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Experience of Using Complex Modifiers to Increase Corrosion Resistance of Pipe Steels

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Abstract. The article presents the test results of complex microcrystalline modifiers containing calcium, barium, strontium, rare earth metals. Complex modifiers were used in the processing of steel for 17G1S-U pipes in order to reduce its contamination with non-metallic inclusions, including corrosive ones. The use of modifiers allowed to reduce metal contamination by non-metallic inclusions of all kinds. The most experimental non-metallic inclusions were obtained during metal processing with INSTEEL®5.1 and INSTEEL®9.4 modifiers. In addition, the use of experienced modifiers ensured the production of complex oxysulfides of calcium, cerium and lanthanum with low oxygen content and thermal expansion coefficients, which increases the corrosion resistance of steel.

Introduction

Increased corrosion resistance requirements are made modern pipe grades. One of the main reasons for the low corrosion resistance in aqueous media of many types of metal products is the increased contamination of steels with non-metallic inclusions (NMI) containing calcium in the form of an oxide or sulfide component [1-11]. These NMI are called corrosion-active non-metallic inclusions (CANMI). The rate of local corrosion of the metal increases with an increase in the density of CANMI in the metal and, accordingly, the service life of the pipelines decreases. Thus, an increase of CANMI in steel from 2 to 5-10 pcs/mm^2 leads to an increase of the local corrosion rate of oil field pipelines from 0.5 to 10 mm/year or more [1-3]. The permissible content of CANMI is not more than 2 pcs/mm^2 of microsection area for metal products with increased requirements for corrosion resistance. This particle content does not lead to an abnormal acceleration of corrosion processes.

The technology for the production of rolled steel at Ural Steel JSC does not provide the conditions for the production of metal with a regulated level of CANMI, the amount of which varies from 1 to 6 pcs/mm^2.

The aim of the work

The aim of this work is to develop a set of technological recommendations for the production of steel with a reduced content of metal contamination by CANMI (less than 2 pcs/mm^2) through the use of complex microcrystalline modifiers manufactured by NPP Technology LTD.

Methods and materials

A promising direction for improving the quality of metal products is the use of complex alloys containing calcium, barium, strontium and rare-earth metals (REM) [9, 12-21] for the modification of NMI.

A series of experimental-industrial trials was implemented using INSTEEL® complex modifiers (NPP Technology LTD production) to develop an effective steel production technology with a regulated level of CANMI.

The experiments were carried out on steel melts grade 17G1S-U. Steel modification was carried out after vacuum treatment on comparative melts with SC40 grade silicocalcium, and on experimental melts a wire with fillers was used:

- INSTEEL®1.5 (Ca+Ba)
- INSTEEL®9.4 (Ca+Ba+Sr)
- INSTEEL®5.1 (Ca+P3M)
- INSTEEL®10.1 (Ca+Ba+Sr+REM).

During the experiments, samples were taken and their contamination of the metal with NMI was evaluated, microspectral analysis of sheet metal was carried out.

Results and Discussion

The Industrial experiments on steel production using INSTEEL® complex modifiers in the form of flux-cored wire were carried out during September-October 2018 in the electric steelmaking shop of Ural Steel JSC. The analysis of production data on experimental and comparative melts showed that their secondary metallurgy processing and steel teeming passed without remark. The table 1 shows the summary technological parameters of steel modification and the results of calculating the absorption of calcium by metal.

Table 1. Averaged parameters and steel modification results

Parameter		Melting parameter values with modifiers				
		CK40	INSTEEL® 1.5	INSTEEL® 9.4.	INSTEEL® 5.1	INSTEEL® 10.1
Metal yield. t		125.85	123.71	118.89	114.45	133.24
Basicity of ladle slag		2.54	2.09	2.15	2.43	2.51
FeO content in ladle slag. %		0.77	1.04	0.84	0.80	0.65
Temperature before modification. °C		1558	1560	1562	1556	1560
Composition before modification. %	C	0.09	0.08	0.08	0.082	0.090
	S	0.004	0.004	0.003	0.008	0.007
	Al	0.026	0.015	0.029	0.033	0.028
	Ca	0.0007	< 0.0005	0.0006	0.0006	<0.0005
After modification. %	C	0.09	0.08	0.08	0.085	0.087
	S	0.003	0.003	0.002	0.005	0.005
	Al	0.036	0.039	0.042	0.044	0.037
	Ca	0.0015	0.0009	0.0014	0.0012	0.0016
Modifier consumption (by filling). kg	CK40	38.11	-	-	-	18.20
	INSTEEL	-	50.27	38.06	50.69	50.88
Calcium introduced. kg		15.24	15.33	7.88	5.68	14.56
The time from the introduction of the modifier to the start of steel teeming. min		30.5	36.0	37.0	31.00	32.50
Calcium absorption. %		7.10	3.64	12.53	12.16	11.44

Statistical analysis of the results showed that the absorption of calcium is determined mainly by the initial oxidation of the steel (estimated by the aluminum content in the steel) and ladle holding time. Additional factors affecting the absorption of calcium by the metal may be the basicity of ladle slag and its oxidation.

