IDENTIFYING THE PHYSICO-CHEMICAL ELABORATION MECHANISMS FOR STEEL THAT AFFECT THE PURITY OF SEMIFINISHED PRODUCTS FOR PIPES

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In order to identify the physico-chemical mechanisms of genesis and the development of non-metallic inclusions in semifinished products for the manufacture of pipes, samples were taken from laminated pipes and analyzed by electronic microscopy (SEM-EDS) and the results were correlated with data regarding the applied technology (history of the batches from which the samples originated). The results highlighted the technological causes of the non-metallic inclusions and identified 4 mechanisms of genesis and developments of the non-metallic inclusions in three aggregates of the steel manufacturing process: oven furnace (LF), the dispensed and the crystallizer from continuous casting (TC).

Keywords: non-metallic inclusions, inclusion purity, steel, pipes

1. Introduction

Defining the purity of steels [1,2,3,4] is based on two types of expressions: on one hand "clean steel" and related, "cleaner steel" and on the other hand "pure steel" and "steel purity". It should be noted that "steel purity" means the maximum amount of unwanted elements in the composition of the steel (P, S, H, N, O, sometimes Cr, Cu, Ni, As, nonmetallic inclusions) while "clean steel" means only pure steel with no nonmetallic inclusions (NMI). Non-metallic inclusions are particles that have been trapped in the base matrix of the steel during its solidification process, and constitute inhomogeneities that will have a different behavior from the base mass in the heating-deformation processes of the steel

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(due to the different melting temperature and their different coefficient of expansion which involves different plasticity). These behavioral differences are primordial for the defects of the semifinished products (cracks, fissures) occurring in the solidification, plastic deformation processes or in the material exploitation processes.

2. Inclusion purity indicators for semifinished products for pipes

Depending on the compounds they incorporate, non-metallic inclusions may be oxides, sulphides, nitrides, oxisulfides, carbonitrides, phosphides, and depending on their morphology, they may be globular, filiform, polyhedral, deformable or not. The size of non-metallic inclusions (equivalent diameter) is a first indicator that provides a measurable image of steel purity: some authors [1] consider a limit of 100 µm below which NMIs are considered microinclusions and others [4,5,6] lower this limit to 50 µm; those beyond this limit are considered macroinclusions. If microinclusions can have a beneficial effect up to a maximum of 5 µm, limiting the excessive growth of grains, macroinclusions are not desirable in any case. In steels for pipes there is a limit of NMI size at 100 µm, or even below [4,7,8], but the total volume of these NMIs is also important. Non-metallic inclusions that are hard and un-deformable usually lead to fatigue cracks in the material [9].

From the point of view of their origin, NMIs are of exogenous type (from interaction with refractory material, added material) or endogenous type (from metallurgical reactions - dewaxing, deoxidation, desulphurisation). Looking at the problem through the nature of the INM, there is a measure of the state of inclusion: the chemical composition of the steel relative to the unwanted elements that form or will form the INM from the liquid state of the steel: P, S, C, N, O. All these chemical elements, as well as others (Q_{total}, H), are now possible to measure in real-time (less than 200 seconds) in order to take the necessary technological precautions. For example, a limitation of the Q_{total} content to a maximum of 30 ppm, S to 30 µm and N to 50 ppm is currently desirable for pipes for pipes and pipes [7]. The content of Q_{total}, however, provides only information about the amount of microinclusions. Macroclusions are difficult to capture through the current sampling system. The chemical composition of steel, however, says few things about the solidity of steel, therefore indirect methods of measuring steel purity (high resolution microscopy, image analysis, qualitative and quantitative chemical microanalysis) are needed in the calibration phases of technological processes and post factum expertise for unwanted events (in this case, it is possible to highlight both micro and macroinclusions, which are the most dangerous.

There are statistical indicators of the purity of steels that industrial and experimental practice of some manufacturers have imposed on them. For steels treated with Al, Al-Si or Si, a superpure steel must simultaneously fulfill several criteria [10]:

- Number of non-metallic inclusions/cm^2 < 500;
- Maximum diameter of each inclusion: max. 10 μm;
- Dimensional fraction over 5 μm: < 10%.

