The influence of additives of lanthanum hexaboride nanoparticles on the cast structure of high-chromium steel of austenitic and martensitic classes

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Abstract. The paper presents the results of studying the influence of lanthanum hexaboride, modified with nanosized powder, on the cast structure of martensitic and austenitic steel, aluminium and silicon killed. A study was carried out on high-chromium steel 08H18N12 and 10H9MFB. As the addition, there were used compressed tablets containing different amounts of nanosized powder of lanthanum hexaboride and carbonyl iron. The conducted research allowed to conclude that the use of lanthanum hexaboride atomizes the dendritic structure of high-chromium steel of martensitic and austenitic classes. Furthermore, it is established that lanthanum hexaboride can be an effective means of introducing boron into high-chromium steel, including nitrogen-containing one. In addition to the above, lanthanum hexaboride actively interacts with sulfur and thus forms primary lanthanum sulphides which are the substrate for forming complex oxysulphides.

1. Introduction

High-chromium steel has gained wide application as a corrosion- and heat-resistant material or as a high-impact material for critical structures if being alloyed with nitrogen.

All compositions of high-chromium steel are actually characterized by an oversize grain which not only prevents the ultrasonic control but also reduces its mechanical properties. It is obvious that the finite grain size in austenitic steel is associated with the as-cast grain size due to the lack of phase transformations, and in martensitic steel, it is associated with structural heredity when direct and reverse martensitic transformations occur. Therefore, austenitic and martensitic steel needs modification that ensures atomization of as-cast grains - dendrites. In particular, modification with rare-earth metals.

Modification with rare-earth metals is widely investigated [1-8] and provides great opportunities to improve the structure and properties of steel and, in particular, it affects the processes of subsequent machine processing [9, 10]. Modification of steels with boron and lanthanum compounds attracts special interest but the influence of boron-lanthanum compounds is currently rather little investigated. At the same time, preliminary calculations showed that such a compound as lanthanum hexaboride

(LaB6) should become a rather strong modifier of the first order already at the introduction of the 0.15% substance due to reducing the surface tension of steel. The objective of this work was to study the influence of the cast structure modification with lanthanum hexaboride, the compound which is new to metallurgy.

2. Materials and methods

This paper refers to charge materials of high-chromium steel 08H18N12 and 10H9MFB as raw materials. For modification, there were used compact tablets of 12 mm in diameter and of 6-8 mm in height, containing nanosized powder of lanthanum hexaboride, which was obtained through mechanical dispersion, as well as micron-sized carbonyl iron powder.

The smelting of experimental samples was carried out in the Tamann furnace with corundum crucibles of 80 ml in volume. After melting the charge material, weighed about 400, with deoxidant additives and reaching the temperature of 1600 °C, modifier portions were added into metal on the alundum tube. After the 10-minute equalizing the furnace was turned off and metal solidified in a crucible. The ingot was cut into samples for analysing the macro - and microstructure, chemical content, non-metallic inclusions.

We studied 6 ingots (3 samples per each type of steel) with the estimated boron content of 0% (samples A0 and M0), 0.05% (samples A1 and M1) and 0.1% (samples A3 and M3).

The obtained samples were used to produce transverse and longitudinal polished sections with the help of a Buehler bench-top abrasive cutting machine with the Buehler H-R/Al2O abrasive disk. Grinding and polishing samples were carried out with the Buehler Phoenix 4000 machine.

Quantitative and qualitative analyses of non-metallic inclusions and structural components were conducted with the use of the Axiovert 200 MAT motorized optical microscope equipped with the Thixomet image analyzer. Non-metallic inclusions in the samples were analyzed by ASTM E1245.

3. The results of experimental studies and their discussion

The first phase of studying the obtained samples of modified steel included the study of their chemical composition. Table 1 shows the results of analysing the chemical composition of melted austenitic and martensitic steel ingots.

