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Effects of Cr - Ni 18/9 Austenitic Cast Steel Modification by Mischmetal

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Abstract

This paper presents the results of Cr - Ni 18/9 austenitic cast steel modifications by mischmetal. The study was conducted on industrial melts. Cast steel was melted in an electric induction furnace with a capacity of 2000 kg and a basic lining crucible. .The mischmetal was introduced into the ladle during tapping of the cast steel from the furnace. The effectiveness of modification was examined with the carbon content of 0.1% and the presence of δ ferrite in the structure of cast steel stabilized with titanium. The changes in the structure of cast steel and their effect on mechanical properties and intergranular corrosion were studied. It was found that rare earth metals decrease the sulfur content in cast steel and above all, they cause a distinct change in morphology of the δ ferrite and non-metallic inclusions. These changes have improved mechanical properties. R_{02}, R_m, and A_5 and toughness increased significantly. There was a great increase of the resistance to intergranular corrosion in the Huey test. The study confirmed the high efficiency of cast steel modification by mischmetal in industrial environments. The final effect of modification depends on the form and manner of placing mischmetal into the liquid metal and the melting technology, ie the degree of deoxidation and desulfurization of the metal in the furnace.

Keywords: Austenitic cast steel, Modification, Mischmetal, Mechanical properties, Intergranular corrosion

1. Introduction

The most commonly met and dangerous type of corrosion is the intergranular corrosion of highly alloyed steels and chromium-nickel cast steels, which are the main constructional materials used in power engineering.

The most common theory explaining the intergranular corrosion is the theory, which explains the phenomenon of steel sensitization to this corrosion type by evolving chromium carbides of $M_{23}C_6$ in the sigma phase or other phases rich in chromium at the boundary grain of corrosion resistant steels during their annealing at 400 – 800°C. At these temperatures the chromium diffusion ability is so small that the chromium necessary for the creating phases is taken from the border zone in consequence of which its content decreases to a quantity smaller than 13%, and the austenite converts into ferrite. These zones are depassivated and corrode heavily. The degree of sensitization to the intergranular corrosion depends at the same time not only on the amount of evolving phases but also on their dispersion, chemical composition and the state of stress caused by their evolving.The effect of content chromium reduction defined by Bain [1] was confirmed in papers [2 – 4]. The intergranular corrosion is relatively often the cause of severe failures as it leads to damaging the device with no initial symptoms (Fig.1).

Providing high durability and reliability of equipment for power engineering forces to unceasing research and improvement of technological methods enabling improving resistance to this kind of corrosion. The most effective method would be the one, which would allow significant improvement of corrosion resistance keeping the casting and mechanical properties at a satisfactory level.

Of the many different ways to increase resistance to intergranular corrosion of austenitic chromium-nickel steels there is a method recognized as the most effective one which significantly reduces the carbon content, i.e. to less than 0.02%. The tests of austenitic steels used in nuclear power show that it is not so certain. They point at results presented in [4], which show that the steel AISI 316 with a content of 0.012% C after annealing and sensitizing at 650°C for 100 h was intensely corroded in the Huey test.It was the result of the presence of many $M_{23}C_6$ carbides at the borders of the austenite grain and chromium depletion in the border areas, which had a ferrite structure composed of 84.7%Fe, 12.3%Cr, 1.9%Ni and 1.2%Mo. With lower carbon contents (0.009%) there was only observed the presence of precipitates of the Laves phase rich in Mo, Cr, Fe and Si, which also exacerbated the corrosion resistance. Cast steels with such low carbon contents are not suitable for casting because of the significant deterioration of the fluidity. Mechanical properties of cast steels are also decreased. Therefore, the negative impact of reduced carbon content in austenitic chromium-nickel cast steels should be compensated by a correction of their chemical composition in the desired direction. So the chemical composition of cast elements must be complemented with the elements that substantially improve the casting properties, and additionally affect the corrosion resistance favourably. One of such elements is copper, which added in an amount of 1-1.5% significantly increases the fluidity of cast steel.