In the case of steels developed for pipes, a MIDAS purity index of <10 characterizes a clean steel [11]. The quality of the steel can also be influenced by the purity of the ferroalloy that is added during secondary refining and deoxidizing of the product which can also introduce inclusions into the melt. [12,13]

3. Electron microscopy investigations on the state of inclusionary purity

Inclusion purity investigations were performed on a batch of 18 continuously cast steel samples that were rolled into pipes. The production flow and the technology used to obtain the continuous castings was of the "minimill" type. This manufacturing technological flow comprises: the "eccentric bottom taping" arc furnace - EBT; liquid furnace treatment plant of the "ladle furnace" type - LF; the wire and tube injection system filled with reagent material in wire feeding - WF; the liquid degassing treatment plant of “vacuum degassing” type - VD; continuous casting machine - MTC. The products of this technological flow are the steel billets in the forms of: round billets with diameters: 177, 220, 250, 280 and 350 mm and the blums with section: 260 x 340 mm of various grades of steel: (EN 10216-2, ASTM A106, ASTM A179) for the purpose of manufacturing hot-rolled or cold-rolled seamless pipes.

Within this technology there are technological processes defined by parameters whose effect is also to ensure the purity of the semifinished products: dewaxing melting under foaming slag, retention of primary slag in the EBT aggregate, deoxidation by precipitation and by diffusion, desulphurisation, controlled decanting, refining under vacuum, controlled modification of the nature and form of non-metallic inclusions, protection against secondary reoxidation.

The results of the 18 purity investigations with the electron microscopic (SEM-EDS) are shown in Table 1. It was considered useful to carry out purity analyses in particular to evaluate the microporous state to know the overall purity of the material. The analysis carried out led to the general conclusion that microcarrier purity at micro level (INM <50 μm) is generally good and at macroscopic level (INM> 50 μm) some sporadic defects appear (only one sample from 18 - sample 3) probably due to some dysfunctionalities in the technological process, especially in the protection part of the liquid steel against the interpenetration of the casting powder and the reoxidations.

Table 1.

Results of purity investigations by electronic microscopy

Sample	Chemical Composition, %						Size and shape of NMI, µm	Mineralogical composition
	O	Na	Al	Si	S	Ca		
1	27,02	5,79	1,37	0,60	0,05	0,60	Multiple polyhedric clusters, ~ 50	Casting powders with reoxidations
2	34,07	2,84	2,03	0,71	0,04	0,18	Multiple polyhedric clusters, ~ 40	Ti=21,40 Casting powders with reoxidations
3	25,97	4,98	0,29	0,20	0,08	0,25	Multiple polyhedric clusters, 30 - 100	Casting powders with reoxidations
4	35,90	-	26,30	0,37	0,26	32,15	Lightly rounded polyhedra agglomerations < 20	Mg = 1,86 - Calco-alumina + sulfides and possibly refractory material
5	26,25	-	23,45	0,49	0,29	16,92	Partially globular < 10	Mg = 2,09 - Calco-alumina + Ca modified sulfides and refractory material
6	30,61	-	19,43	0,42	0,14	27,20	Partially globular < 20	Calco-alumina + Ca modified sulfides
7	33,23	-	24,17	0,51	0,40	26,93	Partially globular < 10	Mg = 1,97 - Calco-alumina and refractory material
8	42,62	-	20,40	1,10	0,22	22,61	Partially globular < 10	Mg = 2,03 - Calco-alumina + sulfides and possibly refractory material
9	38,08	-	24,81	0,16	0,55	32,52	Partially globular < 10	Mg = 2,06 - Calco-alumina + sulfides and possibly refractory material
10	17,79	-	6,08	3,20	0,45	4,24	Partially polyhedral < 10	Mg = 1,02 – Fe oxides from reoxidation, Calcoaluminates + Sulphides
11	16.89	-	3.39	0.74	0.36	1.21	Polyhedral < 10	Mg = 1,53 - Fe oxides from reoxidation, + Sulphides
12	37.87	K= 0.40	23.13	3.56	0.22	22.97	Partially globular < 10	Mg = 2,75 - Calco-alumina + sulfides and possibly refractory material
13	30.42	4.53	39.16	1.17	-	1.19	Polyhedral < 20	Casting powder Deoxidation alumina and Fe oxides
14	19.97	3.99	29.65	1.45	0.06	0.72	Polyhedral < 20	Casting powder Deoxidation alumina and Fe oxides
15	41.25	2.28	49.79	0.50	-	1.76	Polyhedral	Casting powder