Table 1. Chemical composition of the initial steels and the results of analysing the chemical composition of the samples

	C,%	Cr,%	Ni,%	Mn,%	Si,%	B,%	La,%	N,%	Al,%
Martensitic steel charge material	0.09	9.3	0	0.41				0.044	0.03
M0	0.169	9.05	0.023	0.308	0.168	0.0009	0	0.044	0.042
M1	0.132	8.67	0.214	0.257	0.269	0.018	0.0016	0.042	0.061
M3	0.147	8.74	0.023	0.267	0.276	0.043	0.0022		0.045
Austenitic steel charge material	0.07	19.5	11.5	1.1				0.044	0.044
A0	0.058	17.27	12.02	1.16	0.423	0.0011	0.0026	0.26	0.063
A1	0.076	16.76	11.76	1.13	0.433	0.015	0.0025	0.28	0.086
A3	0.083	16.76	11.82	1.01	0.55	0.047	0.0025	0.24	0.1

The comparison of the chemical composition of the steel samples with the charge material showed that boron-addition of the lanthanum hexaboride of 0.05% provided the content of boron equal to 0.018% (recovery of 36%), and the boron-addition of 0.1% led to the boron content of 0.043% (recovery of 43%) in martensitic steel. Adding lanthanum hexaboride of 0.05% to austenitic steel

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increased the boron content up to 0.015% (recovery of 30%) and adding 0.1% increases the boron content up to 0.047% (recovery of 47%), which indicates a good recovery of boron from lanthanum hexaboride both in martensitic and austenitic steel. It is necessary to draw attention to the big difference in nitrogen content in martensitic and austenitic steel and high content of aluminium and silicon in both steels, providing low activity of oxygen and nitrogen.

Regardless of the steel composition, the content of aluminium and silicon, the size of the investigated modifier additive, the chemical analysis showed almost a complete absence of lanthanum in the metal of all ingots with lanthanum hexaboride additives. Poor recovery of lanthanum from LaB_6 is possibly due to the high degree of LaB_6 powder dispersion.

The influence of hexaboride on the non-metallic phase is quite noticeable. Introduction of LaB_6 has significantly increased the volume fraction of the non-metallic phase, the size of the inclusions and reduced the distance between the inclusions, which indicates a significant increase in the density of the inclusions. The volume fraction of non-metallic inclusions in austenitic steel samples increased by 0.1% and 0.15%, which roughly corresponds to the increase in the boron weight fraction by 0.05-0.1% in that case if the modification product is boron nitride.

All studied samples contain aluminium oxides. However, the oxides of silicon, manganese and chromium are contained mainly in the austenitic steel in which the content of these elements is 2-3 times higher than in martensitic steel. The boron nitrides, like lanthanum sulphides, are present only in the modified steel ingots. In this case, lanthanum sulphides in complex oxysulfides are found in the axes of dendrites, and manganese sulphides - in interaxial spaces.

A more detailed qualitative analysis was carried out using electron microprobe analysis (EMPA). The two samples most contaminated with non-metallic inclusions were investigated: M3 and A3. This analysis confirmed the presence of oxides, sulphides, oxysulphides in the M3 sample, and also revealed the presence of vanadium nitrides and a group of carbides. The A3 sample revealed the presence of silicates, oxides and oxysulphides.