In order to improve resistance to intergranular corrosion there are also applied:

- Solutioning at temperatures of 950 - 1150 ° C '
- Stabilizing annealing at temperatures of 800 - 880 ° C,
- Stabilizing additions of titanium, niobium or tantalum,
- Correction of the chemical compositionpermitting getting two-phase structure of austenite + ferrite,
- modification.

In casting practice, a number of these methods are used together. In this study we investigated the effect of mischmetal modifications on the properties of cast steel Cr - Ni type 18/9 stabilized with titanium.

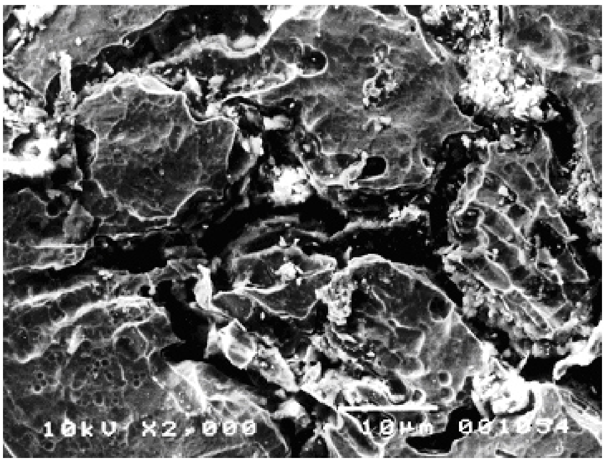

Fig. 1. Damages to the surface of pump rotor of 0,27 % C, 21,4 % Cr, 6,3 % Ni, 2,3 % Mo cast steel caused by erosion and simultaneously developing intergranular and pitting corrosion in the mine water containing approx. 50 mg/dm^3 chloric ions

2. Experimental procedures

The study was conducted on industrial melts. Cast steel was melted in an induction electric furnace with a capacity of 2000 kg and a basic lining crucible.

Feedstocks used were:

- Home scrap,
- Armco Fe-containing C = max. 0.05%,
- Ferrochromium-FeCr 0.06,
- Granulated nickel Ni 98.6,
- Ferrotitanium FeTi 30A16

Cast steel was deoxidated and desulphurized in the furnace by ferroalloys FeSiMn17A and FeSiCa20-3 and immediately before tapping by means of aluminum A5.

Modification was made by means of the mischmetal composed of 49.8% Ce, 21.8% La, 17.1% Nd, 5.5% Pr, 5.35% and the rest of REM. Mischmetal in particulate form was introduced in portions into the ladle during tapping of steel from the furnace. 2.5 kg of mischmetal were added per 1000 kg of liquid metal.

For the tests the cast steel of the chemical composition given in Tab.1 of two melts was chosen. The test specimens were taken from ingots sample after heat treatment. There was used: solutioning: 1050 ° C / 1 hr. / water and sensitization: 650 ° C / 1 hr. / air. For the Huey test of resistance to intergranular corrosion samples measuring 25 x 20 x 5 mm were used.

3. Test results

Structure of the cast was biphasic - austenitic-ferritic. The ferrite content was determined by magnetic method of 6.5 and 7.0% respectively (Table 1).

Application of the modifications reduced the sulfur content of about 0.005% o (Table 1). Delta ferrite morphology had significant change. In the unmodified cast steel δ ferrite made skeletal dendritic systems (Fig.2a). Application of this modification resulted in fragmentation and a partial or almost complete elimination of this form of occurrence of δ ferrite (Fig.2b). There was observed higher δ ferrite pickling ability in unmodified cast steel caused by the presence of numerous precipitates of carbide phase (Fig.3) and decrease of alloying elements in the ferrite matrix. In the modified cast steel the etching ability is clearly less what could result from a more limited process of evolving of these phases. There was also a significant change in morphology of non-metallic inclusions. In the unmodified cast steel beside inclusions of TiC, Ti (C, N), Al_2O_3, and trace amounts of (Fe, Mn) S inclusions there occured inclusions aggregations of lamellar structure (Fig.4a). Ray microanalysis (EDS) showed that these are Ti_2S titanium sulphides (Fig.4b).Ti_2S sulphides do not occur in the cast steel modified by mischmetal. Non-metallic inclusions with high dispersion are generally evenly distributed throughout the matrix