							< 20	Deoxidation alumina
16	56.96	-	25.12	0.31	0.05		Globular ~ 50	Mg = 11.51 - Alumina from deoxidation and refractory material
17	54.00	-	28.89	0.58	-		Globular~ 30	Mg = 14,38 - Alumina from deoxidation and refractory material
18	51.07	-	23.08	0.87	0.16		Globular~ 30	Mg = 2,01 - Deoxidation alumina, calcoaluminates and refractory material

Fig. 1 shows the images of the typical inclusions investigated for the sample with the highest inclusions.

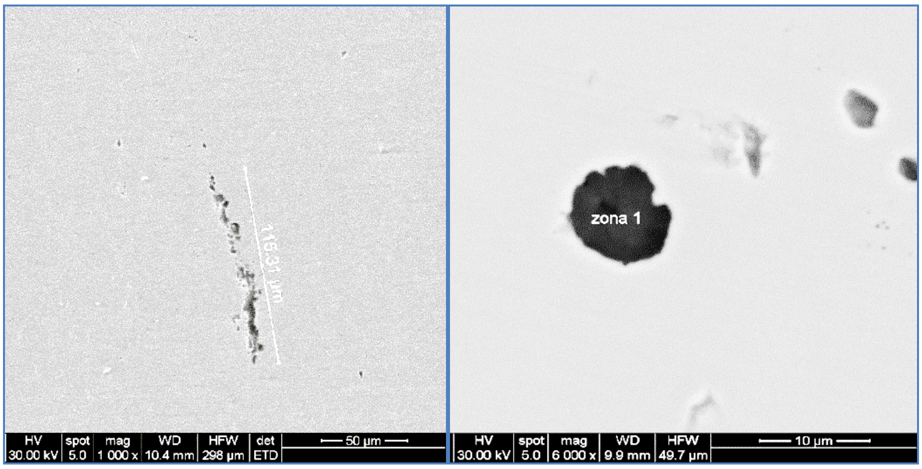

Fig.1. Typical Inclusions - Batch 3

In Figs. 2 and 3 are presented the EDS spectrum and the map of homogeneity of the spherical inclusion elements of Fig. 1.

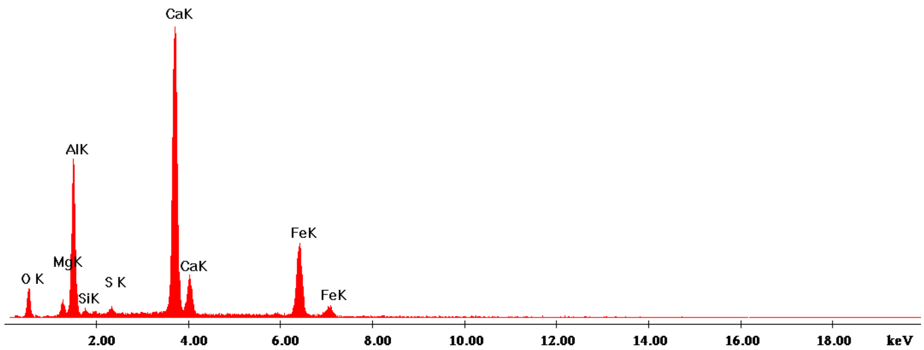

Fig.2. The energy dispersive X-ray spectrum (EDAX) obtained on the spherical inclusion microarray of Fig. 1 - zone 1. The presence of **O, Mg, Al, Si, S, Ca** and **Fe** elements is observed in this microarray;

The evaluation of the purity status for the 18 samples showed:

- Inclusions determined at micro level are in the size range 10-50 µm;
- The average size of inclusion at micro level is ~ 15 µm;
- At the macro level (NMI> 50 µm) sporadic non - metallic inclusions with a size of ~ 100 µm appear;
- the form of macroscopic inclusions is generally a polyhedral cluster;
- SEM-EDS assessments have shown that nonmetallic inclusions have a variable oxygen content (16-56%), aluminum (0-40%), calcium (0-32%), iron (0-80%), sulfur and sporadic presence of marker elements (Na, Cl, K);
    - the different chemical composition of these non-metallic inclusions also reveals a different mineralogical composition, simple oxides of Fe, Si, Al, Ca, partially globulised alumina, insufficiently modified, only partly modified sulphides.

