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DEGRADATION OF CERAMIC MATERIALS IN THERMOTECHNICAL PLANTS

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ABSTRACT

It is demonstrated that the degradation of materials is currently a poorly studied scientific area. We propose a definition of degradation and a classification of the types of degradation. It is investigated, using a technical model, the destructive interactions between the ceramic materials of the tundish refractory lining, in a continuous steel casting plant. We hereby present the experimental results regarding:

- the importance of the steel penetration depth in the refractory ceramic mass;
- the assessment of mineralogical degradation;
- the analysis of chemical degradation.

It is shown that the results of laboratory - pilot scale research can be extended to the industrial level.

KEYWORDS: materials, degradation, continuous casting, ceramic - liquid steel interaction

1. Introduction

The research on the ways to maximize the performance in metalworking engineering must be currently designed and operationalized on the coordinates of two modern evolution concepts (models):

- global knowledge;
- durable and sustainable development of the society.

In such a context, it becomes necessary for the metalworking engineer to investigate the inter-conditioning and interactions existing in the convergence areas of the three systems:

- the social system - S.S. (the quality of life in relation to the socio-cultural needs);
- the natural-ecological system - N.E.S. (the quality of environment in relation to the prevention of environmental pollution);
- the technological system - T.S. in connection with the qualitative maximization of the technological parameters of manufacturing and use of metal materials.

The material degradation is the major process (phenomenon, event) that causes the material quality alteration throughout its lifecycle (l.c.). Degradation is a multisystem (inter- or intra-) process because:

- it directly determines the durability of materials and products, i.e. their social utility;
- it influences the process of primary material transformation into secondary material (waste or residue), which are polluting substances;
- it can have a negative effect on the quality of material manufacturing processes and the durability of the components used in the industrial equipment and plants [3, 4].

The importance of knowing the degradation of materials derives from the fact that it penetrates the whole life cycle, i.e. the entire flow [design of material] [transformation of material into pollutant residue] (Fig. 1).

Possible degradation during the designing activity	Possible degradation when providing resources	Possible degradation during the manufacture of metal materials		Possible degradation when using the materials	Possible degradation in the relationship with the environment
		Melting, casting and solidification	Solid metal processing		

Fig. 1. *Succession of possible material degradation processes over the lifecycle phases*

The final quality of metal material is clearly influenced by the quality of the melting, casting and solidification processes [1, 2]. From the phenomena to be investigated in this case, a significant role is played by the steel quality degradation at continuous casting (C.T.) in continuous casting plants (C.C.P.), resulting from two processes-phenomena which are very important for the ferrous materials engineering [3, 4]:

- degradation of metal bathes caused by impurities;

- degradation of the ceramic materials used for building the C.C.P., caused by the melted steel - ceramic destructive interactions (it is about the ceramic materials that make up the refractory lining of the tundish, an important component of the C.C.P.).

The authors believe that there are several categories of degradation [10], as follows:

a) depending on the lifecycle phase:

a.1.) technological degradation caused by the degradation of processes during the material manufacture; this one may be called process degradation;

a.2.) use degradation

b) depending on the determinant causes:

b.1.) objective degradation caused by some processes that cannot be avoided, but only reduced; in this category fall such examples:

- degradation caused by the metal melts impurification with inclusions and degradation caused by the destruction of ceramics by the melted steel - refractory ceramic lining interactions;

- metal corrosion in the environment or in the working environments, which exercise destructive actions [11].

b.2) subjective degradation, caused by dysfunctions between the measures adopted in designing and process management (imposed specifications) and the actual operationalization conditions [5, 7].

2. Purpose of research. Studied materials. Research methodology elements

2.1. Purpose of research

In general, research can target the extensive area of degradation knowledge, i.e. the area of double interest for degradation, which is the sphere of phenomena occurring between:

The area of metallurgical melts (area of major interest for the metallurgical technology of steelmaking-casting-solidification), where the endogenous inclusions generation processes occur.

The area of the ceramic materials of the plant lining (area of interest for the manufacturer of ceramic materials), which is analyzed from two points of view:

- the ceramic material as participant in generating exogenous inclusions based on physical-chemical interactions with the metallurgical melts;
- the ceramic material as component subject to internal degradation caused by the corrosive interactions with the metallurgical melts.

2.2. Studied materials

The degradation interactions are developing along two material vectors:

- the melted steel, and
- the ceramic material of the refractory lining.

a) steel grades

Three steel grades have been studies (Table 1).

b) studied ceramic mixtures

The ceramic mixtures (C.M.) were prepared using materials whose compositions are shown in Table 2.

