led to a horizontally positioned graphite mould. Temperature inside the furnace before the centrifugal casting was 1550 °C. The charge had to be completely melted and homogenized before the casting. The chamber rotated at speed of 270 rpm for a period of 110 s with a rise time of 1.5 s. After the casting, Ar (6N) was let into the chamber and the steel was cooling down for a period of one hour. The casting was in a form of a rod of c. 225 mm length, 20 mm diameter, and with a conical extension on the inlet into the mould.

## 3. RESULTS

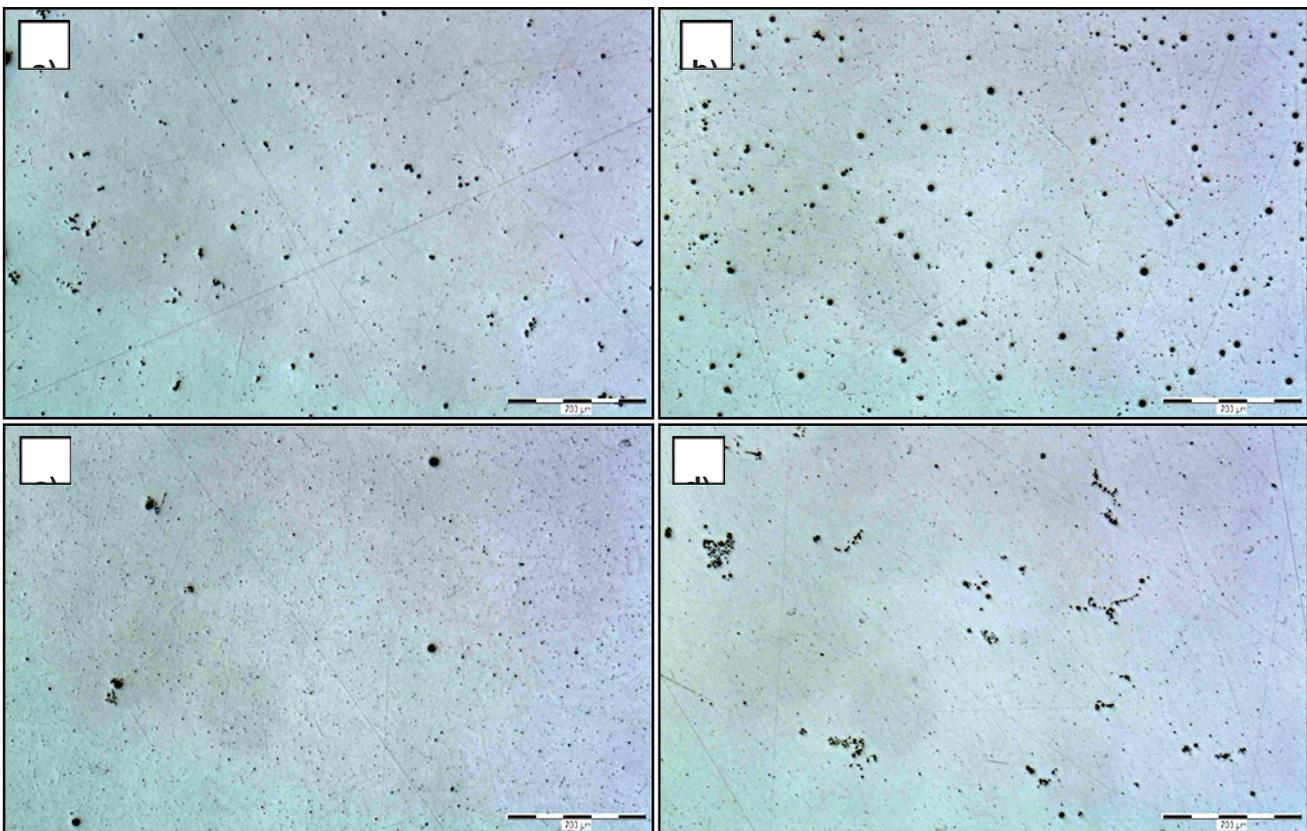
**Table 1** shows the results of chemical analyses; it can be seen that 42CrMo4 steel delivered from VHM had higher contents of carbon, manganese, nickel, molybdenum and copper than the same commercially delivered steel grade from the Ferona company.

