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INVESTIGATION OF EFFECT OF MODIFICATION BY RARE-EARTH METALS ON QUANTITY AND MORPHOLOGY OF NON-METALLIC INCLUSIONS OF ELECTRIC SLAG COKE CASTINGS MADE OF STEEL H11

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ABSTRACT

Improving the physical and mechanical properties of castings from alloyed steels and alloys is achieved in various ways, such as: increasing the purity of metal by non-metallic inclusions, creating favorable crystallization conditions that affect the formation of macro and microstructure, reducing the development of liquation processes, etc. Currently, high-energy processes, including electroslag technologies, are widely used. Application of this technology makes it possible to significantly improve quality of steels due to reduction of content of harmful impurities as a result of refining action of slag in process of electrode remelting, besides, it performs protective function in process of metal remelting and pouring into mold. After overflowing the metal from the crucible into the shape, the flux accumulates in the upper part of the casting and acts as a thermal extension, which has a favorable effect on the crystallization process. The purpose of this work is to study the physical and chemical processes that occur during the interaction of harmful impurities - sulfur, phosphorus and oxygen, with components that are part of slag and with rare earth metals, which are modifiers, as well as to study the effect of the amount, morphology and distribution of non-metallic inclusions on the mechanical properties of castings from steel H11 when using electric slag coke casting. In the course of the work, based on the calculated reactions, the influence of Ca and Al on the desulfurization, dephosphorization and deoxidation of steel, as well as the effect of rare earth metals on the formation of sulfide, oxysulfide and phosphide compounds, which are prone to the formation of large conglomerates, which contributed to their accelerated surfacing in the upper part of the casting and, as a result, to a decrease in the total number of non-metallic inclusions in steel. The number of non-metallic inclusions in the modified steel decreases by more than 4 times compared to the non-modified steel, and the toughness increases from 0,20 to 0,32–0,30 MDzh/m^2.

Keywords: electroslag technology, non-metallic inclusions, modification, mechanical properties.

INTRODUCTION

Currently, high-energy processes are widely used, including electric slag technologies, the use of which allows to significantly improve the quality of steels by reducing the content of harmful impurities as a result of the refining effect of slag in the process of remelting the electrode. In addition, slag performs a protective function in the process of remelting and pouring metal into the mold. After overflowing the metal from the crucible into the shape, the flux accumulates in the upper part of the casting and acts as a thermal extension, which has a favorable effect on the crystallization process. Improvement of physical and mechanical properties of castings from alloyed steels and alloys is achieved in various ways, such as: improvement of metal purity by non-metallic inclusions, creation of favorable crystallization conditions affecting formation of macro and microstructure, reduction of development of liquation processes, etc. [1, 2]. One of the ways to improve the quality of steel castings is the use of electroslag technology. This paper considers the possibility of reducing the content of non-metallic inclusions, changing their morphology and distribution in castings made of steel H11 in the process of electroslag chill casting. Therefore, the purpose of this work is to study the physical and chemical processes when introducing rare earth metals into the melt, as well as to study their effect on the structure and properties of castings of steel H11 obtained by electrosmelt chill casting [3, 4]. A further method of improving these characteristics is to refine and modify the melt during melting and pouring it into the mold [5].

MATERIAL AND METHODS

Castings from instrumental steel H11 were obtained by the method of electroshlag chill casting on experimental equipment, which included: an electric holder, a lifting column, a crucible with a rotary device to which a chill, a power source and a control panel were attached. Melting of the consumable electrode was carried out using slag АНФ-295. During melting, the current intensity was 2,5 kA, voltage – 43–50 V.

Studies of the effect of morphology and distribution of non-metallic inclusions on the mechanical properties of steel castings were H11 carried out using the following methods and research equipment:

- metallographic - by electron microscopy using electron microscopes JEOL JSM 7001F, "HITACHI

TM-1000" and optical microscopy using a light microscope "Carl Zeiss Axio Vision";

- Energy dispersion and chemical analysis in a JEOL JSM 7001F raster electron microscope equipped with an Oxford Instruments energy dispersion spectrometer;
- Rockwell hardness analysis and Brinell hardness analysis.

Improvement of physical and mechanical properties of castings from alloyed steels and alloys can be achieved due to application of electric slag technology due to two-stage treatment of melt: in slag bath (1 stage) and in crucible with metal melt (2 stage) [6]. As a result, optimal conditions are created for processes of deoxidation, desulfurization, dephosphorization of steel and reduction of non-metallic inclusions in it.

In the process of electric slag remelting, which is realized due to the gradual melting of the electrode in the slag bath and the passage of the resulting droplets through it, there is a significant decrease in the sulfur content, and a decrease in the phosphorus content due to the presence of calcium oxide in the slag. Melt accumulated in crucible is preliminary deoxidized with aluminium in amount of 0.2% to residual oxygen content of 0,0002–0,0001 % in order to avoid increased consumption of rare-earth metals for this process. Modification and refining are carried out with rare-earth metals in mishmetal composition in amount of 0, 15-0, 20 % [7].