(Fig. 5a). Numerous titanium nitrides were growing up on pads of oxysulphides REM (Fig. 5b). REM oxysulphides inclusions often took shape close to spherical (Fig. 6). Microanalysis (EDS) revealed the presence of arsenic in these inclusions (Fig.6, 7). The change of δ ferrite morphology and non-metallic inclusions has been beneficial to the change in mechanical properties (Table 2).There was a significant change in fracture morphology of the impact resistance samples (Fig. 8). In samples with unmodified cast steel, cleavage fracture was dominating (Fig. 8a). The presence of Ti_2S sulphide concentrations (Fig. 8b) was adversely affecting the cracking process. Delta ferrite fragmentation and the morphology change of the nonmetallic inclusions in cast steel modified by mischmetal contributed to the occurrence of ductile fracture mechanism of the samples (Fig. 8c).

There has been a significant change in the tested cast steel resistance to intergranular corrosion in boiling 65% nitric acid (Huey test). Specimens of cast steel after solution heat treatment and sensitization annealing were examined. The Vc corrosion rate after the fifth period of cooking samples from non-modified cast steel was 433.5 $g/m^2 \cdot 24h$ and modified 34.0 $g/m^2 \cdot 24h$. The nature and extent of corrosion attack has changed (Fig. 9). The surface layer of the samples with unmodified cast steel δ ferrite separation of dendritic systems have undergone intensive corrosion (Figure 9a). However, in samples of modified cast steel only minor intergranular corrosion aggregates have occured. (Figure 9b).

Table 1.
Chemical composition of tested steel and delta ferrite content in casts

Cast steel		Content in % mas.									Contents of delta ferrite
		C	Mn	Si	P	S	Cr	Ni	Ti	Al	%
Without modification		0,10	1,49	0,82	0,018	0,016	17,9	9,3	0,62	0,17	6,5
Modified by mischmetal	Before adding mischmetal	0,11	1,50	0,65	0,018	0,015	18,56	8,9	0,58	0,15	–
	After adding mischmetal	0,11	1,52	0,68	0,018	0,010	18,62	8,8	0,50	0,14	7,0

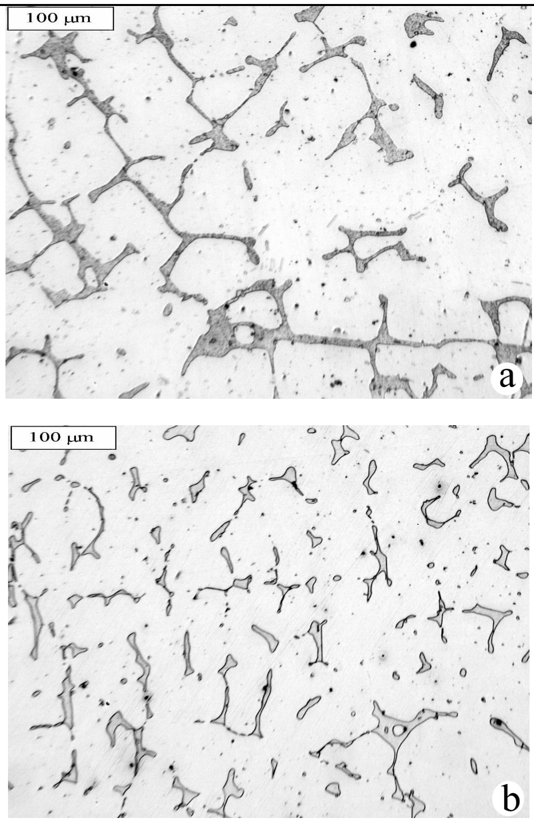

Fig. 2. Cast steel microstructure: a – non modified, b – modified by mischmetal. Heat treatment: solution heat treatment + sensitization. Etched: Mi15Fe. LM