The samples were taken from the upper and bottom parts of the castings. **Fig. 1** documents inclusions in the castings. There is a higher occurrence of the inclusions in the bottom part of the castings. The inclusions are distributed in the volume of the castings quite uniformly. In the cerium-alloyed sample, inclusions of larger dimensions occurred particularly in the upper part of the casting - **Fig. 1c**), than in the sample unalloyed with cerium - **Fig. 1a**), or local clusters of smaller oxide and oxide-sulphide inclusions were formed - **Fig. 1d**).

**Table 1** Chemical analysis of 42CrMo4 steel - OES SpectromaxX, GDOES (weight %)

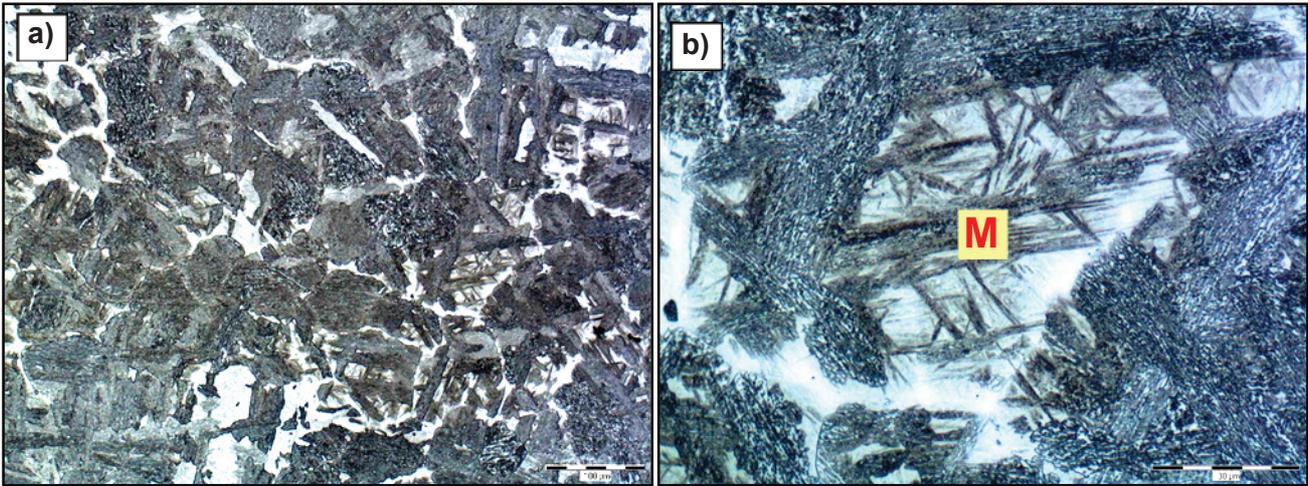
Steel	C	Mn	Si	Ni	Cr	Mo	Al	S	P	O	N	Cu	Co
VHM	0.526	0.86	0.279	0.150	1.08	0.257	0.023	0.0052	0.0073			0.120	0.014
Ferona	0.45	0.69	0.277	0.042	1.07	0.195	0.026	0.009	0.0082	<0.001	0.0063	0.028	0.0098
Casting	0.439	0.68	0.277	0.035	1.07	0.194	0.047	0.012	0.011	0.0042	0.0057	0.029	0.0071

Steel	Ti	Nb	V	Mg	B	Sn	As	Bi	Zr	Ce	Fe
VHM	0.0033	<0.004	0.0052	0.0031	0.0016	0.011	0.0109	0.0098	0.0016	<0.002	96.6
Ferona	0.002	<0.004	0.0036	0.0031	0.0015	0.0043	0.0055	0.0085	<0.0015	<0.002	97.2
Casting	0.0025	0.0054	0.0044	0.0031	0.0020	0.0033	0.0066	0.011	0.0021	0.045	97.1