Figure 1 presents the results of inclusions EMPA in the sample A3. There were found the oxides of aluminium, aluminium and chrome, sulphide-coated manganese, complex inclusions BN-(Cr, Mn, Al)$_m$O$_n$, complex oxides of Al, Si, Mn, Cr with and without lanthanum sulphides. The location of complex inclusions BN-(Cr, Mn, Al)$_m$O$_n$ (Fig. 1) in the axes of dendrites deserves attention rather than on interdendritic borders. The chemical composition of the studied inclusions is given in Table 2.
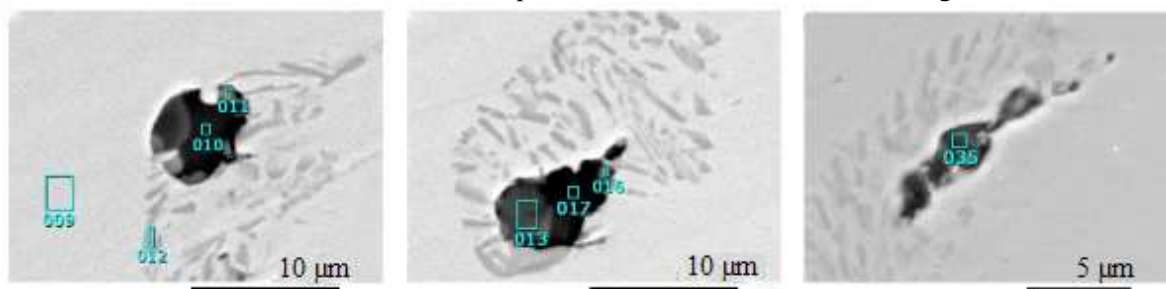

Figure 1. The result of a micro-X-ray spectral analysis of BN-(Cr, Mn, Al)$_m$O$_n$ complex inclusions in a sample of austenitic steel with a calculated boron content of 0.1%

Table 2. The chemical composition of BN-(Cr, Mn, Al)$_m$O$_n$ complex inclusions in a sample of austenitic steel with a calculated boron content of 0.1%

#	O,%	Al,%	Si,%	S,%	Cr,%	Mn,%	Fe,%	Ni,%	Mo,%	B,%	N,%	Ti,%
009					20.9		66.7	12.4				
010	48.1	8.20	7.13	1.60	3.55	28.09	3.31					
011	9.73		1.37	19.6	8.54	41.04	17.5	2.17				
012					35.9	1.56	53.1	7.49	1.94			

#												
013	44.97	18.0	0.45	0.37	12.8	22.48						0.89
016	13.78		1.44	14.41	7.77	36.21	14.07	1.67				
017	19.44	1.33	0.77	0.61	5.65	5.58	4.99	0.46	10.65	35.05	26.11	
035			0.10		5.47		15.9	2.39		42.20	33.94	

Similar inclusions are found in the M3 ingot: the oxides of aluminium, chromium, silicon, but non-metallic phases are characterized by niobium borides, especially at boundaries and tripoints (Fig. 3). The chemical composition of the M3 sample inclusions is given in Table 4.
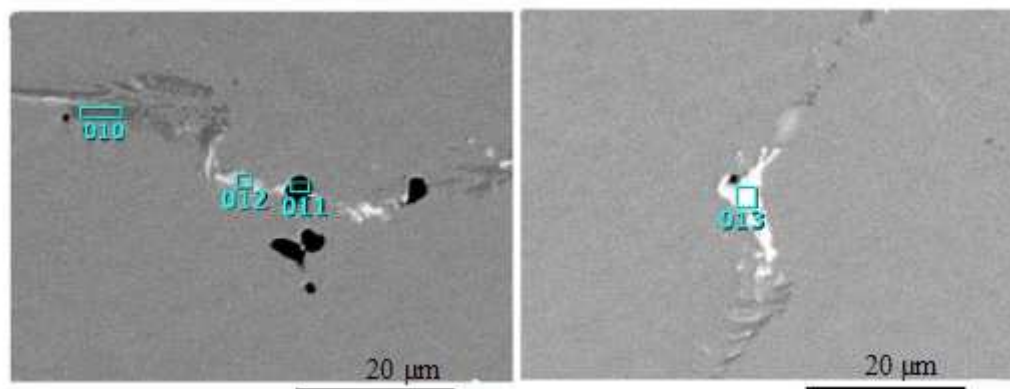

Figure 2. The result of a micro-X-ray spectral analysis of non-metallic inclusions in a sample of martensitic steel with a calculated boron content of 0.1%

Table 3. The chemical composition of non-metallic inclusions in the martensitic steel sample with the estimated boron content of 0.1%.

