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PHYSICO-CHEMICAL PROCESSES FROM THE X70 STEEL MAKING AND CONTINUOUS CASTING THAT INFLUENCE ITS PROPERTIES

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ABSTRACT

The paper presents the processes of elaboration and casting that favourably influence the properties of microalloyed steel.

High strength microalloyed steel used to manufacture main oil and gas pipelines must meet, in addition to special technical conditions, economic conditions, which contribute to the protection of the environment. Secondary treatment in LF and RH installations as well as automatically controlled continuous casting can also help improving the physical, mechanical and corrosion properties of the products obtained from these steels. The making of X70 steels at OLD1-(Liberty Steel Group), according to existing technology, is the peak of performance at the current stage.

Blowing oxygen and argon into the converter is done according to a Blowing Pattern that takes into account the gas flow and the distance from the head of the blowing lance to the surface of the metal bath. Deoxidation and microalloying of the X70 steel take place in the casting ladle and during the secondary treatment in LF and RH.

For deoxidation and microalloying, some ferro-alloys which have strictly limited content of harmful elements (P, S) are used. LF microalloying materials such as: Mn-99%, Al-99%, FeTi-70%, FeV-80%, FeNb-65%, Ca-99% or SiCa-60/30% are introduced into the steel as tubular ferro-alloys and not chunks. In this way, a superior assimilation and homogeneous diffusion of the elements into the metal bath are achieved.

Secondary treatment of the X70 steel for chemical and thermal homogenization of the metal bath is achieved by advanced metal bath desulfurization using synthetic slag, lime and bauxite. Vacuum degassing with RH procedure is done to reduce hydrogen from 8-9 ppm to less than 2 ppm. At the continuous casting of these steel types, the bubbling is not used because it is intended that the floating of inclusions be easier on the surface of the metal bath.

KEYWORDS: properties, deoxidation, microalloying, steel, LD converter

1. Introduction

The launching point in the research and development of high-strength micro-alloy steels was represented by the brands used in the construction of major oil and natural gas pipelines, the steels developed and processed for use in extreme conditions, from the Arctic to the desert areas, from depths greater than 2000 m, to the altitudes necessary to cross mountain ranges, buses that extend thousands of kilometres and which must satisfy, in addition to the special technical conditions that ensure their safety in use, economic conditions and protection of the environment.

By performing the tasks elaborated on the basis of the mathematical models and by optimizing the parameters of the main processes in the elaboration and casting of the high strength mechanical steels, their properties can be improved. The steel industry has responded to current requirements by developing new steel brands that can be used in different

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industrial sectors and which have a common set of characteristics

These steels are called HSLA - high strength microalloyed steels [1]. All these features are found in high strength microalloyed steels, which are produced and developed under different brands by the major steel producers around the world [2]. This category also includes X70 steel according to API-5L-91.

X70 steel, by its characteristics, is suitable for the manufacture of main pipes in the current state of their technologies. Medium alloy steel would have required a higher consumption of alloying elements and thus higher production prices.

2. The experimental part

The main reference properties for X70 steels:
- high mechanical strength;
- high weldability;
- high resistance even at low temperatures;
- good plasticity characteristics;
- good resistance to atmospheric and marine corrosion;
- high economic efficiency in terms of production costs.

Tables 1-4 present the main mechanical properties and chemical compositions of X70 steel type.

Table 1. *Variation of mechanical strength of X70 microalloyed steels according to API-5L / 95*

Yield Strength [MPa]	Tensile strength [MPa]	$Rp_{0.2}$/Ts
485-615	570-700	0.93

Table 2. *X70 microalloyed steels, according to API-5L / 95*

Chemical analysis	Acceptance limits	Over tolerant limits	Target	Chemical analysis	Acceptance limits	Over tolerant limits	Target
Element	Max (%)	Max (%)	Target (%)	Element	Max (%)	Max (%)	Target (%)
C		0.09	0.07	Mo		0.13	0.12
Mn		1.65	1.55	Ni		0.20	
P	0.02	0.018	0.02	Cu		0.10	
S	0.01	0.05	0.03	B		0.0005	0.0003
Si		0.40	0.30	Ca		0.0015	0.001
Al		0.05	0.04	N		0.007	0.006
Nb	0.07	0.06	0.05	V+Nb+Ti	0.15	0.15	
V	0.10	0.008		V+Nb	0.14	0.14	
Ti		0.025	0.02	Ce	0.39	0.39	
Cr		0.20					