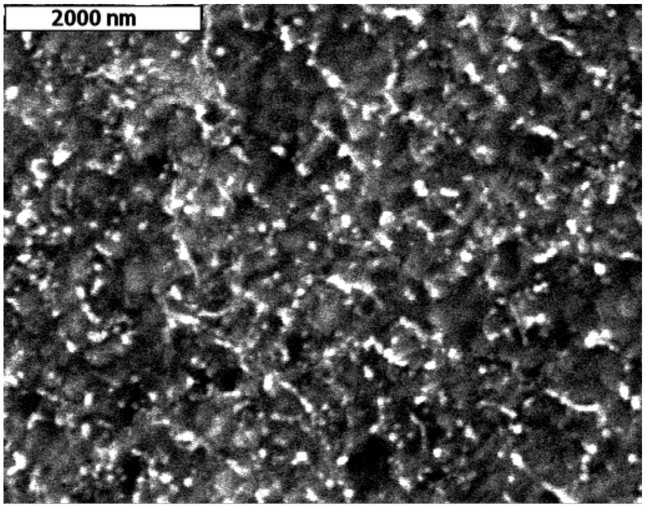

Fig. 3. Carbide phase separation in the delta ferrite in unmodifiedcast steel. Heat treatment: solution heat treatment + sensitization. Etched: Mi15Fe. SEM