#	B,%	O,%	Al,%	V,%	Cr,%	Fe,%	Nb,%	Mo,%	Ti,%
010				0.78	33.02	62.55		3.64	
011		42.78	39.38		2.16	13.41	2.27		
012	33.49			0.54	5.67	41.81	18.49		
013	31.79				1.11	3.97	60.75		2.38

Analysis of the macrostructure showed that smelted ingots express in in different degrees all typical crystallization areas: columnar, close-grained different-oriented dendrites. Comparing the area of the zones of differently oriented dendrites in the austenitic steel samples revealed that the introduction of lanthanum hexaboride greatly enlarges this area. The martensitic steel sample with the same content of lanthanum hexaboride has a structure which is similar to the 'cone of deposition'. These changes are probably connected with the fact that lanthanum oxysulphide plays the role of germ and disordered dendrites crystallize thereon and form characteristic structures of the deposition cone or zones of differently oriented dendrites while interacting with advancing solidification fronts.

Hexaboride additives in martensitic and austenitic steel have not noticeably affected the area of the columnar dendrites but expand the zone of differently oriented dendrites of the 'cone of deposition' and atomize the grain in these zones (Fig. 3).
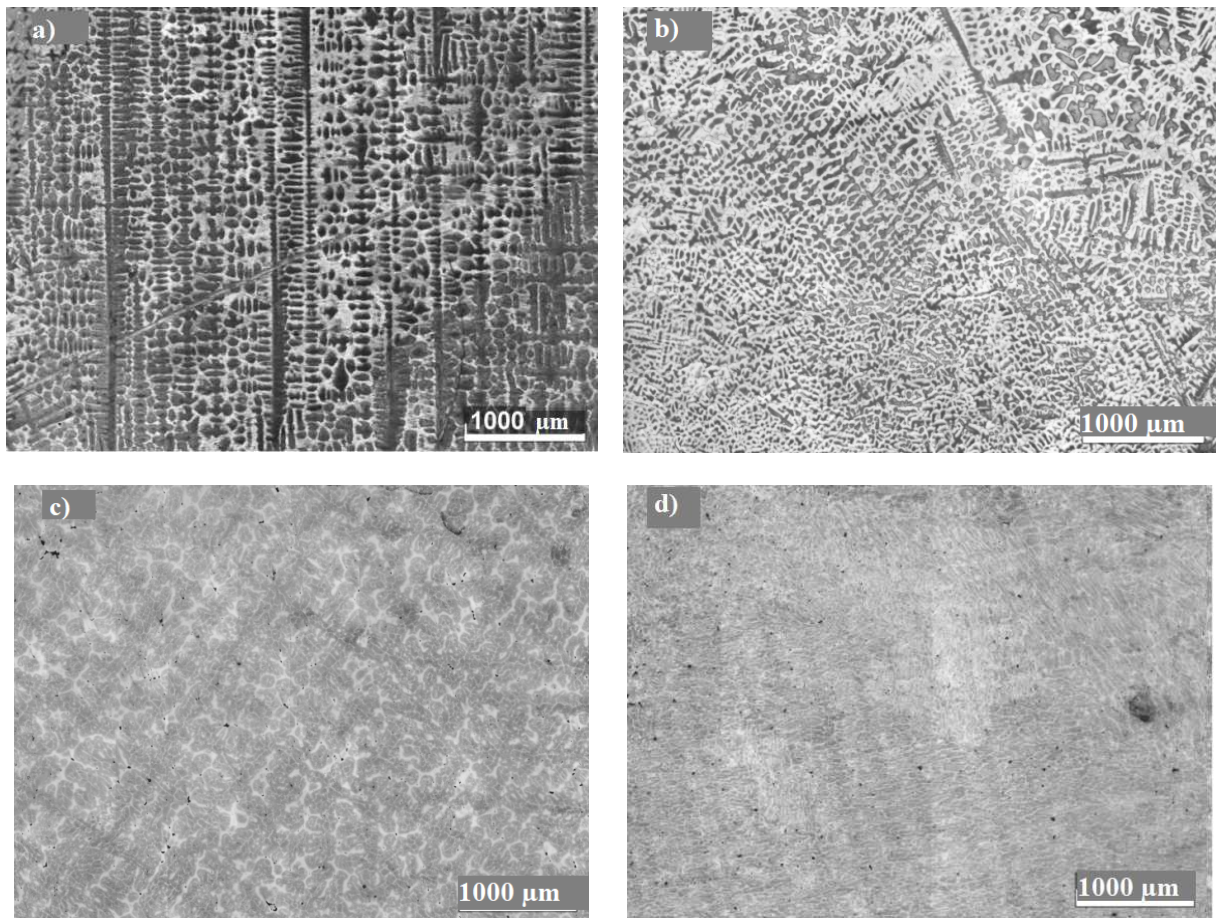
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Figure 3. The structure of samples of austenitic steel with a calculated boron content of 0% (a), 0.1% (b) and martensitic steel samples with a calculated boron content of 0% (c), 0.1% (d)