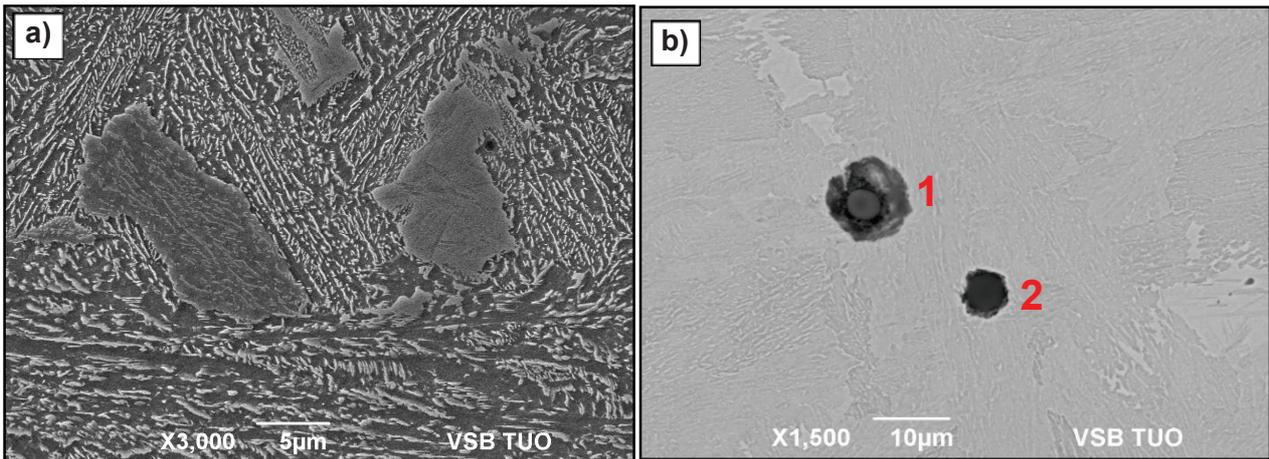


**Fig. 1** Microstructure of 42CrMo4 steel (Ferona) after melting and centrifugal casting into graphite mould. State: after polishing, non-etched. **Fig. 1a) and 1b)** without cerium, **Fig. 1c) and 1d)** with cerium addition. On the left: top part of the casts, on the right: bottom part of the casts (rod Ø 20 mm). Scale: 700 µm

The microstructure of the 42CrMo4 steel (Ferona) after casting is mainly bainitic (a matrix) with a certain proportion of martensite (marked with a letter **M** in **Fig. 2** in light areas, where laths and needles growing inwards the grain and generally orientated can be visible. Both of these phases were also confirmed by microhardness testing. At 0.05 kg load, light areas of martensite exhibited hardness ranging between 692 - 888 HV, bainite had hardness ranging between 341 - 416 HV. In this sample structure, presence of oxide-sulphide inclusions of MnS and FeS, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> was found - inclusion 1 in **Fig. 3b**). In area 2, there were oxide inclusions of Al<sub>2</sub>O<sub>3</sub>, CaO, MgO and SiO<sub>2</sub>.



**Fig. 2** Baititic - martensite microstructure of 42CrMo4 steel (Feronia) after casting into graphite mould. State: Etched. Scale: **Fig. 2a**) - 100 μm, **Fig. 2b**) - 30 μm. M - martensite