An increase in calcium absorption (in comparison with standard technology) was obtained in cases of metal processing with INSTEEL®9.4. INSTEEL®5.1 and INSTEEL®10.1. respectively. by

76.5. 71.3 and 61.1% rel. The use of INSTEEL®1.5 did not cause an increase in the absorption of calcium in comparison with SC40 (silicocalcium). which. apparently. is associated with the increased oxidation of ladle slag in the experimental melts.

The results of the study of metal samples from experimental and comparative melts for contamination of steel with NMI (according to state standard of Russia 1778-70) and CANMI are shown in table 2.

Table 2. The results of the assessment of contamination of steel NMI

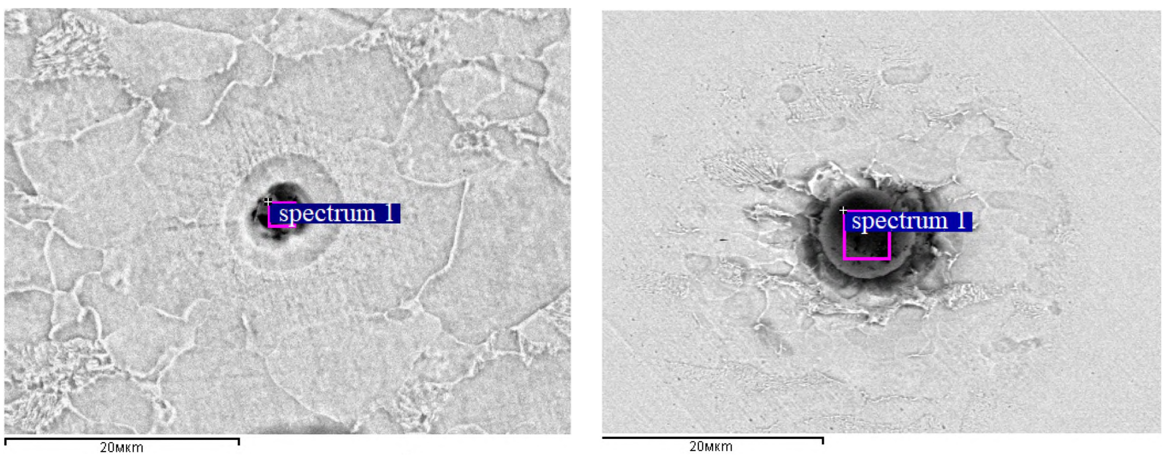
Applied modifier	Contamination with NMI according to state standard 1778-70						The average score of metal contamination by CANMI. pcs/mm^2	
	Point oxides		Fragile silicates		Non-deformable silicates			
	Maximum score	Average score	Maximum score	Average score	Maximum score	Average score	CANMI 1	CANMI 2
SC40	1.0	0.75	4.5	1.3	4.5	2.30	1.78	1.88
INSTEEL® 1.5	0.50	0.50	2.0	0.40	3.5	1.50	1.51	0.62
INSTEEL® 9.4	1.0	0.53	3.0	0.77	4.0	1.33	1.15	0.70
INSTEEL® 5.1	0.5	0.50	2.0	0.40	3.0	1.25	1.03	0.92
INSTEEL® 10.1	0.5	0.50	1.5	0.30	2.5	1.35	1.46	1.54

From the data of table 3 it follows that the maximum score of NMI and the average level of contamination for the main types of NMI reduction is provided when processing steel by experimental modifiers. Wherein. the most significant decrease in NMI is observed for fragile silicates. which is a positive fact. because this type of inclusions has an acute-angled shape and is a stress concentrator.

The use of all 4 experimental modifiers allowed to reduce the contamination of the metal with CANMI. The purest rolled product of this type of NMI were obtained by metal processing with INSTEEL®9.4 and INSTEEL®5.1. The greatest complex effect on reducing the contamination of steel by NMI was observed when using wire with INSTEEL®5.1 filler.