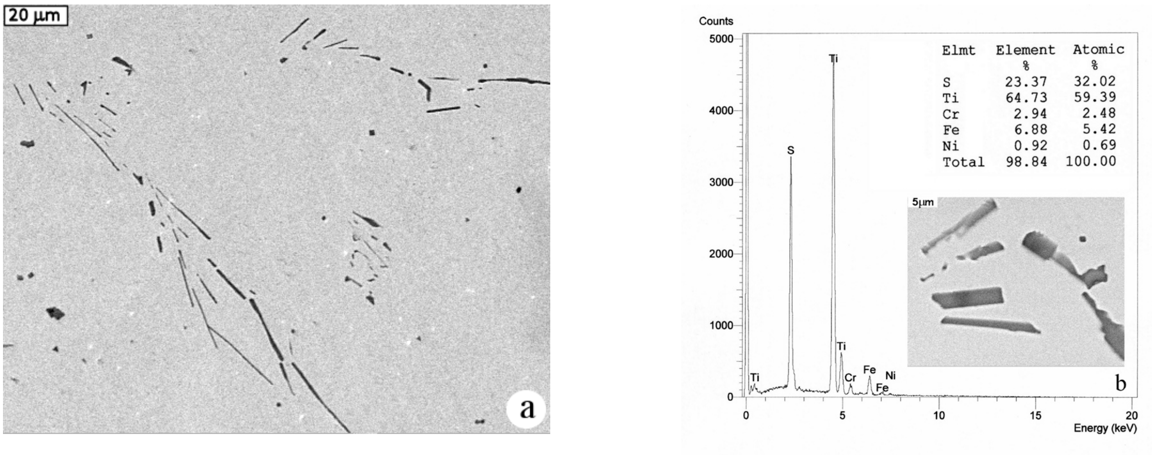

Fig. 4. Non metallic inclusions in non modified cast steel. Not etched. SEM

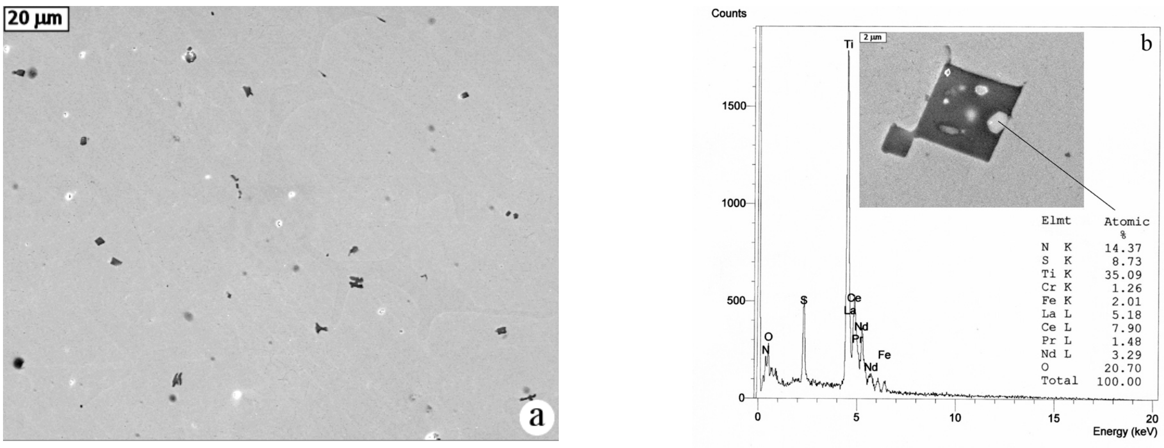

Fig. 5. Non-metallic inclusions in cast steel modified by mischmetal. Not etched. SEM

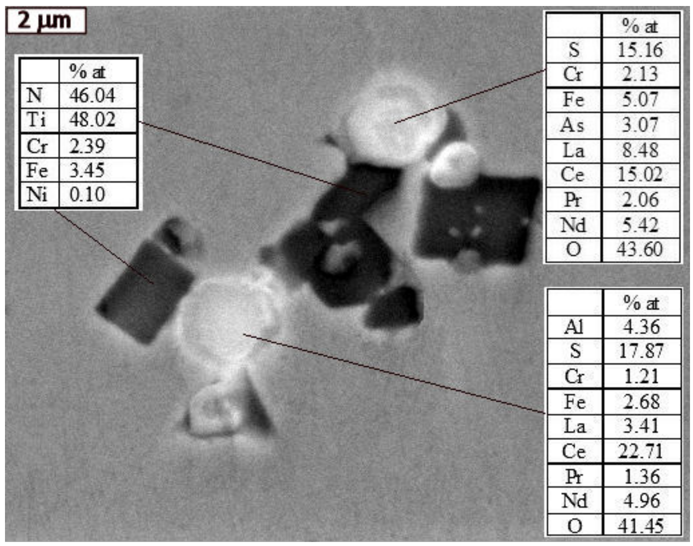

Fig. 6. Most commonly occuring non-metalic inclusions in cast steel modified by mischmetal. Not etched. SEM