Table 3. *X70-M21 microalloyed steels, according to the Arcelor Mittal Galati-Metallurgical Handbook*

	C	Mn	Si	P	S	Al	N_2	H_2	Cu	Cr	Ni	Mo	Nb	Ti	V	Ca
Min (%)	0.06	1.45	0.25			0.02						0.12	0.045	0.015		0.0005
Max (%)	0.075	1.6	0.4	0.01	0.002	0.05	0.007	2 ppm	0.1	0.2	0.2	0.13	0.055	0.025	0.008	0.0015

Table 4. *X70-T15 microalloyed steels, according to the Arcelor Mittal Galati-Metallurgical Handbook*

Chemical analysis		C	Mn	Si	Al	P	S	N_2	Mo	Cr	Nb	Ti	Ca	H_2 [ppm]
T15	min (%)	0.060	1.600	0.200	0.020				0.110	0.25	0.055	0.015	0.0005	max.2
	max (%)	0.075	1.750	0.350	0.060	0.015	0.005	0.007	0.120	0.35	0.065	0.025	0.0015	
	Target (%)	0.068	1.680	0.280	0.040	0.012	0.003	0.006	0.115	0.30	0.060	0.020	0.0010	

2.1. Steelmaking and continuous casting of X70

The following materials, installations and some specific operations are used in the X70 steelmaking process [3-5]:

• Technologically selected scrap iron;

• Desulphurized cast iron at% S = 20 ppm and advanced slag removed;

• Converter with functional bubbling and slag retention, calibrated;

• Clean casting pot with functional bubbling;

• Recycled steel is not inserted in the metal load;

• Bubbling only with argon for the entire duration of the breath;

• Intermediate stop for advanced slag evacuation and resumption of blowing with additional quantity of 1-ton lime [8];

• Minimum 3 minutes post bubble (oxygen activity ≤ 700 ppm and phosphorus ≤ 0.006%);

• The calculation of the necessary alloys is made on the lower limit of each element;

• Electrolytic manganese will be used during the evacuation and the ferroalloys will be administered with 1-minute breaks between them;

• Steel bubbling after evacuation will be done through a porous plug without the discovery of the metal bath;

• LF treatment (advanced steel bubbling, heating and desulphurization);

• Advanced desulfurization with lime, bauxite and synthetic slag;

• Correction of chemical analysis and microalloys with tub ferroalloys of Nb, V, Ti and SiCa;

• HR treatment for 15 minutes minimum vacuum degassing;

• The batches do not bubble for about 15-20 minutes before casting begins to float inclusions in the slag [5].

Table 5. *Chemical compositions corresponding to X70 steel making batch (%), according to the OLD1- Arcelor Mittal Galati spectral laboratory analysis*

Cod ACH / Element	Desulphurized cast iron	End of blowing	Steel after evacuation	Steel in LF, first sample	Steel in LF, second sample	Steel in LF, the third sample	Steel in LF, fourth sample	Steel in LF, last sample	Final sample from distributor
C	4.7196	0.0555	0.0524	0.0602	0.0677	0.0761	0.0723	0.0742	0.0728
Mn	0.5105	0.0824	1.2704	1.3102	1.3115	1.5012	1.4937	1.4843	1.4696
Si	0.6787	0.0010	0.2086	0.1661	0.2510	0.2813	0.2631	0.2646	0.2729
P	0.0767	0.0048	0.0052	0.0059	0.0064	0.0069	0.0066	0.0068	0.0070
S	0.0036	0.0090	0.0069	0.0044	0.0030	0.0014	0.0013	0.0013	0.0012
Al	0.0031	0.1753	0.0151	0.0232	0.0308	0.0316	0.0342	0.0393	0.0444
Ni	0.0016	0.0081	0.0086	0.0085	0.0084	0.0086	0.0085	0.0085	0.0085
Cu	0.0063	0.0112	0.0136	0.0136	0.0138	0.0146	0.0146	0.0144	0.0145
Cr	0.0186	0.0063	0.0088	0.0093	0.0097	0.0110	0.0108	0.0112	0.0157
Ti	0.0318	0.0001	0.0006	0.0007	0.0015	0.0209	0.0224	0.0206	0.0166
Mo	0.0010	0.0009	0.1172	0.1184	0.1182	0.1246	0.1251	0.1251	0.1245
Nb	0.0010	0.0003	0.0014	0.0013	0.0016	0.0420	0.0422	0.0451	0.0466
V	0.0072	0.0004	0.0014	0.0015	0.0017	0.0020	0.0019	0.0017	0.0018
Ca	0.0000	0.0166	0.0001	0.0001	0.0033	0.0103	0.0047	0.0039	0.0006
Sn	0.0042	0.0008	0.0010	0.0011	0.0013	0.0014	0.0014	0.0012	0.0015
B	0.0006	0.0000	0.0001	0.0001	0.0002	0.0002	0.0002	0.0002	0.0003
N	0.0000	0.0057	0.0024	0.0010	0.0011	0.0069	0.0033	0.0006	0.0047
Pb	0.0010	0.0005	0.0020	0.0022	0.0022	0.0024	0.0028	0.0027	0.0026
Zr	0.0010	0.0003	0.0019	0.0020	0.0020	0.0025	0.0024	0.0024	0.0024
Zn	0.0017	0.0042	0.0060	0.0065	0.0043	0.0028	0.0089	0.0059	0.0020
Co	0.0010	0.0021	0.0024	0.0024	0.0023	0.0026	0.0025	0.0025	0.0025
Fe	93.9087	99.6261	98.2768	98.2643	98.1609	97.8518	97.8813	97.8875	97.8962

