METABK 55(4) 757-760 (2016)
UDC – UDK 669.1:546.3:620.17:620.18=111

INFLUENCE OF SELECTED RARE EARTH METALS ON STRUCTURAL CHARACTERISTICS OF 42CrMo4 STEEL

Received – Prispjelo: 2015-11-06
Accepted – Prihvaćeno: 2016-03-30
Preliminary Note – Prethodno priopćenje

The influence of rare earth metals (REM) addition on solidification structure of the low-carbon 42CrMo4 steel was investigated. Alloys were prepared by means of a centrifugal casting. The addition of cerium, praseodymium or mischmetal in the steel produced greatly improved solidification structure with a suppressed columnar grain zone, finer grain size in the equiaxed grain zone. The additions occurred in the steel bath in the form of REM oxide and/or oxide-sulphide inclusions and as dissolved REM segregated along with other elements at prior grain boundaries and interdendritic spaces. Microstructure (light microscope), SEM/EDX chemical microanalysis, and TOF-SIMS analysis – mapping of elements in the structure of alloys were obtained.

Key words: Low-carbon 42CrMo4 steel, rare earth metals, centrifugal casting, structure, inclusions

INTRODUCTION

The improvement of quality and utility properties of large forgings intended for heavy-duty use can be achieved by addition of non-ferrous metal alloys in the form of so-called mischmetal during steel production, leading to refinement of the microstructure of produced steel ingots, which are subsequently forged. The microstructure refinement, or grain refinement, has a large influence on the resulting mechanical properties of steel. Besides the typical alloying elements (e.g. Ti, Nb…) [1, 2], the selected non-ferrous metals include also rare-earth metals (REM). Just a small amount is enough for the grain refinement and structure modification.

The fine-grained structure in steels can be achieved by application of EGR (Elkem Grain Refiner) based on cerium, in some case by using Ce + La based mischmetal [3-5]. This process was applied on a laboratory scale with pilot equipment and also in casting ingots of a weight of 2 [6] to 5 tons, possibly in 10 t continuous casting. An influence of deoxidation of medium-carbon steel microalloyed by cerium on the morphology of sulphide inclusions and mechanical properties of the steel is also well known [7].

The results [8] on the grain refinement of fully austenitic stainless steels using Fe-Cr-Si-Ce pre-alloy are interesting. A substantial reduction of the dendritic arm spacing was achieved due to formation of Ce-Al oxide inclusions in the liquid steel before solidification. Another experience [9] ensued from experiments with low-alloyed steel, when ferrite nucleation on cerium sulphide inclusions occurred.

The advancement in the development and application of the grain refinement using cerium sulphide and titanium compounds in carbon steels is described in [10]. The inclusions (dispersoids) are usual oxides, sulphides, nitrides, phosphides and carbides of metals, most frequently titanium and cerium. Alloys for the grain refinement, containing cerium as a reactive element, are commercially available already and can be used as a substitute for mischmetal and strengthen the effectiveness of inclusions and nucleation with regard to the austenite and ferrite morphology in steels. A reasonable rate of REM content in steels in industry is between 0,2 to 0,5 wt. %.

Effect of cerium sulphide particle dispersions on acicular ferrite microstructure development in steels is described in [11]. Effect of REM on mechanical properties of low alloyed steel can be found in [12].

Influence of cerium, praseodymium and mischmetall on the formation of oxide-sulphide inclusions and segregation of elements in 42CrMo4 steel castings has been investigated in this paper.

MATERIALS AND EXPERIMENT

The commercial steel 42CrMo4 was used in the form of a rod with 35 mm diameter as an input material. Thin foils of 0,1 mm thickness, dimensions of 25 x 25 mm of pure cerium, pure praseodymium (Alfa Aesar, Germany - 3N purity) and mischmetal were used for microalloying. Melting was carried out in a medium-frequency furnace SuperCast with centrifugal casting in vacuum or Ar inert atmosphere. The samples were melt-

J. Drápala, S. Brožová, I. Szurman, K. Konečná, G. Kostiuková, J. Vontorová, VŠB – Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Czech Republic.
P. Jonšta, Vitkovice Heavy Machinery, a.s., Ostrava – Vítkovice, Czech Republic.
K. Sobotková, Tescan Orsay Holding, a.s., Brno, Czech Republic.

ed 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 or praseodymium addition was put into a turned-out hole in one of the cylinders so that it could be completely melted and dissolved homogenously 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 1 550 °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 cooled down for a period of one hour. The castings were in a form of rods of 225 mm length, 20 mm diameter, and with a conical extension on the inlet into the mould.