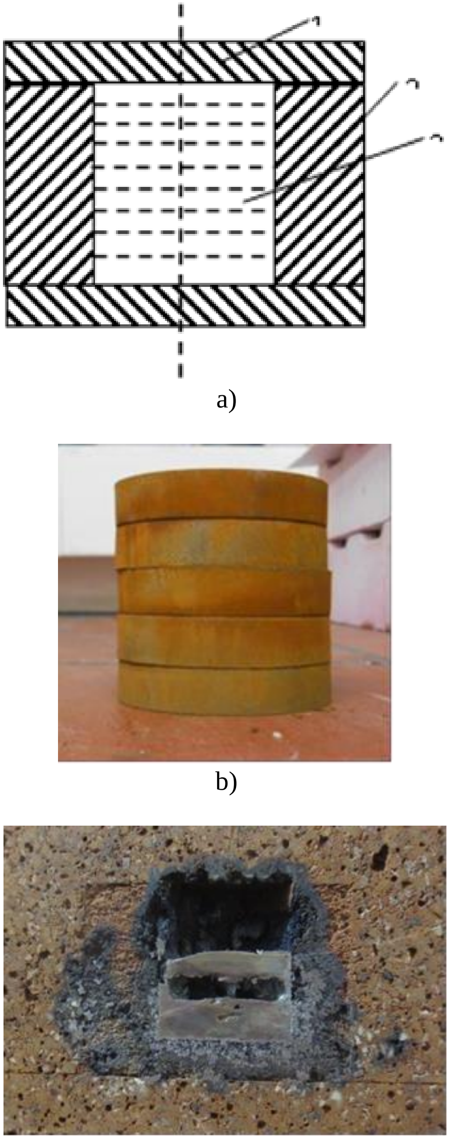
Table 2. *C.M. compositions*

Designation	Symbol	Composition				
		MgO %	CaO %	SiO_2 %	Fe_2O_3 %	Al_2O_3 %
Pure magnesia	M.C.M.	93.4	3.1	2.9	0.5	0.1
Low silica magnesia	L.S.M.C.M.	80.8	2	14.4	2.6	0.1
Medium silica	M.S.M.C.M.	66.0	1	26.7	5.1	0.6
Lime magnesia	L.M.C.M.	80.4	14	1	4	0.6

2.3. Research methodology elements

The Physical-Technological Investigation Model is a pilot plant for studying the ceramic - liquid steel interaction processes.

In fact, it is a crucible made according to the general scheme shown in Figure 2.2.



a)

b)

c)

Fig. 2. *Elements of designing and modelling: a) Sketch of the crucible: 1 - cover; 2 - crucible body (refractory lining made of ceramic mixture - C.M.); 3 - Steel under investigation. b) Steel discs. c) Sample cut for analyses*

The experimentation technology

- the crucible is filled with discs of the steel to be studied;

- the crucible returns to the oven to heat and melt the steel at 1600 °C for 10 hours;

- the assembly is left for two days for cooling and solidification;

- the area (sample) to be studied is cut out.

The research equipment

In the research, two analytical methods of investigation were used:

- mineralogical investigations (reflected light microscope and SEM scanning electron microscope) and

- chemical analysis (X-ray fluorescence spectrometer).

The research situations (E1...E12) resulted from the combination in various variants of the two materials marked with special symbols (Tables 1 and 2).

The grid of research situations with the experiment numbers (E) are shown in Table 3.

Table 3. *Symbolization of experimental cases*

	M.C. M.	L.S.M. C.M.	M.S.M. C.M.	L.M.C. M.
L.C.S.	E 1	E 2	E 3	E 4
V.L. C.S.	E 5	E 6	E 7	E 8
B.S.	E 9	E 10	E 11	E 12

The parameters used for assessing the degradation were:

- penetration depth of steel in the ceramic material mass, ap [mm];

- mineralogical degradation, assessed by mineralogical transformations of ceramic components;

- chemical degradation, assessed by the chemical composition changes.

The cooling rate, v_r, of the melted steel in the ceramic mass and its influence on the degradation could not be established experimentally for objective reasons, which is why the authors used assessments based on the thermophysical properties of the ceramic materials. They started from this idea since the cooling rate of the melt is dependent on the thermal diffusivity coefficient “a” [m/s] of the ceramic material:

$$v_r = f(a) \tag{1}$$

In turn, the coefficient “a” is given by the equation:

$$a = \lambda / c \cdot \rho \tag{2}$$

Where “λ” is the thermal conductivity coefficient [w/m·degree], “c” is the specific heat [J/kg·degree], and “ρ” is the density [kg/m^3].