Measurement of interaxial distances in cast grains (dendrites) has shown some reduction of values from 200 µm in the A0 sample to 120 µm in the A3 sample when comparing ingots, comparable in composition, deoxidant content, conditions of melting and solidification. Similar dynamics is observed in the samples of martensitic steel: 200 µm in the M0 sample and 100 µm in the M3 sample. It is obvious that the boron concentration of 0.015-0.047 %, as a modifier of the 1st order, atomizes the dendrite structure by reducing the surface tension. Our early works [11] showed that the introduction of rare earth metals into the liquid metal leads to forming not only columnar but also differently oriented dendrites, the axes of which include sulphides and REM oxysulphides that lead to the abnormal distribution of sulfur in the ingot: sulfur-rich 'cone of deposition', sulfur-depleted area pipe and off-center segregation. Thus, the clusters of REM oxysulphides can be captured by the growing dendrites and form rough macrodefects in the ingots periphery.

We can assume that the atoms of dissolved lanthanum form oxides and sulphides in molten steel in the conditions that are fundamentally different from the interaction of deoxidants and desulphurizers, injected in the form of a powder or introduced into steel in the form of a wire. Usually, the particles (drops, bubbles) of aluminium, REM or calcium are surrounded with zones supersaturated with a reactant and discontinuity of the liquid metal, being places of origin for new phases – the products of deoxidation and desulphurization. When introducing, dissipating and dissolving nanoparticles, the selection of the new phase becomes possible only on the natural boundaries of the liquid metal with a coating, slag and gas bubbles. It seems that such conditions drastically reduce not only the probability

of desulphurization and deoxidation of liquid metal but modification of the 2nd order with the use of the reaction products as substrates for nucleation of crystallization centres.

In view of the small size of the crucible, the zone of lanthanum supersaturation near the surface of dissolving tablets is comparable to the size of a metal bath, and to identify the oxide phase it is enough to find discontinuity of the liquid metal caused by the dissolving particles of carbonyl iron. Removal of oxides having a high melting point occurs before solidification starts. Lanthanum and manganese sulphides are formed during solidification and sulphides and oxysulphides are not removed, but lanthanum sulphides are formed during the dendrite axes formation, and manganese sulphides appear in interaxial spaces which affects their distribution.

4. Conclusion

The use of lanthanum hexaboride atomizes the dendritic structure of high-chromium steel of martensitic and austenitic classes.

Lanthanum hexaboride in the form of nanoparticles can be an effective means of introducing boron into high-chromium steel, including nitrogen-containing one.

Boron nitride is a component part of primary complex inclusions which are located in the axes of dendrites. The introduction of boron in the form of lanthanum hexaboride can prevent the formation of the tertiary boron nitrides which are usually located along the boundaries of high-chromium steel dendrites.

Lanthanum hexaboride actively interacts with sulfur and thus forms primary lanthanum sulphides which are the substrate for forming complex oxysulphides. The process of desulphurization was not observed due to the small sizes of the crucible and the high rate of solidification.

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