In our research 42CrMo4 low-carbon steel was selected – see Table 1.

Table 1 **Chemical composition of 42CrMo4 steel / wt. %**

C	Mn	Si	Ni	Cr	Mo	Al	S	P
0,44	0,68	0,28	0,036	1,07	0,19	0,024	0,01	0,012
Cu	Co	V	Mg	Sn	As	Bi	Ca	Fe
0,027	0,024	0,04	0,0026	0,034	0,0066	0,0072	0,0011	Bal.

Table 2 **Chemical composition of cored wire filled with mischmetal steel / wt. %**

C	Ce	Cr	Si	Fe
0,10	12,23	33,18	21,5	Balance

RESULTS AND DISCUSSION

Microstructure analyses

The samples were taken from the upper and bottom parts of the castings. Figure 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.

The microstructure of the 42CrMo4 steel after casting contained mainly acicular ferrite (AF) – see Figure 2 as a matrix with a certain proportion of martensite (M).

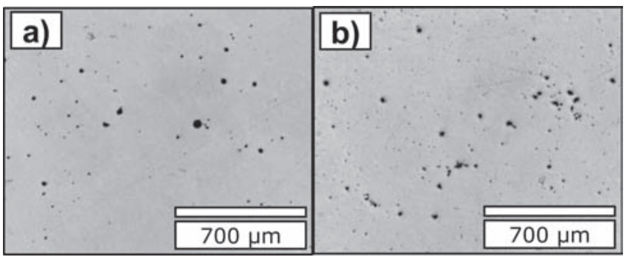

Figure 1 Microstructure of 42CrMo4 steel (without REM) after melting and casting. State: polished, non-etched (Light Microscope - LM). a) top part, b) bottom part of the casting with inclusions

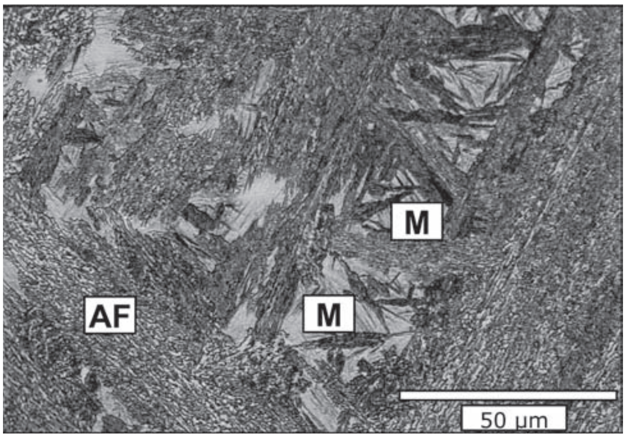

Figure 2 Microstructure of 42CrMo4 steel (with mischmetal) after etching (LM). State: as cast. M – martensite, AF – acicular ferrite

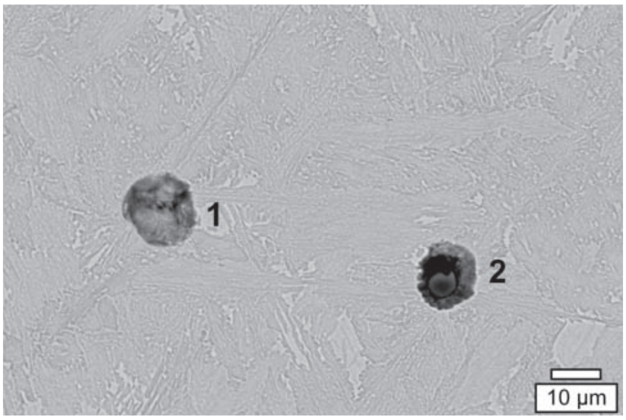

Figure 3 Microstructure of 42CrMo4 steel (without REM). State: as cast. a) acicular ferrite (Secondary Electron Imaging - SEI), b) two inclusions (Backscattered Electron Imaging/ Energy Dispersive X-ray Spectroscopy - BEI/EDX)