The values that have been used are shown in Table 4.

Table 4. *Thermophysical properties*

Material	λ [w/m·gr d.]	c [J/kg·gr d.]	P [kg/m^3]	a·10^3 [m^2/s]
MgO (A.C.M.)	5.02	1.35	2750	1.4
CaO	3.3	1.06	2400	1.25
SiO_2	1.68	1.05	2000	0.8
L.S.M.C.M.				1.28
M.S.M.C.M				1.20
L.M.C.M				1.37

3. Experimental results. Data processing

The degraded area condition (microscopic appearance) of the ceramic material led to results similar to the ones shown as examples in Figure 3.

The mineralogical structure of the degraded layer revealed a number of complexes, but mainly magnesio-wüstite (Fig. 4-6).

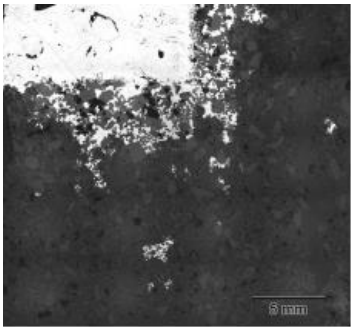


Fig. 3. *Appearance resulted after the E11 experiment: 1 - steel; 2 - penetrated ceramic material*

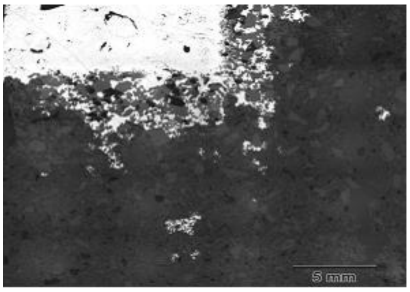


Fig. 4. *Result of research for highlighting the multi-oxide inclusions*

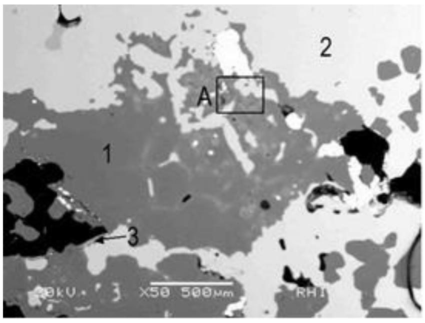


Fig. 5. *Detail of Figure 4: 1 - magnesio-wüstite; 2 - iron; 3 - FeO*

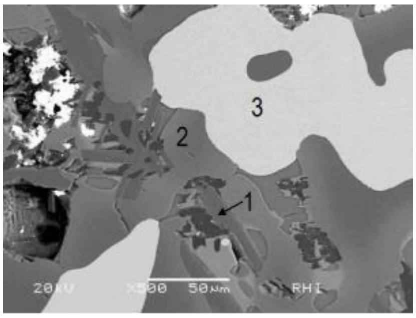


Fig. 6. *Detail of Figure 5: 1 - multi-oxide; 2 - magnesio-wüstite; 3 - iron*

The steel penetration depth, a p, [mm], in the ceramic mixture depends on the steel nature and the ceramic mixture nature (Table 5 and Figure 7).

Table 5. *Penetration depth values, a_p [mm]*

	L.C.S.	V.L.C.S.	B.S.
M.C.M.	7.5	5.5	4.0
L.S.M.C.M.	9.0	8.5	6.0
M.S.M.C.M.	11.0	9.5	7.0
L.M.C.M.	6.5	4.5	3.5

The degradation degree of C.M. has been assessed using the degradation degree of MgO, gd.Mg [%]:

$$g_{d.MgO} = \frac{(MgO)_i - (MgO)_d}{(MgO)_i} \cdot 100 \qquad (3)$$

In the above relationship, $(MgO)_i$ is (MgO) in initial condition, and $(MgO)_d$ are the distances (d1 – d4) from the contact interface.

The changes in chemical composition are caused by the processes:

- reaction;
- diffusion of FeO in MgO with the formation of the magnesio-wüstite compound (Mg, FeO).

The processes mentioned above are in line with the theory of steel processes. [6, 9, 12] The concrete explanation is given in Figure 8.

The experiments were carried out in case of interaction between C.M. and L.C.S. (E2).

The tabular and graphical data processing is presented in Table 6 and Figure 9.