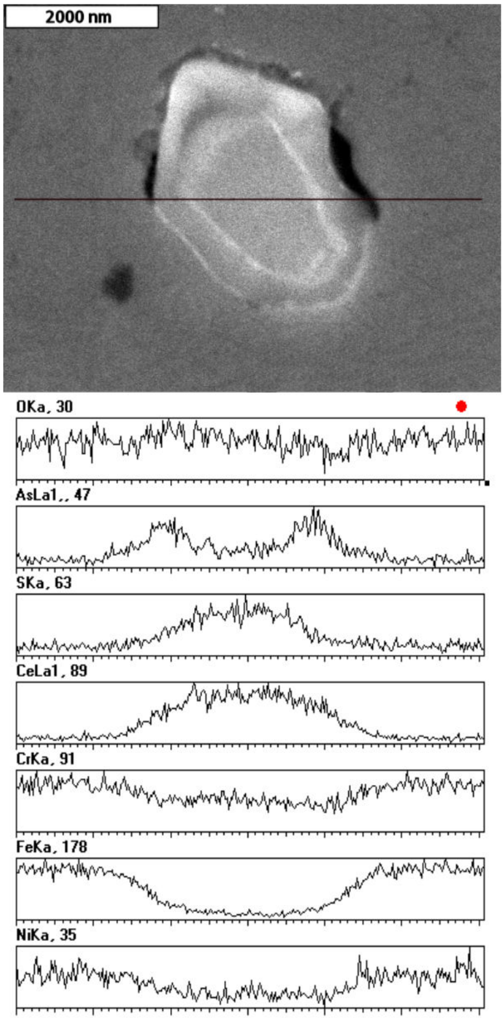

Fig. 7. Linear distribution of elements in theinclusion containing cerium and arsenic. SEM

Table 2.
Mechanical properties of cast steel. Heat treatment: solution heat treatment

Cast steel	R_{02}	R_m	A_5	Z	Impact strength KCU2 J/cm^2
	MPa		%		
Without modification	224	502	42,0	61,0	118
Modified by mischmetal	238	541	48,0	60,0	145

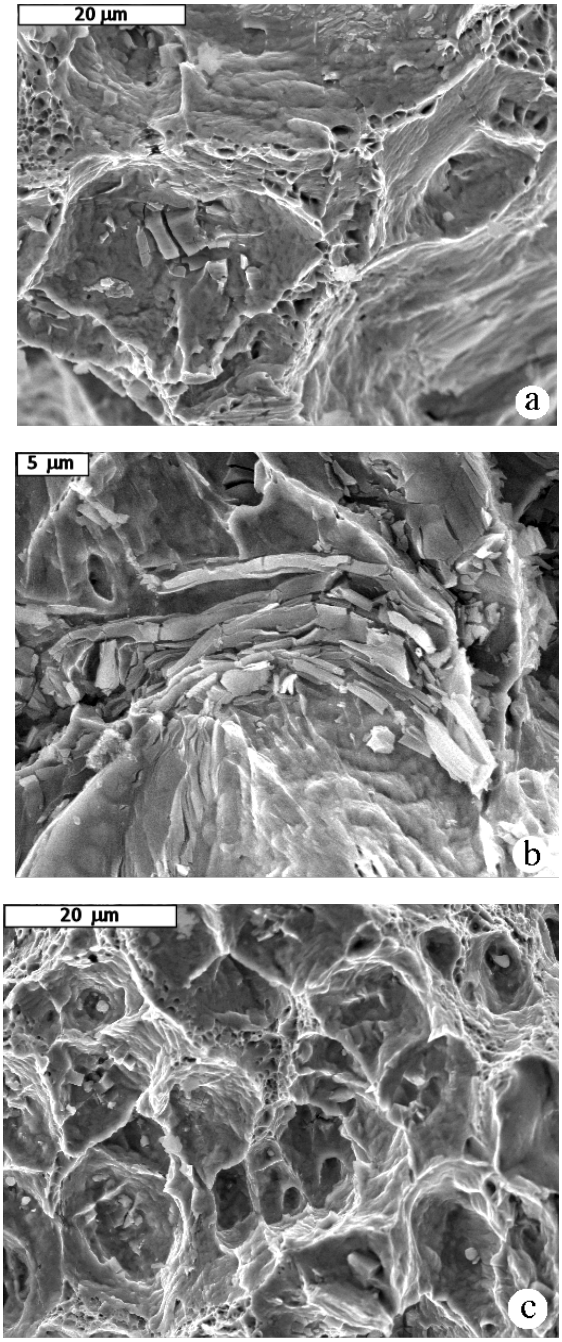

Fig. 8. Fracture surfaces of charpy specimens of unmodified cast steel(a, b) and modified by mischmetal (c). Heat treatment: solution heat treatment. SEM