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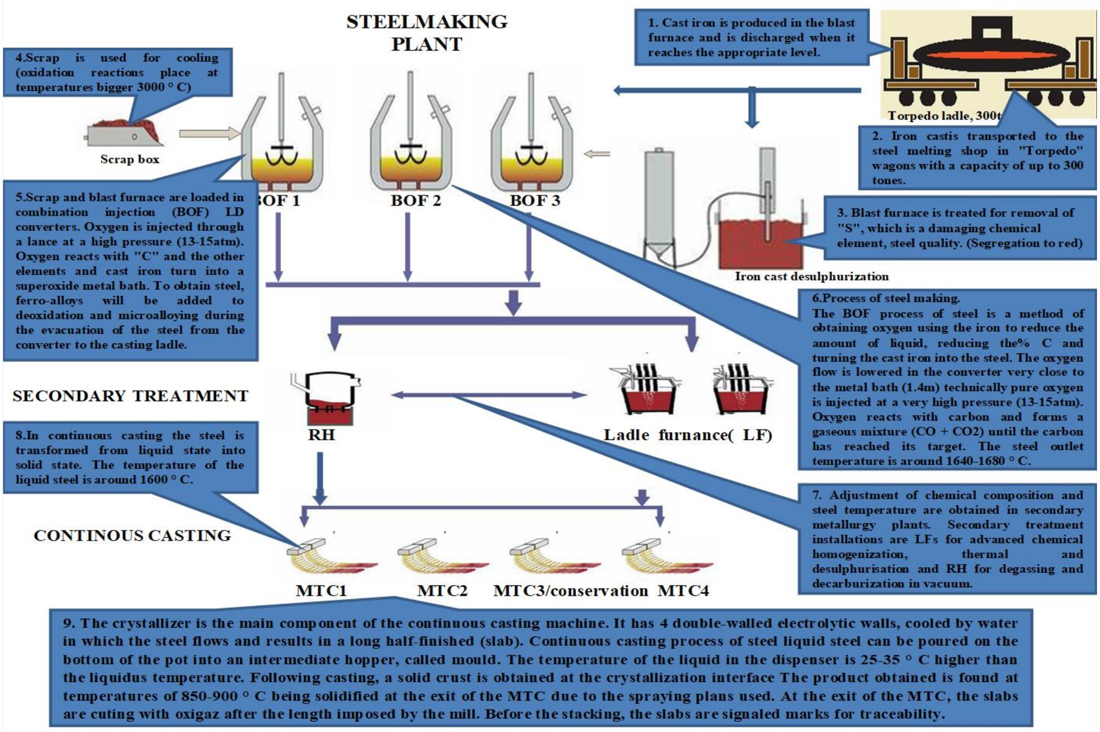

Fig. 1. *General presentation of the technological flows of making and casting steel* [1, 4]

2.2. Physico-chemical processes in steelmaking and casting of X70

In a LD converter with combined oxygen and argon blowing, Fig. 2, the basic reactions that take place are oxidation, and the movement of the metal bath is mainly generated by the energy transmitted by the oxygen jet hitting the metal bath and by the blowing energy, due to carbon monoxide (CO) formation and release [6].