Table 3 **Chemical microanalysis of inclusions – see Figure 2 b) / at. %**

	O	Mg	Al	Si	S	Ca	Cr	Mn	Fe
1	26,04		1,67	0,64	28,7		2,1	22,7	18,2
2	62,86	1,20	23,55	0,54	0,25	10,8			0,79

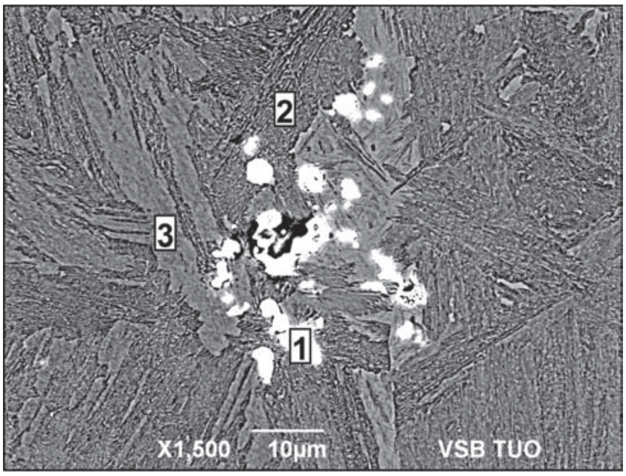

Figure 4 Microstructure of 42CrMo4 steel (with mischmetal), Scanning Electron Microscopy - SEM/EDX. 1 – inclusions, 2 – AF, 3 - M

Table 4 **Chemical microanalysis (EDX) – see Figure 4 / at. %**

Element	O	Si	S	Ca	Cr	Mn	Fe	Mo	Ce
Area 1	42,2		19,85	4,2			6,78		27,2
Area 2		0,98			1,35	0,70	97,0	0,16	
Area 3		1,43			3,28		94,6	1,69	

Both of these phases were also confirmed by microhardness testing. At 0,5 N load, light areas of martensite exhibited hardness ranging between 692 – 888 $HV_{0,5}$, AF had hardness ranging between 341 – 416 $HV_{0,5}$. In this sample structure, the presence of inclusions of MnS and FeS, FeO, Al_2O_3 and SiO_2 was found – inclusion 1 in Figure 3. In area 2, there were oxide inclusions of Al_2O_3, CaO, MgO and SiO_2.

Figure 4 shows SEM/EDX analysis images of the 42CrMo4 steel casting microalloyed with mischmetal The inclusions are dispersed unevenly in the structure and they are usually smaller than 5 µm.

TOF-SIMS analysis

Measurements on the Reflection electron microscope/Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) with the Schottky auto-emission cathode were performed in Tescan Orsay Holding in order to observe the micro-segregation of particular elements present in the studied steel. The distribution of the particular elements in the structure in a defined limited amount of samples was mapped through a gradual ion milling of 300 layers (c. 4 µm) from the area of 100 x 100 µm. The attention was focused above all on localities with REM containing inclusions.