When modifying steel with rare-earth metals, it is necessary to take into account the possibility of formation of refractory compounds between impurities in liquid metal and introduced elements [8].

Liquid metal droplets passing through the slag layer were refined. Desulfurization and dephosphorization of the melt occurred as a result of the presence of calcium compounds in the slag. Since calcium is a strong desulfurate and a dephosphorator, these processes proceeded through the following reactions:

$2Ca + S_2 = 2CaS \quad \Delta G^o = -702\,500 + 193{,}34T$ J/mol
$3Ca + 2P = Ca_3P_2 \quad \Delta G^o = -873\,140 + 433T$ J/mol

It should be borne in mind that the refining properties of the slag reduce the sulfur content several times compared to the electrode to be melted, the amount of phosphorus is reduced to a lesser extent. Under the slag layer, the melt accumulated, gradually filling the crucible. After reaching a given volume of liquid metal 5 minutes before the end of melting, the steel was deoxidized with aluminum to avoid the consumption of rare earth metals for this process. As a result, a reaction occurs, resulting in a significant decrease in the oxygen content of steel:

$4Al + 3O_2 = 2Al_2O_3 \quad \Delta G^o = -426\,700 + 194{,}17T$ J/mol

Upon completion of the deoxidation process, the liquid metal was modified with rare earth metals in the mishmetal composition [9]. In this case, reactions with the main element - Ce, which is part of mishmetal, are considered. The processes of desulfurization and dephosphorization of steel were carried out by the reactions:

$4Ce + 3O_2 = 2Ce_2O_3 \quad \Delta G^o = -913\,150 + 168{,}5\,T$ J/mol
$4Ce+3O_2+2S= 2Ce_2O_3S \quad \Delta G^o = -876\,850+155{,}9\,T$ J/mol
$2Ce + 3S = Ce_2S_3 \quad \Delta G^o = -689\,309 + 145\,T$ J/mol
$2Ce + S_2 = 2CeS \quad \Delta G^o = -516\,930 + 97\,T$ J/mol
$2Ce + P_2 = 2CeP \quad \Delta G^o = -367\,940 + 25{,}43\,T$ J/mol

Based on calculations, it was found that when the modifier is introduced, refractory compounds are formed: oxides, oxysulfides, sulfides, as well as rare earth metal phosphides. These compounds are not wetted with liquid metal, tend to be coarse as a result of their possible collision and the formation of conglomerates. Particles float into a small profitable part of the casting, which is under a layer of slag, thereby cleaning the steel from gases and non-metallic inclusions.

In order to avoid prolonged interaction of the modifier with the slag, since it has high activity, the modifier was introduced through a quartz tube with a diameter of 50 mm and a length of 1 m placed in the molten metal. Uniform distribution of the modifier over the entire volume of the liquid bath was ensured due to the intensive movement of the metal during the remelting process. After the smelting, the crucible turning device was turned on, and liquid steel was poured over together with slag, which was used in the smelting process into a chill. The overflow rate was selected to provide a laminar flow of metal on the surface of which liquid slag is present. In the process of overflow, first of all, slag contacts the chill, this leads to the formation of garnish on the surface of the casting with a thickness of 1.5–2 mm. The remaining slag accumulates at the top of the casting and acts as a thermal extension, which has a favorable effect on the crystallization process. After cooling to 350-300 ° C, casting was removed from the chill and further cooling took place in a sand bath. Such cooling conditions are necessary to reduce the amount of internal stress since steel is H11 martensitic steels.

After such cooling, the hardness of the castings was 400-450 HB, which made mechanical processing difficult. To reduce hardness, annealing was performed according to a conventional mode [10, 11].

The study and evaluation of non-metallic inclusions were carried out on an optical microscope on untwisted microspheres with magnifications × 500 and × 800. At least 15 visual fields on each microslip were viewed. In each field of view, the size of inclusions with an eyepiece-micrometer was measured. Next, the area of each inclusion was determined in ocular scale units. The inclusion areas were summed up in all sample fields of view and the contamination of the sample with non-metallic inclusions was calculated.