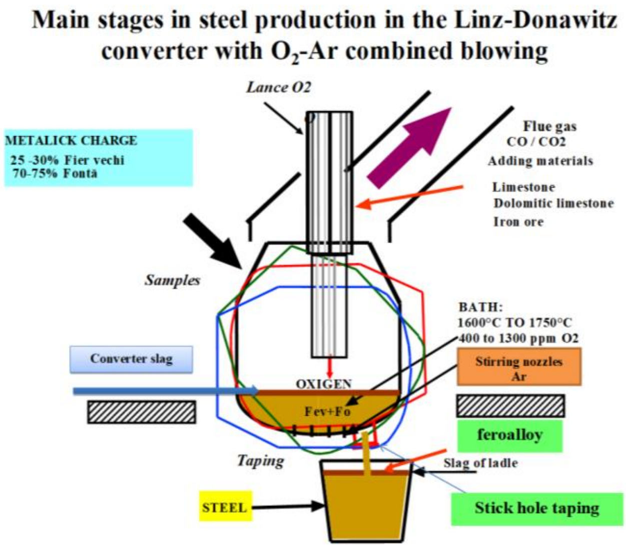

Fig. 2. *Linz-Donawitz converter with combined blowing of the O_2 - Ar* [1, 8]

In the initial phase of the process when the silica oxidation takes place, the formation of CO remains less intense. In the main decarburization phase, the formation of CO in the reaction areas of the oxygen jets and in the immediate vicinity is extremely pronounced. In the marginal areas of the converter, however, there are dead zones where variations of concentrations occur due to the differences in intensity of the oxidation reactions [7]. In the final phase of the decarburization, the combustion zones are less carbon-fuelled, due to an increased slag of iron and manganese.

In the bubbling process, the inert gas (nitrogen or argon) is injected into the batch through the bottom of the converter. The amount of gas varies depending on the phase of the elaboration process. During de-silica and the main decarburization phase, the gas flow is sufficient to ensure the chemical composition and homogeneous temperature of the metal bath. In the final phase of decarburization and especially in advanced decarburization, the CO formation is too weak to generate the movement of the metal bath.

In this period the flow rate of the bubbling gas is increased to ensure the transport of carbon in the reaction areas of the oxygen jets and at the same time to prevent the slag from further oxidation of other elements. In the whole process, the reactions are close to equilibrium, balances that are reached in the post-bubbling phase and the variation of the main elements concentration and of their oxides are shown in Fig. 3.

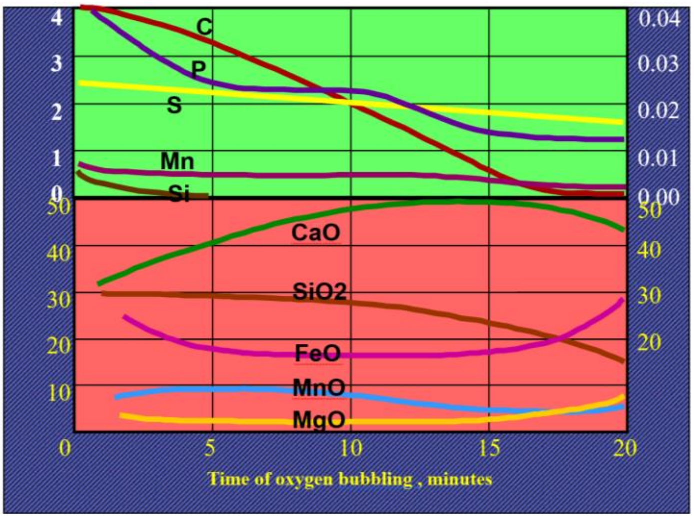

Fig. 3. *Variation of different element and the resulting oxides concentration in the converter* [4]