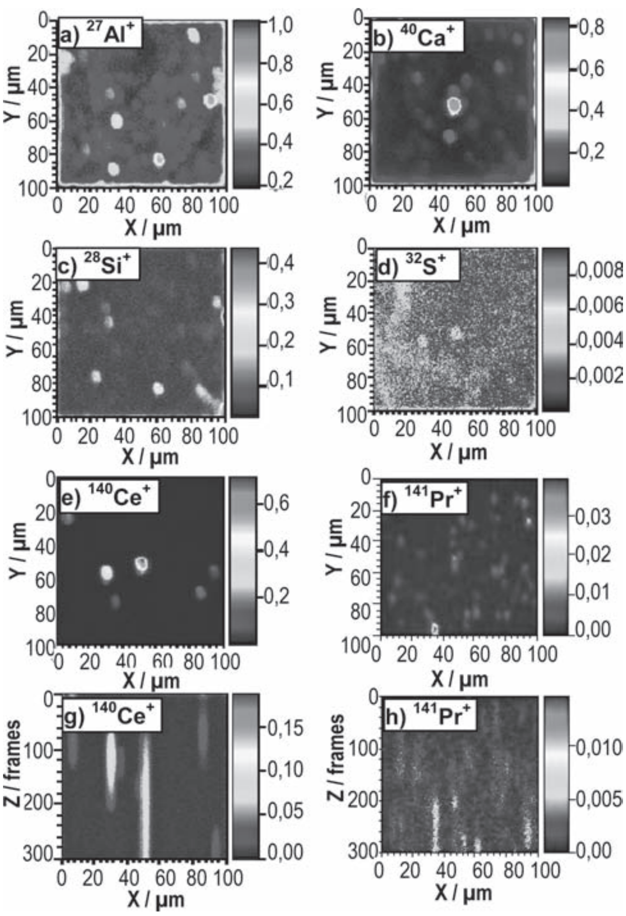

Figure 5 Maps of the selected elements Al, Si, P, S, Ca, Cr, Ce and Pr in 42CrMo4 steel castings (100 x 100 µm area); a) – h) top view on the analyzed sample; i) and j) side view on the analyzed sample. For the side view, the signal was integrated from 60 milled layers for Al from 80 layers for Si from 300 layers for P, S, Ca, Cr, Ce and Pr.

Table 5 **Chemical microanalysis (EDX) of areas with acicular ferrite (AF) and martensite (M) / wt. %**

Element	Si	Cr	Mn	Fe	Mo
AF	0,41	1,17	0,64	97,54	0,28
M	0,68	2,49	1,45	93,29	1,88

Table 6 **Average values of the chemical composition of particular types of inclusions in the structure (SEM/EDX analysis) / at. %, RE = Ce, Pr**

	N	O	Al	Si	S	Ca	Cr	Mn	Fe	As	RE
A		39,6			18,3	3,2			12,2		27,2
B		48,2	3,6	0,4	1,05				28,5		17,1
C		16,3		0,7	0,26		0,8	1,1	57,3	9,3	7,6
D	22,2	11,8		0,6	1,0				38,6		25,8
E							2,1	1,3	96,6		

An absolute total concentration of elements was not determined, because this is an inhomogenous sample. According to the colour scale in the maps of elements the number of the elements in the defined measuring point can be estimated - see Figure 5.

Following the statistical evaluation, the SEM/EDX analyses have imply that in the martensite area the enrichment of elements in comparison with AF area occurred, namely 0,27 % for Si, 1,32 % for Cr, 0,51 % for Mn and 1,6 for Mo / wt. % - see Table 5.

Five different types of inclusions were found in the structure of samples – see Table 6.

In type A inclusions the oxygen content was about 40 at. %, sulphur about 18 at. %, and REM about 27 at. %. Moreover, calcium and iron were present here. The chemical composition of the observed phases was as follows: $(Ce,Pr)_2O_2S$ + FeO + CaS. Type B inclusions contained Al_2O_3 + SiO_2 oxides in addition, the sulphur content was low (c. 1 at. %), calcium was not present, Fe content was about 28 at. %. In some of the observed inclusions (C type), antimony (0,7 at. %) and phosphorus (6 at.%) were found in addition. In this case, there is a complicated interaction between Fe, Si, Cr, Mn and Ce with O, As, P, Sb and S elements. A high nitrogen content was observed in tiny inclusions (D type), which showed evidence of the presence of cerium nitride (CeN) and iron nitride. Further, oxygen was also present in a form of cerium and iron oxides. Tiny E type inclusions presented Fe and Cr carbides.