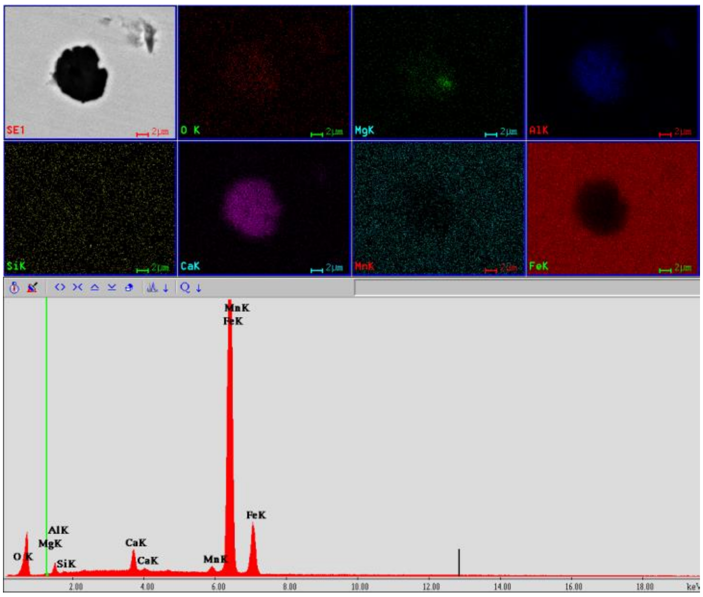

Fig. 3. **a)** At the bottom of the image is the energy dispersive X-ray spectrum (EDAX) obtained on the entire microarray of Fig. 1 including spherical inclusion. The presence of the elements: **O, Mg, Al, Si, Ca, Mn** and **Fe** in this micro-area is observed; **b)** In the upper left corner of the image, the aspect of the analyzed microarray is also shown in Fig. 1; **c)** the other image frames show the characteristic X-ray distribution in the microarray in the top left frame of the image.

4. Establishment of genesis and development of non-metallic inclusions

In order to complete the necessary information to determine the genesis and the development of the investigated non-metallic inclusions, the data related to the applied technology (the history of the batches from which the investigated samples originate) were taken into consideration.

On the basis of all these data the causes of the occurrence of these non-metallic inclusions were identified, each sample (batch) having even multiple causes for the occurrence of these inclusions..

Fig. 2 shows the causal frequency for the sample batch analyzed.

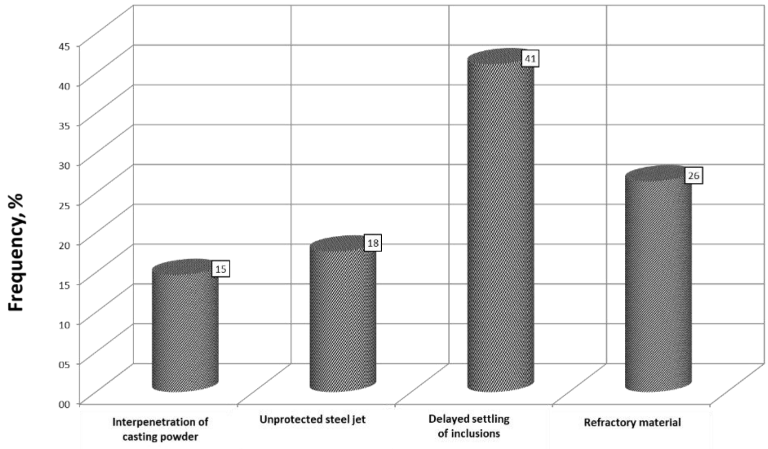

Fig. 4. Frequency of causes of occurrence of non-metallic inclusions

The data presented in Fig. 4 shows the following:

a) the most common cause (41%) that causes NMI is delayed settling; this phenomenon is related to four possible insufficiently controlled processes:
   - an incomplete NMI decanting in the LF / VD treatment pot (inconsistent bubbling) eventually with an unfinished de-oxidation;
   - an incomplete NMI decanting after SiCa immersion (too intense bubbling, too low thermal regime);
   - an incomplete NMI decanting in the distributor (too low steel level and too sudden level variations, inadequate distributor geometry);
   - an unfinished NMI decanting even in the crystallizer (too low steel level and too sudden level variations, inadequate geometry of nozzles);

b) Detection of refractory material (based on MgO) in the analyzed non-metallic inclusions implies a possible low durability of the pot-distributor assembly and a possible inappropriate thermal regime;

c) Unprotected steel jet (with massive generation of Fe and Fe) includes several possible phenomena: oxygen pot openings, reoxidations due to insufficient protection of the two jets, low levels in the two steel tanks, and even interpenetration of airborne casting / coating dust;

d) the cause of the casting / coating dust interference due to the inconsistent level in the distributor / crystallizer remains a significant phenomenon.

For each of the 18 batches, a mechanism of genesis and development of the non-metallic inclusions analyzed was proposed, depending on the technological stage traveled (Table 2).

Table 2.

Mechanisms of genesis and development of non-metallic inclusions

Sample Nr.	LF treatment (in the pot)	CC Distributor (Continuous Casting)	CC crystalliser (continuous casting)
1	Opening with oxygen (Formation of $FeO+Al_2O_3$)	Low level (Poor settling)	Large / sudden level changes (interpenetration of casting powder)
2	Opening with oxygen (Formation of $FeO+Al_2O_3$)	Low level (Poor settling)	Large / sudden level changes (interpenetration of casting powder)
3	Opening with oxygen (Formation of $FeO+Al_2O_3$)	Low level (Poor settling)	Large / sudden level changes (interpenetration of casting powder)
4	Delayed inclusionary settling Intense shearing of the liner	Low level (Poor settling) Intense shearing of the liner	-
5	Reduced Ca treatment Delayed inclusionary settling Intense shearing of the liner	Shearing of refractory liner	-
6	Reduced Ca treatment Delayed inclusionary settling	-	-
7	Reduced Ca treatment Delayed inclusionary settling Intense shearing of the liner	Shearing of refractory liner	-
8	Reduced Ca treatment Delayed inclusionary settling Intense shearing of the liner	Shearing of refractory liner	-
9	Reduced Ca treatment Delayed inclusionary settling Intense shearing of the liner	Shearing of refractory liner	-
10	Opening with oxygen (Formation of $FeO+Al_2O_3$) Delayed inclusionary settling	Reoxidation Delayed inclusionary settling	Reoxidation Delayed inclusionary settling
11	Opening with oxygen (Formation of $FeO+Al_2O_3$) Delayed inclusionary settling	Reoxidation Delayed inclusionary settling	Reoxidation Delayed inclusionary settling
12	Reduced Ca treatment Delayed inclusionary settling Intense shearing of the liner	Shearing of refractory liner	-
13	Reduced Ca treatment Delayed inclusionary settling	Reoxidation Delayed inclusionary settling	Large / sudden level changes (interpenetration of casting powder) Reoxidation Delayed inclusionary settling
14	Reduced Ca treatment Delayed inclusionary settling	Reoxidation Delayed inclusionary settling	Large / sudden level changes (interpenetration of casting powder)

			Reoxidation Delayed inclusionary settling
15	Reduced Ca treatment Delayed inclusionary settling	Delayed inclusionary settling	Large / sudden level changes (interpenetration of casting powder) Delayed inclusionary settling
16	Reduced Ca treatment Delayed inclusionary settling Intense shearing of the liner	Delayed inclusionary settling Intense shearing of the liner	Delayed inclusionary settling
17	Reduced Ca treatment Delayed inclusionary settling Intense shearing of the liner	Delayed inclusionary settling Intense shearing of the liner	Delayed inclusionary settling
18	Reduced Ca treatment Delayed incidence settling Intense shearing of the liner	Delayed incidence settling Intense shearing of the liner	Delayed inclusionary settling

The data presented in Table 2 shows the existence of 4 main mechanisms of genesis and development of NMI in the case of the analyzed sample batches and originators:

1. Opening the oxygen casting pot ($FeO + Al_2O_3$ formation) - Low level of steel in the distributor (lean and delayed settling) - Large / sudden variations in the steel level in the crystallizer (interpenetration of the lubricant powder);
2. Inappropriate bubbling in the casting chamber (lean and delayed settling) - Intense shearing of the refractory liner and distributor liner (refractory mixture in steel) - Low level of steel in the distributor (lean and delayed settling)
3. Reduced Ca in the pot (alumina inclusions in the immersion tubes with sudden detachment) - Low level of steel in the distributor (lean and delayed settling);
4. Opening of the oxygen casting pot ($FeO + Al_2O_3$ formation) - Residuals in the distributor and crystallizer (incorrectly protected) - Low level of steel in the distributor (lean and delayed settling) - Turbulent flow in the crystallizer (lean and delayed settling).

5. Conclusions

1. The most common cause (41%) that causes non-metallic inclusions in pipe semifinished products is delayed settling; this phenomenon is related to four possible insufficiently controlled processes;

2. In the production of liquid steel, 4 mechanisms of genesis and development of non-metallic inclusions were identified in relation to the three main aggregates through which it is passed: the furnace vessel (LF), the dispenser and the continuous casting crystallizer (TC) ; Large / sudden variations of steel level in the crystallizer;

3. The four mechanisms identified are based on technological deviations: opening oxygen casting pot; low level of steel in the distributor; inappropriate bubbling in the pouring chamber; re-oxidation in the distributor and crystallizator; intense erosion of the refractory liner and distributor liner; re-oxidation in the distributor and crystallizator; turbulent flow in the crystallizer

R E F E R E N C E S

[1] *S. Kumar*, Inclusion Control for Clean Steel, [http://www.slideshare.net/santosh178/ inclusion-control-for-clean-steel], 2002.

[2] *L. Zhang, X. Wang*, Evaluation and Control of Steel Cleanliness-Review, 85th Steelmaking Conference Prpceeding, ISS-AIME, Warrendale, PA, 2002, pp. 431-452.

[3] *C Mappeli*, Non-Metallic Inclusions and Clean Steel, La Metalurgia Italiana, **vol. 100**, no. 6, 2008, 43-52.

[4] *V. Ludlow*, Oxygen Requirements from an end-user Viewpoint, Oxygen in Steel-Towards cleaner Steels, Institute Of Metals Communications, London, 2001.

[5] *D. Mazumdar*, *S.C. Koria*, Steelmaking, Departament of Materials Science and Engineering, Indian Institute of Technology, Kanpur, Module No. 1, Lecture No.23.

[6] *J.P. Birrat*, Steel Cleanliness and Environmental Metallurgy, Metall Research Technology, **vol. 113**, 2016, pp. 201-225.

[7] *K.S. Satyendra*, Non-metal inclusions in steel, ispatguru.com, 2015.

[8] *T. Ototani*, Calcium Clean Steel, Springer-Verlag Berlin Heidelberg, 1986.

[9] *Y. Tang*, Effect of slag composition on inclusion control in LF-VD process for ultra-low oxygen alloyed structural steel, Procedia Earth and Planetary Science, **vol. 2**, 2011, pp. 89-97.

[10] *A. Scamarda, G. Maccio*, Effect of Calcium in Al-Si Killed Clean Steel, 7th European Electric Steelmaking Conference, Venice, 2002.

[11] *B. Debiesme, I. Poissonnet, P. Choquet, F. Penet*, Steel Cleanliness at Sollac Dunkerque, International Conference Clean Steel 4, Balaton, 1992.

[12] *P. Han, S. Chu, P. Mei, Y. Lin*, Oxide inclusions in ferromanganese and its influence on the quality of clean steels, International Journal of Iron and Steel Research, **vol. 21**, 2014, pp. 23-27.

[13] *G. Coman, S. Ciuca, A. Berbecaru, C. Pantilimon, M. Sohaciu, C. Gradinaru, C. Predescu*, New Martensitic Stainless Steel Hardenable by Precipitation for Hydropower Turbines, University Politehnica of Bucharest Scientific Bulletin Series B-Chemistry And Materials Science, **vol. 79**, 2017, pp. 209-218.