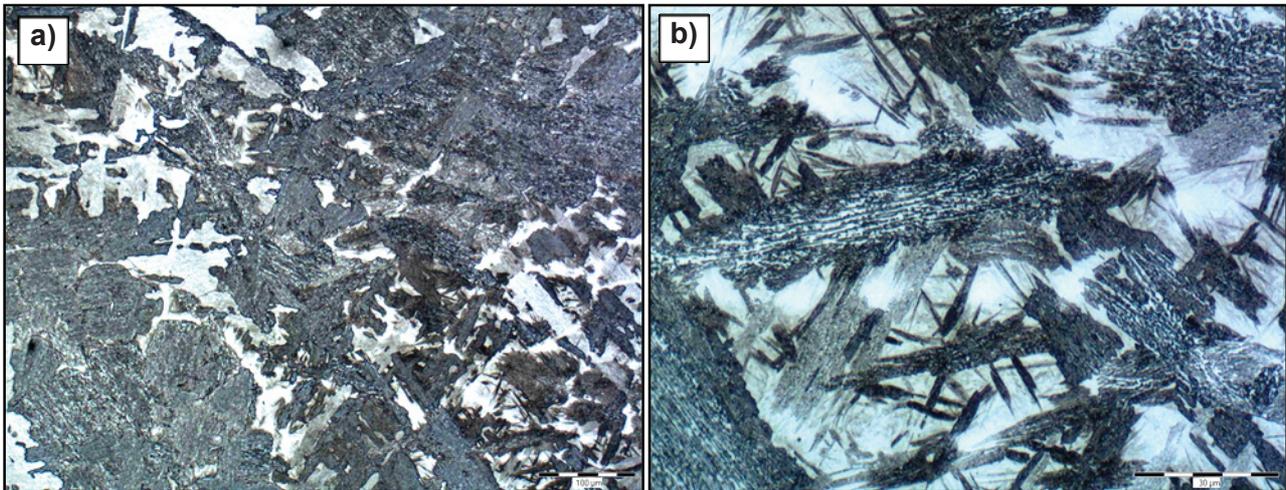


**Fig. 3** Baititic microstructure of 42CrMo4 after melting and casting. a) SEI, b) BEI/EDX - two inclusions

**Table 2** EDX chemical microanalysis of the matrix and inclusions (atomic %)

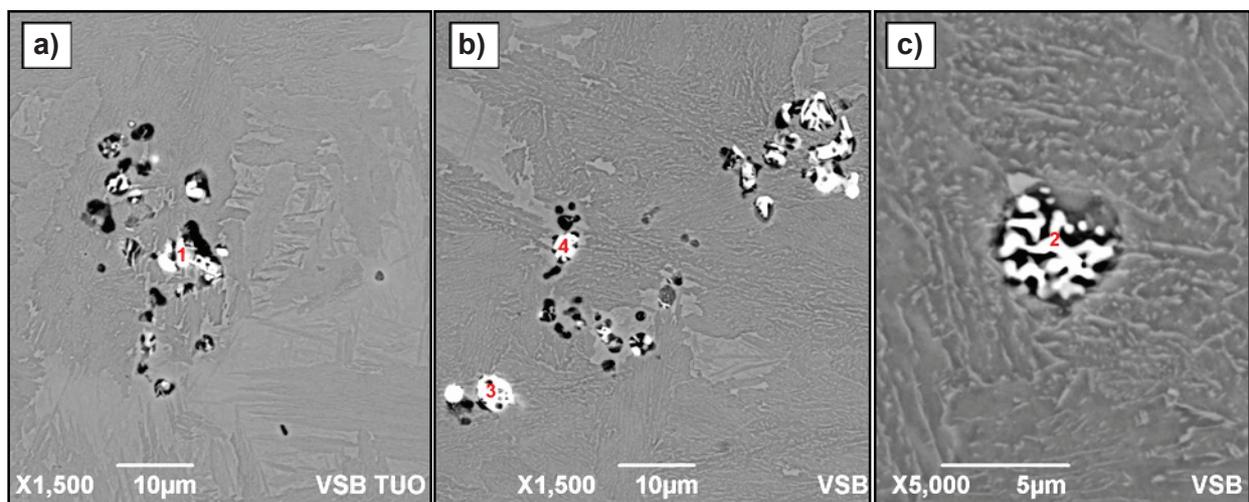
Name	O	Mg	Al	Si	S	Ca	Cr	Mn	Fe
Matrix				1.13			1.51	0.82	96.54
Inclusion 1	26.04		1.67	0.64	28.69		2.12	22.69	18.15
Inclusion 2	65.37	0.61	23.34	0.46	0.21	8.55			1.47

Optical microscopy of the cerium alloyed sample found also a multi-phase structure with prevailing bainite occurrence and minor content of martensite. Martensite needles and laths with a mutual orientation towards each other occurred inside the grains - **Fig. 4**. Martensite was confirmed by micro-hardness testing (648 - 755 HV), too.



**Fig. 4** Microstructure of 42CrMo4 (Feron) with pure cerium addition (0.05 wt. % Ce) after melting and centrifugal casting (top part of the cast). State: after etching. Scale: a) 100 µm, b) 30 µm

Clusters of inclusions as well as isolated inclusions were found in the structure - see **Fig. 5** X-ray EDX microanalysis (see **Table 3**) of the sample micro-alloyed with pure cerium proved uniquely the occurrence of oxide-sulphide inclusions, which were chemically bound with cerium. The size of these inclusions ranged between 1 up to 5 µm. An interaction between cerium, oxygen and sulphur occurred unambiguously.