Oxide inclusions Al_2O_3, SiO_2, Cr_2O_3, resp. $(Fe\text{-}Cr)_xO_y$, and MnS sulphide were identified in the structure of the initial 45CrMo4 steel as a result of the REM/SIMS analysis. Following REM alloying, cerium or praseodymium oxide-sulphides were uniquely identified in the structure; they were not spherical shaped, as expected, but the inclusions appeared as elongated cylindrical formations oriented parallel with the casting axis – see Figure 5 i) and 5 j). The used REM/SIMS method is sensitive enough for identification of many elements, which can be visible in colour maps of individual elements.

CONCLUSION

The results of laboratory melting experiments with subsequent centrifugal casting of 42CrMo4 steel samples are described. SEM/EDX as well as REM/SIMS analysis unambiguously showed occurrence of oxide-sulphide inclusions of approximate composition corresponding stoichiometrically to the formula RE_2O_2S (RE = Ce, Pr). Then, an interaction between cerium, or praseodymium, and oxygen and sulphur occurred defninitely. Sizes of these inclusions ranged from 1 to 5 μm, which were minimally half-sized compared to 42CrMo4 steel without REM micro-alloying.

The found out findings were applied in operational conditions in Vitkovice Heavy Machinery company in four melts and production of ingots of a weight as high as 24 t.

Acknowledgement

This work was solved within the frame of the project TA CR No. TA03010161: „Experimental development of non-ferrous metals utilization for microstructure refinement in the production of steel ingots for forgings in the specific work” and the project No. LO1203: „Regional Materials Science and Technology Centre – Feasibility Program”.

REFERENCES

[1] C. Eijk, O. Grong, F. Haakonsen, L. Kolbeisen, G. Tranell, Progress in the development and use of grain refiner based on cerium sulfide or titanium compound for carbon steel. ISIJ International 49 (2009) 7, 1046-1050.

[2] O. Grong, L. Kolbeisen, C. Eijk, G. Tranell, Microstructure control of steels through dispersoid metallurgy using novel grain refining alloys. ISIJ International 46 (2006) 6, 824-831.

[3] E. S. Dahle, Grain refinement of high alloyed steel with cerium addition. Master Thesis, Department of Materials Science and Engineering, Norwegian University of Science and Technology. Trondheim, 2011. 68 p.

[4] M., Anderrson, J. Janis, et al., Grain size control in steel by means of dispersed non-metallic inclusion – GRAINCONT. Final report. European Commision „Research Fund for Coal and Steel“, 2011, Brussels, Belgium. 132 p.

[5] C. Eijk, INGROS project. Final technical report. SINTEF Materials Technology, Trondheim, Norway, 2004, 77 p.

[6] J. Kasińska, Wide – ranging influence of mischmetal on properties of G17CrMo5-5 cast steel. Metalurgija 54 (2015) 1, 135-138.

[7] M. Guo, H. Suito, Influence of dissolved cerium and primary inclusion particles of Ce_2O_3 and CeS on solidification behavior of Fe-0.20 mass % C – 0.20 mass % P alloy. ISIJ International 39 (1999) 7, 722-729.

[8] J. Appelberg, K. Nakajima, H. Shibata, A. Tilliander, P. Jönsson, In situ of mischmetal particle behaviour on a molten stainless steel surface. Materials Science and Engineering A, 495 (2008), 330-334.

[9] H. L. Liu, Ch. J. Liu, M. F. Jiang, Effect of rare earths on impact toughness of a low-carbon steel. Materials and Design 33 (2012), 306-312.

[10] T. Kasuya, Exchange interactions in rare earth compounds. Journal of Alloys and Compounds 192 (1993), 11-16.

[11] G. Thespis, Effect of cerium sulphide particle dispersions on acicular ferrite microstructure development in steels. Materials Science and Technology 22 (2006) 2, 153-166.

[12] C. Kronholz, O. Depierreux, N. Slomski, K. Richter, H. Dewenter, Effect of rare earth elements in steel and determination of properties by comparing standard and new methods. International Conference COMAT, Plzeň, Czech Republic, 2012, 5 p., on CD ROM.

Note: The paper was translated by Zdeňka Kunčická, Metal Translations, Lipník nad Bečvou, Czech Republic