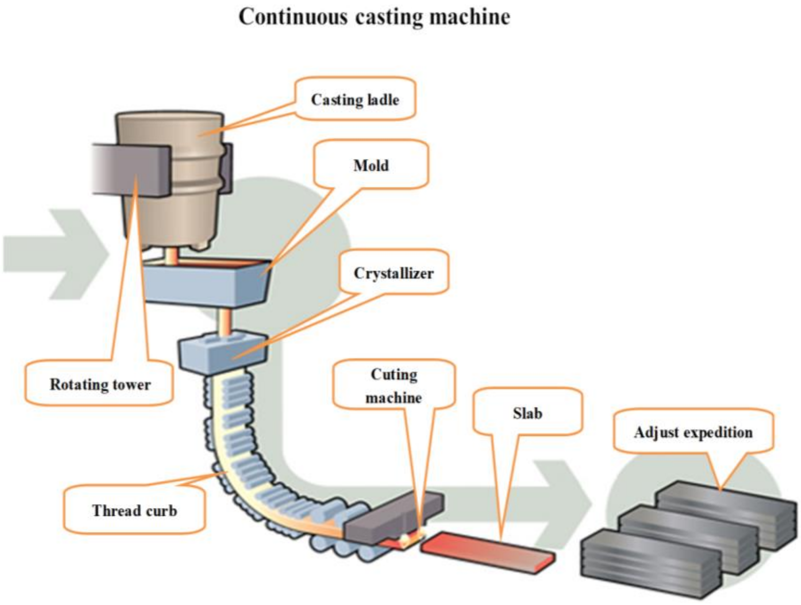

Fig. 4. *Continuous casting machine, the main scheme* [4, 5]

The bubbling process through the bottom of the converter helps the oxidation and slurry reactions of the formed oxides (oxides of silica, manganese, iron etc.) near the equilibrium state, during the main phase of the decarburization [8]. The equilibrium states between the chemical elements in the metal bath and

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the oxygen content are not perfectly achieved during oxygen bubbling. The lime dissolution is accelerated by injecting the inert gas into the metal bath. The addition of fluorine (CaF_2) for the fluidization of the slag is no longer necessary, which leads to increased durability of the refractory lining of the converter.

Examples of the defects types in slabs are presented in Table 7 and Fig. 7, 8.

Table 6. *Baumann analysis bulletin according to the Baumann-OLD1 Laboratory Analysis*

No. heat	No. slab	Quality	Sleb dimensions	Attack type	Casting machine	Level of segregation
911435	3	M21	250/1900	$CuCl_2$+ NH_4Cl	1/1	Class 2
911435	6	M21	250/1900	$CuCl_2$+ NH4Cl	1/2	Class 1

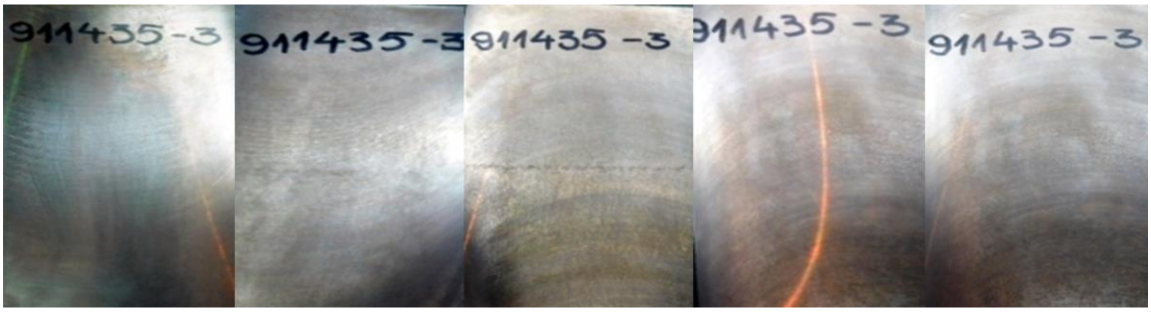

Fig. 5. *Central segregation and defective core class 2, wire 1*

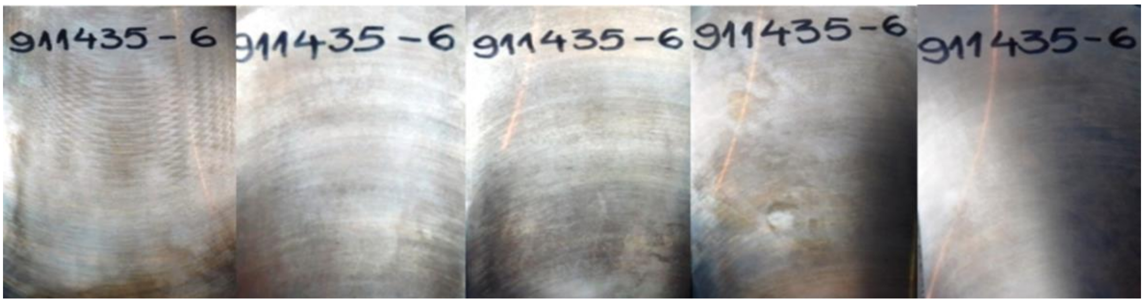

Fig. 6. *Central segregation and defective core class 1, wire 2*

Table 7. *Faults in frames according to API-5L / 95* [4, 5]