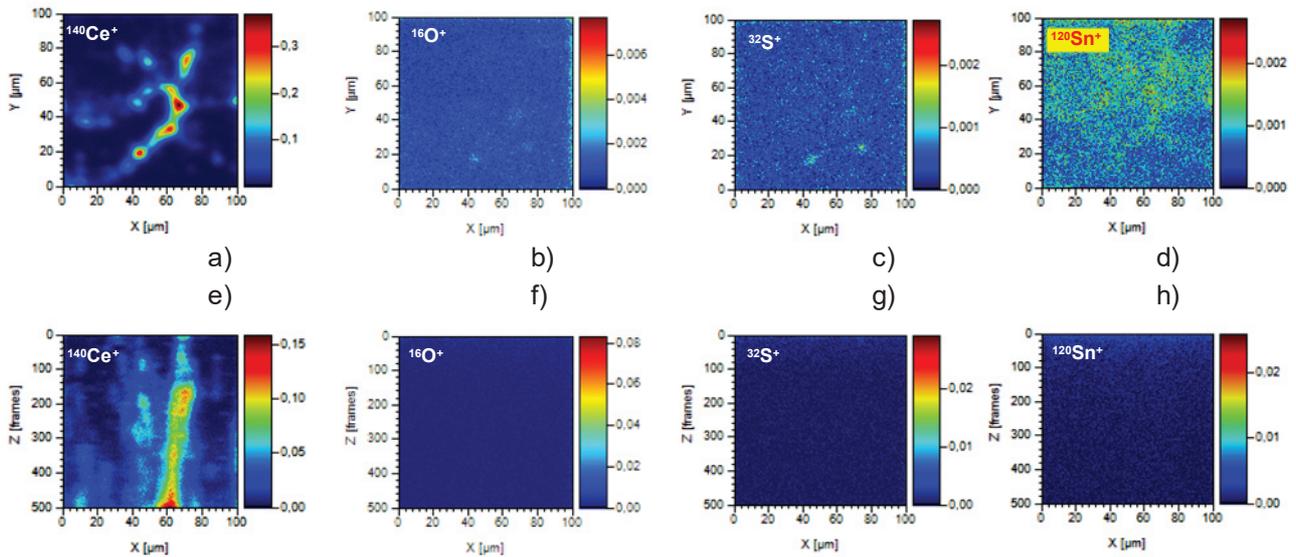
**Fig. 5** BEI/EDX inclusions microstructure analyses of the 42CrMo4 steel with pure cerium addition (0.05 wt. %) after centrifugal casting in the induction furnace- top part of the casting (see **Table 3**)

**Table 3** EDX chemical microanalysis of inclusions in the 42CrMo4 steel with Ce addition (atomic %)

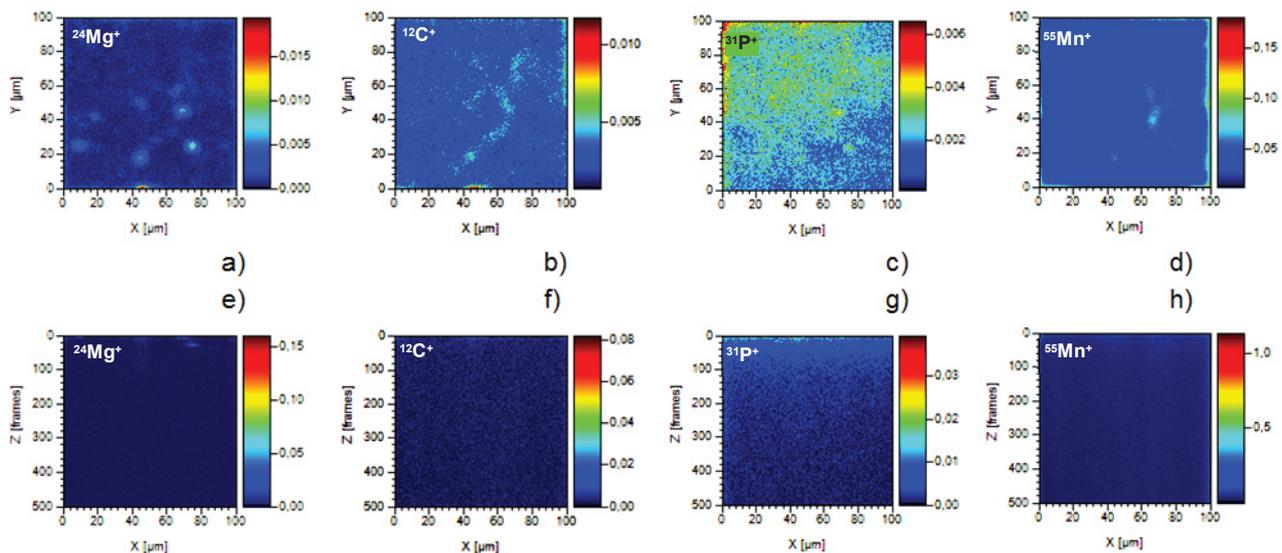
Name	O	Al	S	Ca	Fe	Ce
Inclusion 1	42.38		16.73	1.62	8.40	30.86
Inclusion 2	28.94	1.20	10.22		41.33	18.32
Inclusion 3	32.95		25.66	6.57	7.32	27.50
Inclusion 4		1.57	36.15	8.84	9.27	44.17