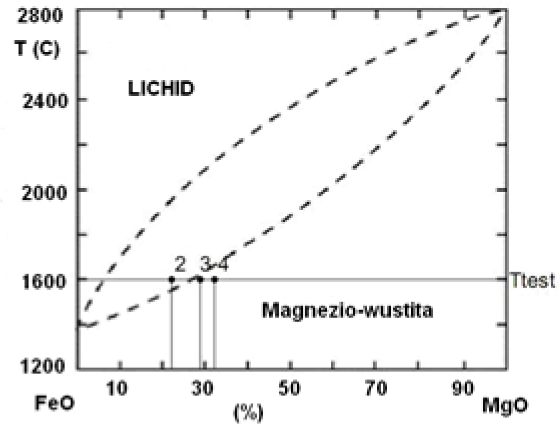


Fig. 8. *Fragment of the FeO-MgO phase diagram [6, 9, 12]:1 – liquid steel at 1600 °C: 2 - magnesia with solid-liquid wüstite; 3 and 4 - magnesia with solid wüstite at 1600 °C*

Table 6. *Results of chemical analyses*

Distance [mm]	Composition		Phases	$g_{d.MgO}$ [%]
	MgO	Fe_2O_3(x)		
$d_1 = 0$	-	100	Metal iron	-
d_2 = 2 mm	22.4	77.6	Magnesia and wüstite	77.6
d_3 = 3 mm	29.2	70.8	Magnesia and wüstite	70.8
d_4 = 4 mm	32.4	67.6	Magnesia and wüstite	67.6

x – Total iron, calculated as Fe_2O_3

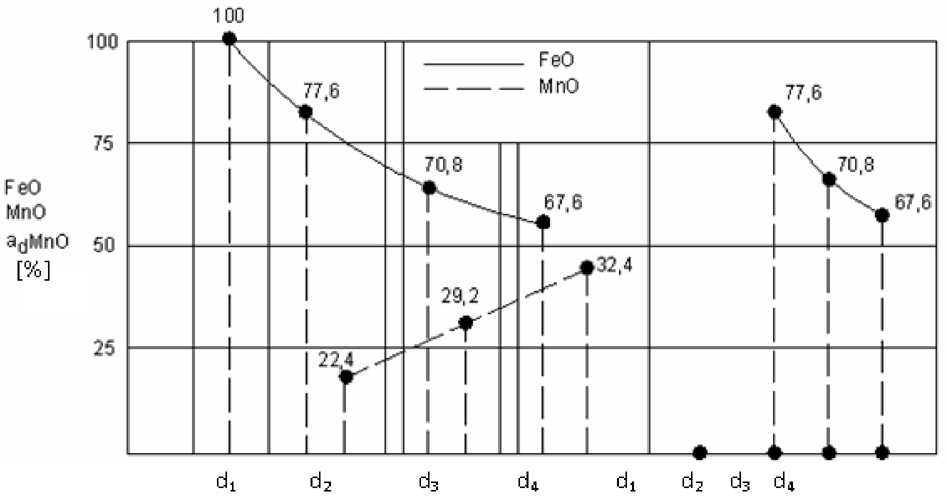


Fig. 9. *Dynamics of chemical and mineralogical transformations*

4. Interpretation of results. Conclusions

The following explanations were found for the influence of ap:

- the depth of penetration is influenced by the fluidity of steel (carbon content variation) and the purity of steel (case of bubbled steel);

- the depth of penetration is influenced by the possible reactions occurring inside the C.M. Therefore, at L.S.M.C.M. it is possible to be generated low-temperature melting constituents:

$$MgO + SiO_2 \rightarrow (MgO \cdot SiO_2)$$

- the depth of penetration is influenced by the ceramic mixture compaction degree. Such a case must be regarded as a subjective deviation from the mixture preparation conformity;

- another reason to be considered is the refractoriness of mixtures, knowing that the melting temperatures of MgO and CaO are higher than that of SiO.;

- it is noted that the degradation of C.M., assessed by ap, can be also influenced by the thermophysical properties of the C.M.;

- the paper points out that the research on material degradation must become a scientifically important segment of materials engineering.

In this respect, the following justifications can be brought forward, knowing that:

- currently, most research topics focus on improving the use performance and less on the degradation phenomena;

- even when the degradation is investigated, the scientists mostly consider the material degradation in the use phase rather than in the primary phases (production and casting);

- this paper demonstrates that the degradation occurs throughout the entire lifecycle of the material;

- the results of pilot-scale research can be extended at the industrial level.

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