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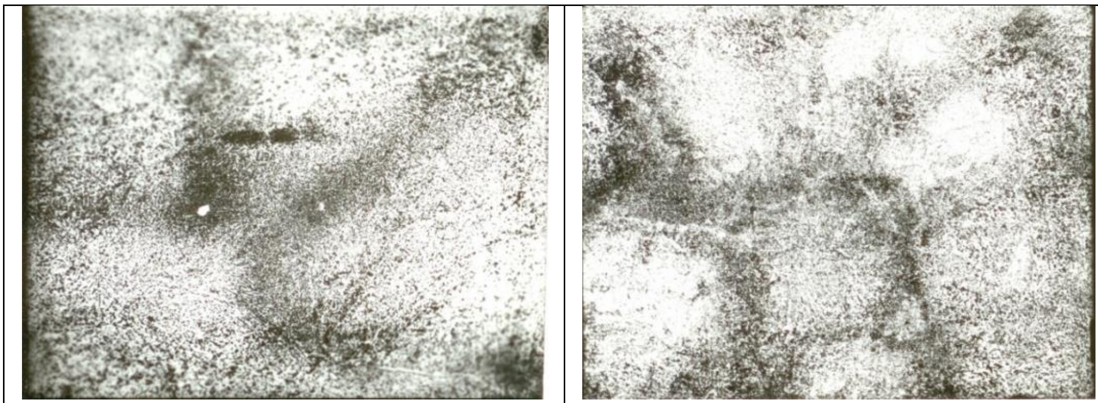
The results of the studies showed that in samples No. 1-3, which were cut from castings obtained without the use of modification, the total contamination with non-metallic inclusions is several times higher than the contamination of samples No. 4-6, in the production of which modification with rare-earth metals as part of michmetal was used (Table-1).

Table-1. Content of non-metallic inclusions and strength properties of steel castings H11 before and after modification.

Processing method	No sample	Percentage of contamination with sulfides and oxysulfides, %	Total percentage of contamination with inclusions, %	Ultimate strength, σ_B, MПa	Impact strength, KCU, MJ/m^2
Without modifyings	1	8,4	9,3	1 325	0,20
	2	6,2	7,4	1 290	0,18
	3	6,5	8,2	1 390	0,22
After modification	4	1,7	2,1	1 630	0,33
	5	1,2	1,6	1 645	0,32
	6	2,0	2,9	1 580	0,30

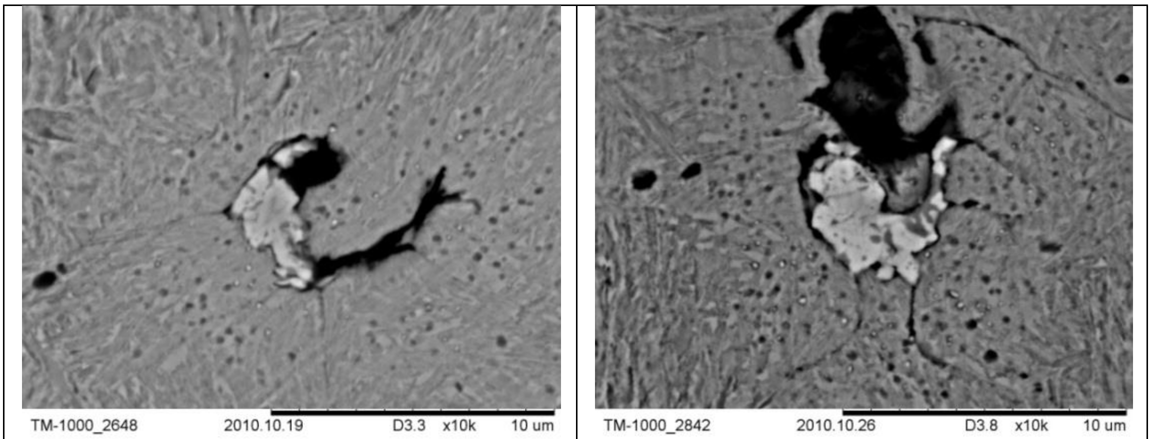
When modifying the melt, grain grinding is observed due to the localization of rare earth elements Ce, Nd, La on the surface of the growing solid phase due to their surface activity (Figure-1).



(a) (b)

Figure-1. Microstructure of tool steel castings after heat treatment: *a* – unmodified, × 400; *b* – modified, × 400.

It can be observed that in unmodified steel there is a large number of large inclusions having an unfavorable form, which in most cases form in interdritic areas (Figure-2) [12].



(a) (b)

Figure-2. Coarse non-metallic inclusions in steel castings H11: *a* – film character, *b* – branched character.