### 3.1. Scanning electron microscopy of steel samples

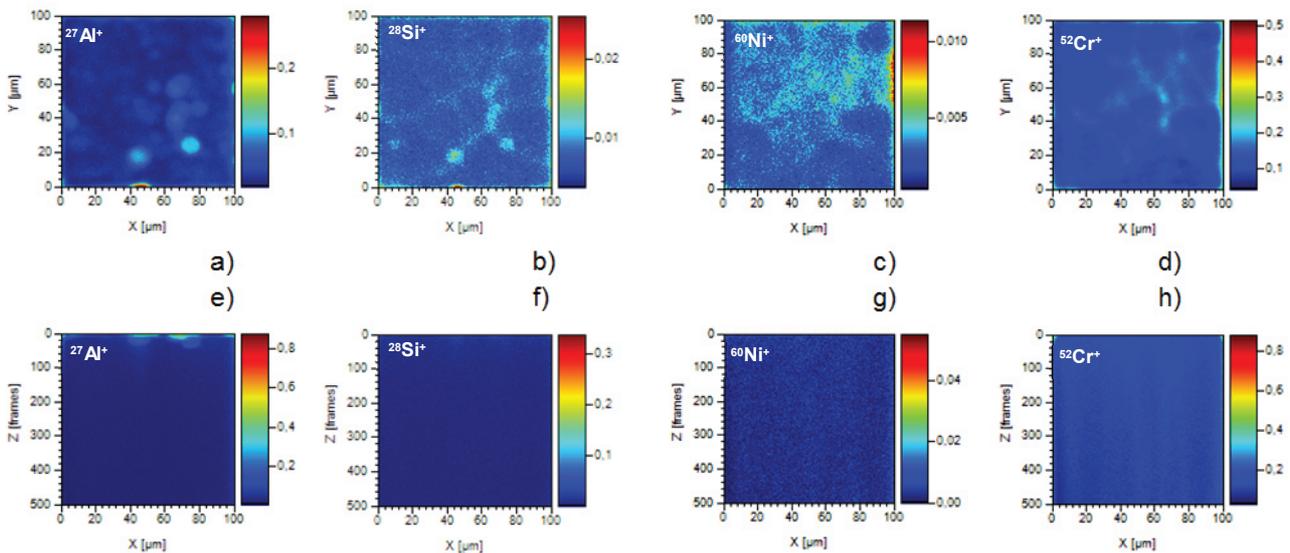
Scanning Electron Microscope (SEM) with Focused Ion Beam (FIB) and Time-of-Flight Secondary Ion Mass Spectrometry (SIMS) was used to obtain element distribution (a map) in the samples of 42CrMo4 steel (VHM); this enabled mapping of particular elements through sequential sputtering of the sample surface using a focused ion beam, while ionizing a part of the material. Testing was performed in cooperation with TESCAN ORSAY HOLDING, a.s., Brno. Three samples of steels microalloyed with mischmetal in a concentration of 1 wt. % were measured using TOF-SIMS on the FERA system, which was equipped with a source of Xe<sup>+</sup> ions. The analyses were focused above all on cerium detection, which should bind O, S, P, Sn, Sb and Mg. As for Sb and As elements, a very low signal was detected. Further, mapping of other elements was carried out, above all Mn, Si, Al, Ni, Cr and Mo - see **Figs. 6 to 9**.