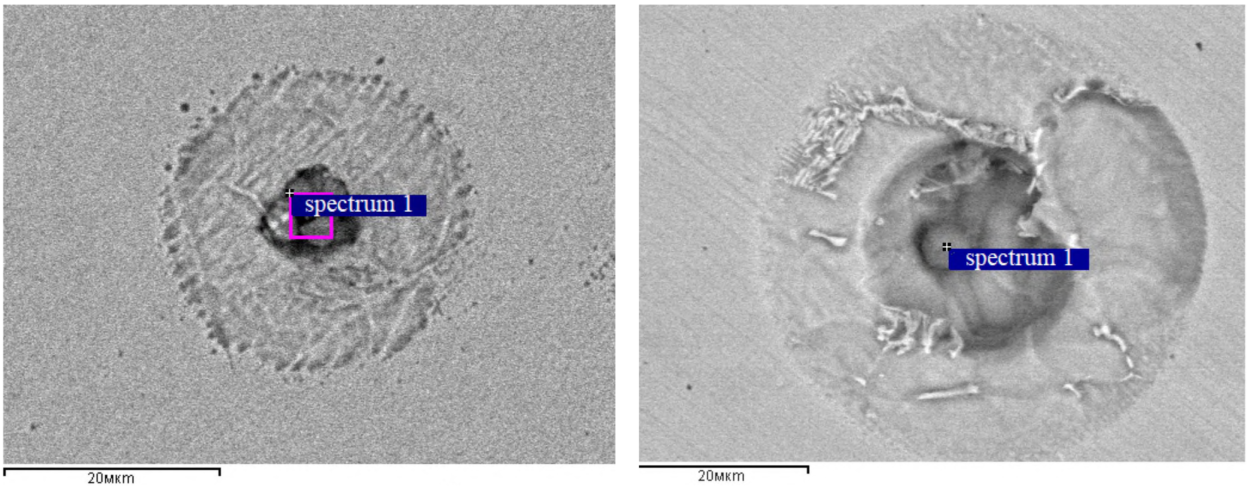
Thus. the use of complex INSTEEL® modifiers (containing Ca. Ba. Sr and REM) provides a significant reduction in the contamination of steel by NMI of all types as a result of the effect on the properties and behavior of NMI. This contributes to more efficient removal of NMI and reduces the harmful effects of NMI on the properties of steel.

Fig. 1 and 2 and Table 4 show the typical results of microspectral analysis of sheet metal samples from comparative and experimental melts using INSTEEL®5.1 to illustrate the effect of experimental modifiers on the morphology and composition of CANMI.



a - INSTEEL®5.1 b - SC40

Fig. 1. Microstructure of steel 17G1S-U and type of CANMI 1. x200
(the compositions are shown in table 4)



a - INSTEEL®5.1 b - SC40

Fig. 2. The microstructure of steel 17G1S-U and the type of CANMI 2. x200 (the compositions are shown in table 4)

Table 4. Composition of CANMI (Fig. 1 and 2)

Element	CANMI compositions by type and modifier			
	CANMI of 1 type		CANMI of 2 type	
	INSTEEL®5.1	SC40	INSTEEL®5.1	SC40
	Fig. 1a	Fig. 1b	Fig. 2a	Fig. 2b
O	12.65	40.42	15.38	19.36
Mg	4.46	2.05	2.81	3.52
Al	11.43	24.42	5.99	8.78
S	4.36	-	18.09	10.99
Ca	5.35	31.17	13.73	9.53
Mn	11.79	-	1.96	2.39
Fe	13.6	1.94	3.63	45.43
La	4.96	-	5.8	-
Ce	31.4	-	32.62	-
Total	100	100	100	100

A comparative analysis of the composition of CANMI (Table 4) allows to conclude that the treatment of steel with an experienced INSTEEL®5.1 modifier leads to a decrease in the oxygen content in CANMI type 1 from 39-40% to 5-24%. In addition. a noticeable amount of cerium and sulfur is observed in the inclusions. which increases the probabilityof the formation of a sulfide shell.

A decrease in oxygen concentration is observed and sulfur compounds are found in a larger amount (from 13 to 36%) compared with a metal modified in 40 (from 9.8 to 12.7 %) when studying the chemical composition of CANMI type 2 in a metal after using experimental modifiers.

The use of complex modifiers with REM leads to the formation of smaller complex oxysulfides of calcium. cerium. lanthanum with a low oxygen content [21-23] in addition to reducing the degree of contamination of the metal with NMI. The sulfide shell of such inclusions serves as a damping element that prevents the formation of metal tears at the metal-inclusion boundary [2. 7. 8. 22. 23]. which prevents the occurrence of microcracks - sources of development of corrosion processes.

Conclusions

The use of complex microcrystalline modifiers produced by NPP Technology LTD provides:

– more complete deoxidation and an increase in the degree of calcium absorption in comparison with that used according to the current technology of SC40 by 61.1-76.5% rel.;

– increased degree of metal desulfurization;

– reduction of steel contamination by oxide inclusions as well in maximum score as in average value;

– a decrease in the content of CANMI in steel and a change in their morphology towards the formation of oxysulfide inclusions favorable in terms of increasing the corrosion resistance of steel.

The effect of the use of experienced modifiers can be used both in the production of standard grade steel grades and in the production of steels with increased requirements for NMI. At the same time. increasing the degree of calcium absorption allows reducing the consumption of experienced modifiers for melting by 40-50% without compromising the quality of steel.

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