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Some methods of increasing the density of metal in order to increase him corrosion resistance

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Abstract. Methods to increase the density of metal in order to increase its corrosion resistance in an aggressive environment are examined in the article. Two steel grades, differing in the content of alloying elements, increasing the resistance to corrosion are selected for the manufacture of experimental metallic materials. Two technologies are chosen as methods for increasing the density, and as a result, corrosion resistance, of the experimental materials obtained: the first is electroslag remelting with rotation of the consumable electrode, the second is centrifugal casting with modification. The microstructure of the metal becomes more homogeneous, the degree of metal refining from non-metallic inclusions increases, the rate of crystallization during metal smelting by the ESR method increases with rotation of the consumable electrode. When ingots are produced by the method of centrifugal casting, they are modified with dispersed WC and TiC particles, which increases the crystallization rate, increases the metal density, corrosion and mechanical properties. The evaluation of their corrosion resistance with the help of the autoclaved test complex "Cortest" is made after obtaining ingots by various technologies.

1. Introduction

The problem of the protection of metal structures from corrosion arose with all severity with the discovery and development of oil and gas fields in the composition of the produced fluid which contains hydrogen sulfide, carbon dioxide or their joint presence. About 350.000 km of commercial pipelines are located in Russia in operation, where 20.000 cases of leakage are observed every day, leading to oil losses and environmental pollution. In this case, about 90% of accidents occur due to corrosion damage to pipe material and stop valves. Thus, the problem of providing materials with resistance to corrosion in an aggressive environment is quite relevant today [1]. One of the important criteria is the density of the resulting metal to increase the resistance of metals to corrosion. Of the known technologies of metallurgical production, electroslag remelting (ESR) and centrifugal casting make it possible to produce a metal with an increased metal density index in comparison with other technologies [2-4]. In addition, a number of properties, including the density of the metal, can be increased by carrying out the ESR, by using the technology of rotating the consumable electrode [5]. The main layer acting on the metal during casting with centrifugal casting is the centrifugal force, which exceeds tens of times the gravity of the metal being poured. In the casting, a dense, fine-grained metal structure without porosity is created thanks to this [4]. An increase in the density and fine-grainedness of the metal produced by this technology can be achieved by the dispersive hardening of the crystallizing melt by refractory particles [6, 7]. These methods of increasing the density of metal using known technologies of metallurgical production were taken by the authors as a basis in this work.

2. Carrying out experiments to obtain ingots using the ESR method

The production of solid ingots using the ESR method using classical technology and technology with rotation of the consumable electrode was performed on the upgraded A-550 unit. For remelting, electrodes were used from experimental steels No. 1 and No. 2 with a diameter of 40 mm having a length of 1500 mm, the chemical composition of the remelted steels is shown in table 1.

Table 1. Chemical composition of experimental steel grades (wt. %).

	C	P	S	Mn	Si	Ni	Cr	Cu	Mo	W	Ti
No. 1	0.195	0.025	0.003	0.449	0.802	0.247	14.107	0.059	0.022	0.038	0.057
No. 2	0.169	0.031	0.005	0.306	0.624	5.497	33.103	0.086	0.142	0.082	0.389

The electrodes were attached to the movable carriage of the electroslag remelting installation using a collet clamp. After fixing the remelted electrode, current-carrying brushes were pressed against it using springs to provide a larger contact surface. The remelting was carried out in a crystallizer with a diameter of 90 mm.
The flux of ANF-6, whose chemical composition is presented in table 2, was filled in the working space of the water-cooled crystallizer before the start. The flux granules were previously sieved and had a fraction of not more than 3 mm; also the flux was pre-calcined for two hours at 400 ℃ to remove residual moisture from it.

Table 2. Chemical composition of the ANF-6 flux (wt. %).

CaF_2	Al_2O_3	CaO	SiO_2	C	TiO_2	Fe_2O_3	S	P
Basis	25				No more			
	31	8	2.5	0.10	0.05	0.5	0.05	0.02