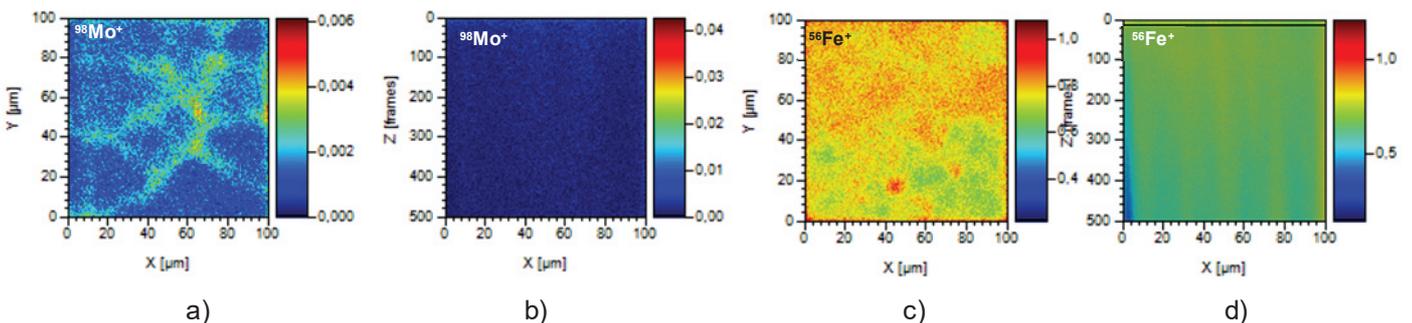
**Fig. 6** SEM and TOF-SIMS analysis - 3D mapping of Ce, O, S and Sn in 42CrMo4 steel after melting with Ce addition. **Fig. 6a) to 6d)** mapping from above, **Fig. 6e) to 6h)** mapping from lateral edge



**Fig. 7** SEM and TOF-SIMS analysis - 3D mapping of Mg, C, P and Mn in 42CrMo4 steel after melting with Ce addition. **Fig. 7a) to 7d)** mapping from above, **Fig. 7e) to 7h)** mapping from lateral edge



**Fig. 8** SEM and TOF-SIMS analysis - 3D mapping of Al, Si, Ni and Cr in 42CrMo4 steel after melting with Ce addition. **Fig. 7a) to 7d)** mapping from above, **Fig. 7 e) to 7h)** mapping from lateral edge



**Fig. 9** SEM and TOF-SIMS analysis - 3D mapping of Mo and Fe in 42CrMo4 steel after melting with Ce addition. **Fig. 9a) and 9c)** mapping from above, **Fig. 9b) and 9d)** mapping from lateral edge

The results from mapping the elements in 42CrMo4 steel using SEM proved, that the presence of cerium and other observed elements in the structure, their distribution and concentration, could be identified quite reliably. The analysis provided the required information for a small limited volume of a sample only, this is a time consuming process.

#### 4. CONCLUSION

The samples of 42CrMo4 steel were remelted in an induction furnace in an inert argon atmosphere at decreased pressure with subsequent centrifugal casting into a graphite crucible with a cylindrical opening of 20 mm diameter and 225 mm length. The samples were cast without alloying, another sample was alloyed with pure cerium with a concentration of 0.05 wt. %. It was found out through metallographical and SEM/EDX analyses that the structure was bainitic with minor proportion of martensite. Oxide-sulphide inclusions were identified in the structure, whereas higher occurrence was observed in the bottom part of the casting. The cerium addition favourably affected formation of small oxide-sulphide inclusions, binding chemically with them afterwards. There were no significant changes observed in the steel structure after the cerium addition after casting.

The results of mapping of elements using SEM proved that the cerium distribution in the volume is not uniform. Cerium occurs in certain localities, which penetrate inwards the sample along the direction of crystallization. Phosphorus and sulphur concentration was higher near the sample surface than inside the main volume. Other elements, such as Mo, Mn, Cr, Ni, Si, were distributed relatively homogeneously inside the sample volume.

## ACKNOWLEDGEMENTS

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