Surface defects	**Type**	**Causes**
Cracks	longitudinal	longitudinal uneven cooling in the crystallizer
	transversal	transversal adhesion of the steel to the walls of the crystallizer
	lateral	lateral abrasions of the crystallizer walls
	marginal	marginal sealing improper at the beginning
		temperature and high casting speed
		defective alignment of the supporting rolls
Microcavities and non-metallic inclusions		low temperature of steel
		oxidation of steel in crystallizer
		inadequate dry distributor

		inclusions of pouring powder
		impure steel with non-metallic inclusions
		driving crusts of solidified steel in crystallizer
		inadequate deoxidation of steel when making it
Internal defects		
Segregation at the center and defective cores		Improper casting temperature
Non-metallic inclusions	inclusions of pouring powder	
	local inclusions	excessive turbulent local of the steel in the crystallizer
	slag inclusions	refractory exfoliated material
	inclusions in the form of clouds	slag drive from distributor to crystallizer
	inclusions below the surface	

Fig. 7. *Surface cracks*

Fig. 8. *Deep longitudinal cracks*

Following some structural analysis presented in Fig. 9, it resulted that the microstructure noted with 1 shows that the analysed steel purity is very good, max. 1 in conformity with the existing standards. The steel is clean and globular inclusions rarely occur (sulphides modified as a result of their interaction with Al_2O_3 and CaO).

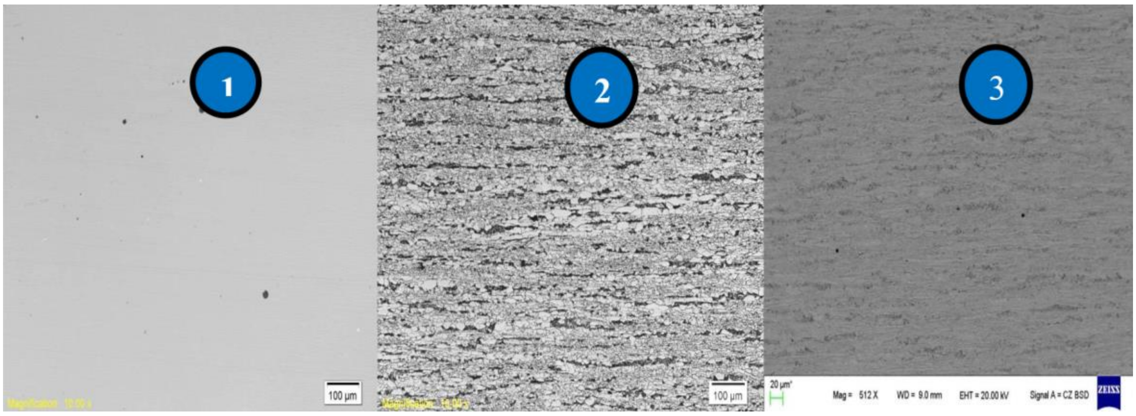

Fig. 9. *SEM images of X70 steel samples (500x), according the, Central Laboratory analysis of Liberty Steel Group Galati*

The microstructures noted with 2 and 3 are fine, with some granulation zones 8-9 and a ferrito-perlitic structure. These structures ensure good deformability [8].

3. Conclusions

For deoxidation and microalloying, iron alloys are used but they have strictly limited content of harmful elements (P, S). LF microalloying materials such as: Mn-99%, Al-99%, FeTi-70%, FeV-80%, FeNb-65%, Ca-99% or SiCa-60/30% are introduced into the steel as tubular iron -alloys and not chunks.

In this way, the superior assimilation and homogeneous diffusion of the elements into the metal bath are achieved.

Secondary treatment of the X70 steel for chemical and thermal homogenization of the metal bath is achieved by advanced metal bath desulfurization using synthetic slag, lime and bauxite. Vacuum degassing with RH procedure is done to reduce hydrogen from 8-9 ppm to less than 2 ppm. At the continuous casting of these steel types, the bubbling is not used because it is intended that the floating of inclusions be easier on the surface of the metal bath.

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