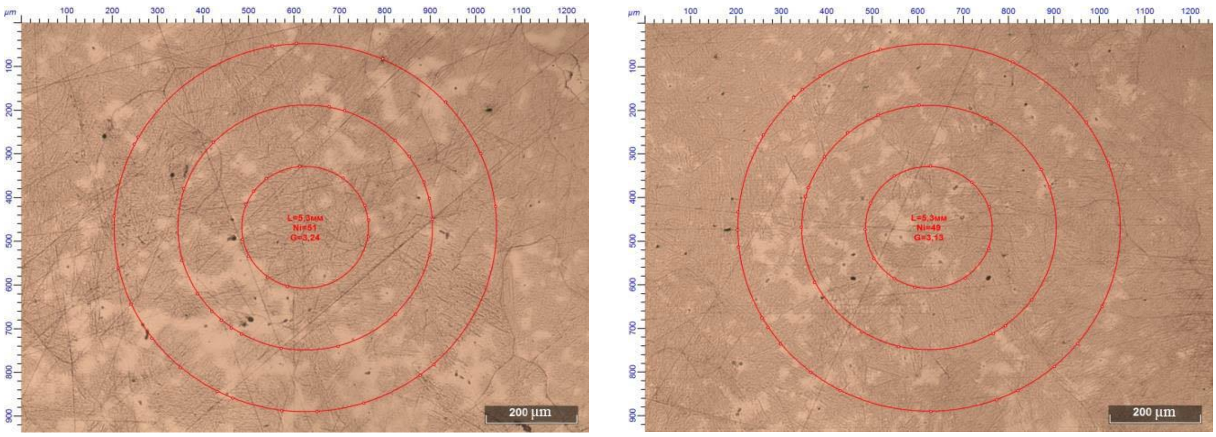
The melting period lasted until the electrode was completely melted down and was 30 minutes. The melted end of the remelted electrode in case of using the classical technology had a conical shape, characteristic for the ESR process. With the use of technology with rotation of the consumable electrode, the beginning of the melting was carried out in a similar way, the rotation started from the moment of formation of the liquid bath. This was evidenced by the absence of current jumps. The rotation speed during the experiments was 100 rpm. Received ingots were given the following marking:
1 - ingot from the experimental grade of steel No. 1, the classical technology of remelting;
2 - ingot from the experimental grade of steel No. 2, the classical technology of remelting;
3 - ingot from the experimental grade of steel No. 1, technology of remelting with rotation of the consumable electrode;
4 - ingot from the experimental grade of steel No. 2, technology of remelting with rotation of the consumable electrode.
Before the extraction of all the ingots obtained, the slag was allowed to cool, and the time for its complete solidification was 8 minutes. After the slag solidified, the ingots were removed from the crystallizer. In all cases ingots had a satisfactory surface quality. Parameters of the obtained ingots of ESR according to different technologies are presented in table 3.

Table 3. Parameters of received ingots of ESR according to different technologies.

	Diameter (mm)	Height (mm)	Weight (kg)
1	90	225	11.27
2		210	10.72
3		230	11.28
4		180	10.47

A study was made of the structure of experimental materials with a microscope for the study of Axio Observer.D1m materials using an image analysis system for solving metallurgical problems and controlling the quality of Thixomet [8]. Examination of samples from experimental ingots of the ESR showed that there are differences in the structure of the ingot microstructures obtained by the classical technology and ingots obtained using the rotation of the consumable electrode. When comparing the structure of the ingot structure from the same experimental grade of steel smelted by different methods (classical technology and rotation of the electrode), it is observed that technology with the use of electrode rotation makes it possible to obtain a structure more uniform and shallower than using classical technology ‘figure 1’.

There are also differences in the structure of the ingot structure from the experimental steel grade No. 1 and No. 2: the structure of the ingot from the experimental steel grade No. 2 when using both melting technologies has a more uniform and fine structure compared to the ingots from the experimental grade No. 2 steel.



(a) (b)

Figure 1. Microstructure of samples obtained by different ESR technologies, ×130: (a) - ingot No. 1, (b) - ingot No. 3.

3. Carrying out experiments on obtaining ingots by the method of centrifugal casting

The experimental steel grade No. 1, whose chemical composition is presented in table 3, was used as the charge materials for experiments on the production of experimental materials. The charge materials were selected in a certain form to ensure maximum filling of the crucible and, as a consequence, to ensure its maximum productivity. The charge was pre-dried at a temperature of 200 ℃ before melting.

Melting of charge materials for the production of cylindrical ingots was carried out in an induction melting furnace SELT-001-40/12-T. The time for complete melting and bringing the liquid melt to the required temperature was 25 minutes. WC and TiC powders having a dimension of 2-4 μm, a density of 15.8 g/cm^3 and 3.21 g/cm^3, respectively, were selected as reinforcing dispersed particles. The crystallization time of the melt in the mould was to be increased in order to ensure an even distribution of the particles over the entire section of the billet, for this, the mould and the poured gutter were preheated to a temperature of 400 ℃, and the temperature of the metal to be filled was 1650 ℃. The launch of a horizontal centrifugal casting plant was carried out after the metal was brought to the optimum discharge temperature and slag removal. The rotational speed of the mould for casting was 700 rpm. The supply of dispersed particles was carried out directly into the mould by a pneumatic metering device. The weight of the metal poured into the mould was 6 kg per ingot.