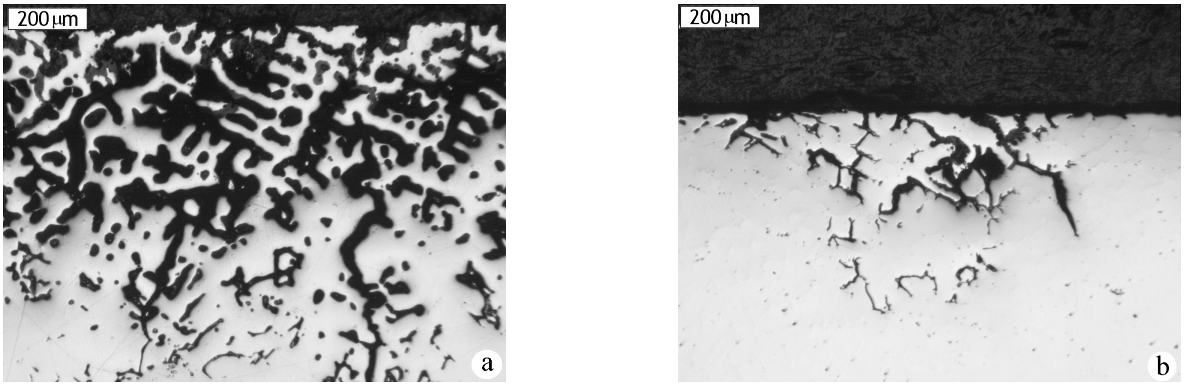

Fig. 9. Propagation of intergranular corrosion in steel samples of unmodified cast steel(a) and modified by mischmetal (b). Huey test corrosion resistance. The condition after the fifth period of cooking. Heat treatment: solution heat treatment + sensitization. Not etched. SEM

4. Conclusions

The study shows that the effect of rare earth metals contained in mischmetal is focused primarily on changing the conditions of crystallization and the sulfur bounding in non-metallic inclusions

Changing the conditions of crystallization prevents the occurrence of δ ferrite with the dendritic systems. Under the influence of modifier δ ferrite crystallizes generally in the form of separate small grains. This effect of modification can be interpreted basing on the "nucleus creating" model and models based on theories of grain growth inhibition [5 – 9]. Change of δ ferrite morphology is important for improving the mechanical properties, and above all to increase the resistance to intergranular corrosion. In the studied cast steel, δ ferrite underwent intensive corrosion in the Huey test. During the sensitization to intergranular corrosion, the carbides evolving concentrate in δ ferrite and its borders. And to a lesser extent on the austenite grain boundaries. Zones with chromium contents of less than critical (13%) will therefore occur primarily in the area of δ ferrite. The presence of δ ferrite of dendritic systems in the unmodified cast steel generally forming a continuous network causes the corrosion to spread very intensively. In the cast steel modified by mischmetal δ ferrite grain are not linked. If, through the reduction of chromium content around them or inside corrosion occurs, it cannot spread further. The observed less advanced process of the evolution of carbide phases in δ ferrite favourably affects the increase of the resistance to intergranular corrosion. This can be due to reducing the carbon diffusion from the interfacial boundary of austenite to ferrite δ by rare earth metals. The high affinity of rare-earth metals with sulphur and oxygen causes a significant change in morphology of nonmetallic inclusions. The unfavorable forms of these inclusions, such as Ti_2S lamellar separations are eliminated. Rare-earth metals reacting with oxygen and sulfur form oxysulphides of high dispersion and shape similar to spherical. Non-metallic inclusions in modified cast steel are apart from that more evenly distributed in the metallic matrix.The change in morphology and distribution of nonmetallic inclusions also preferably improves the mechanical properties in particular, the plastic properties and impact resistance. Thus, the mischmetal modification of Cr - Ni 18/9 cast steel, of a two-phase structure austenitic – ferritic structure enables significant improvement of cast steel properties. Even in cases where for technical reasons the carbon content of cast steel cannot be significantly reduced and is approximately 0.1% and above.

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