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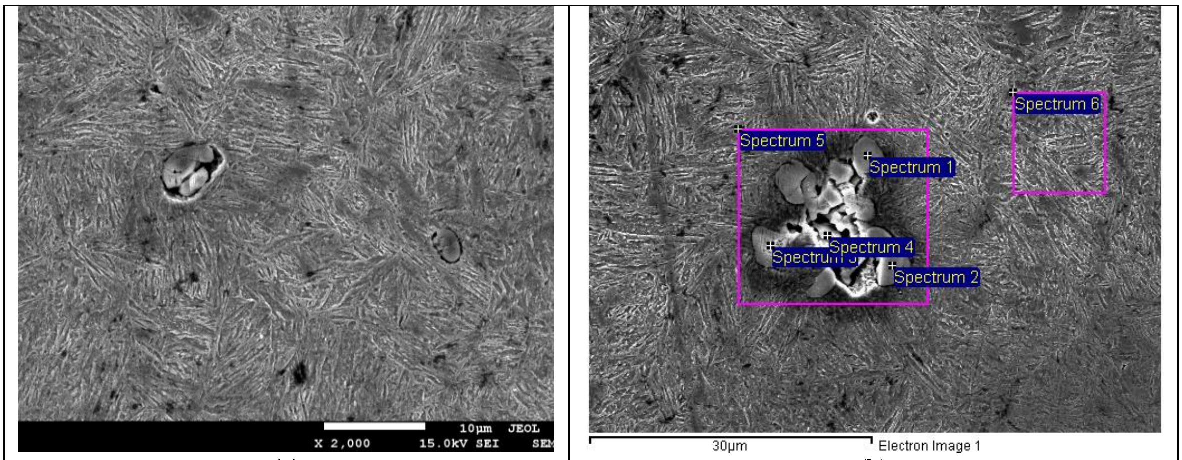
The modification process facilitates the translation of coarse film and branched inclusions into globular oxysulfide formations (Figure-3, a). It should be noted that non-metallic inclusions, due to the lack of wettability, can collide with each other and form large conglomerates, which during the crystallization process float to the surface of the casting, ensuring a decrease in their total content.



(a) (b)

Figure-3. Non-metallic inclusions in steel castings H11 after modification: *a* - globular inclusions, *b* - large conglomerates.

Energy dispersion analysis of non-metallic inclusions indicates a significant content of Ce, Nd, La, O, S in them (Figure-3, *b*; Table-2), which indicates the presence of oxysulfide inclusions, the presence of which was justified based on the calculation of reactions.

Table-2. Chemical composition of non-metallic inclusions.

No range	Chemical composition, %											
	N	**O**	**F**	**Al**	**Si**	**S**	**Cr**	**Fe**	**Ni**	**La**	**Ce**	**Nd**
1	-	11,64	1,48	1,40	-	8,89	-	6,08	0,30	16,78	43,07	10,35
2	10,65	9,08	0,93	11,10	-	7,36	-	1,80	-	14,08	36,96	8,05
3	-	3,00	-	-	0,64	1,23	4,71	86,45	-	-	3,97	-
4	-	3,27	-	-	0,67	1,36	4,52	86,69	-	-	3,49	-
Max.	10,65	11,64	1,48	11,10	0,67	8,89	4,71	86,69	0,30	16,78	43,07	10,35
Min.	10,65	3,00	0,93	1,40	0,64	1,23	4,52	1,80	0,30	14,08	3,49	8.05

It can be clearly observed that the first and second spectra contain a high content of rare earth elements, as well as sulfur, phosphorus and oxygen. This clearly indicates the interaction of rare earth elements with harmful impurities in steel.

When treating steel with rare-earth metals in an amount of 0.15-0.20% according to the calculation, desulfurization and dephosphorization of the melt, grinding of the microstructure, reduction of the total number of non-metallic inclusions, change of their nature, distribution, globalisation and increase of mechanical properties are provided. It is also noted that rare earth metals have a positive effect on the growth rate of primary crystals, thereby grinding the steel structure. All this leads to a significant increase in mechanical properties. So, the time resistance $\sigma_{в}$ increases from 1 350 MPa to 1 640 MPa, and the impact resistance (KCU) from 0,2 to 0,3 MJ/m^2 (samples No. 4-6, Table-1). At the same time, part of rare-earth metals participates in the process of melt refining, and part - in modification.

CONCLUSIONS

In the course of the work on the basis of the calculated reactions, the effects of Ca and Al on the desulfurization, dephosphorization and deoxidation of steel, as well as the effects of rare earth metals on the formation of sulfide, oxysulfide and phosphide compounds in castings of H11 steel obtained using electric sludge coke casting were studied. Analysis of experimental data confirms the correctness of theoretical calculations. It has been found that modification with rare earth metals leads to the formation of sulfide, oxysulfide and phosphide inclusions, which, combining into conglomerates, float into the upper part of the casting, which leads to a decrease in the total number of non-metallic inclusions in

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steel, and the remaining inclusions have a small extent and acquire a globular appearance. The number of non-metallic inclusions in the modified steel is reduced by more than 4 times compared to the non-modified steel. The mechanical properties of steel are significantly increased, since the toughness increases from 0,20 to 0,32–0,30 MDzh/m^2, and the temporary resistance from 1 300 MPa to 1 620 MPa.

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