Five castings were obtained with different concentrations of introduced particles during the run-up of cylindrical ingots from the experimental grade of steel No. 1 with the introduction of dispersed hardening particles. The received markings were given the following marking:

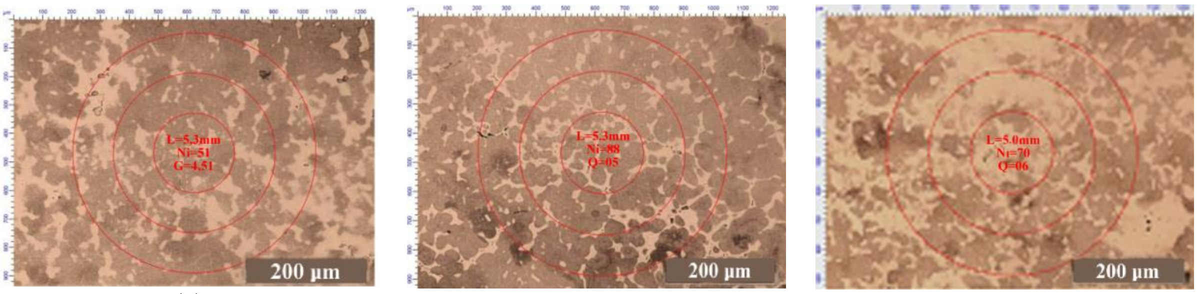
5 - casting without the introduction of dispersed particles (reference sample);
6 - casting with the introduction of WC, concentration - 1 wt. %;
7 - casting with the introduction of TiC, concentration - 1 wt. %;
8 - casting with the introduction of WC, concentration - 2 wt. %;
9 - casting with the introduction of TiC, concentration - 2 wt. %.

The blanks were placed in quartz sand for uniform cooling after the extraction of all the obtained centrifugally cast blanks from the ingot mould. The parameters of the ingots obtained are presented in table 4.

Table 4. Parameters of ingots obtained by the method of centrifugal casting.

	Height of ingot (mm)	Outer diameter (mm)	Inside diameter (mm)	Weight (kg)
5			110	5.69
6			116	5.78
7	65	140	104	5.68
8			106	5.52
9			112	5.65

Examination of samples from ingots obtained by the method of centrifugal casting showed that the introduction of dispersed hardening particles grinds the structure of the metal, making it more uniform, since refractory particles are not soluble in the metal; they are additional centres of crystallization, thereby increasing the rate of solidification of the metal ‘figure 2’. The increase in the grain score does not depend on their composition with an increase in the concentration of introduced dispersed particles.



(a) (b) (c)

Figure 2. Microstructure of samples obtained by centrifugal casting, ×130:
(a) - ingot No.5, (b) - ingot No.6, (c) - ingot No.8.

4. Carrying out works to assess the corrosion resistance of the samples obtained

Samples 4 mm in height, 10 mm in thickness and 40 mm in length were made to conduct work to assess the corrosion resistance of the obtained samples from each ingot using the HONOR SEIKI VL-100CR lathe and carousel. Estimation of corrosion resistance was carried out with the help of the autoclaved test complex "Cortest" in corrosive-aggressive conditions:

- mineralization - 50 g/l;
- pH - 2.5...3;
- partial pressure of CO2 - 3.0 MPa;
- the total pressure - 5.0 MPa;
- test temperature - 120 °C;
- concentration of CO_2 at the beginning / end of the test - 0,086 / 0,055 g/l;

- duration of the test - 120 hours.

Determination of the rate of general corrosion was carried out by gravimetric method in accordance with GOST 9.908 by determining the mass loss of a sample per unit surface during its exposure to an aggressive medium. The data obtained are presented in table 5.

Table 5. Rate of total corrosion of samples from experimental ingots.

Sample marking	Corrosion rate, mm/year
1	0.24
2	0.00
3	0.01
4	0.09
5	0.73
6	0.70
7	0.32
8	1.46
9	0.33

5. Conclusion

The conclusion can be made on the basis of the results obtained, that the most promising method for increasing the metal density in order to increase the corrosion resistance is the ESR technology, while comparing the corrosion rates of the experimental steels Nos. 1 and 2, the data diverge. The experimental grade of steel No. 1 has the best corrosion resistance index when using the ESR technology with the use of the rotated electrode rotation (the corrosion rate of sample No. 3 (0.01 mm/year) is less than sample No. 1 (0.24 mm/year), and the experimental grade steel No. 2 - using classical technology (corrosion rate of sample No. 2 (0.00 mm/year) is less than sample No. 4 (0.09 mm/year).

Cylindrical samples obtained by the method of centrifugal casting with the introduction of hardening particles (samples No. 5-9) have corrosion resistance values lower than ESR ingots. Samples modified with WC tungsten carbide have corrosion resistance values almost equal to the standard (standard 0.73 mm/year, 1% WC - 0.70 mm/year) or less (2% WC - 1.46 mm/year). When the metal is modified with TiC dispersible particles, the corrosion resistance increases: the comparison sample has a value of 0.73 mm/year; the modified samples have 0.32 mm/year (1% TiC) and 0.33 mm/year (2% TiC). It is noteworthy that an increase in the concentration of TiC particles to 2% does not give an additional effect of increasing corrosion resistance.

Thus, according to the work done, it can be concluded that the use of titanium carbide as a modifier in minor amounts allows a more than 2-fold increase in the resistance to corrosion. All experimental samples (except modified with tungsten carbide) have values corresponding to the accepted norm for a number of parts used in the oil and gas industry - 0.5 mm/year.

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