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DOCTORAL THESIS (C.C.)

Summary in English (S.E.)

RESEARCH ON MATERIAL DEGRADATION AT THE CONTINUOUS CASTING (C.C.) OF STEEL

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CONTENTS

Key words:

Steel, refractory ceramic materials, early degradation, chemical analyses, structural analyses

Chapter I
INTRODUCTION
REGARDING THE OBJECTIVE-DIALECTICAL CORRELATION BETWEEN MATERIAL DEGRADATION AND PRODUCT QUALITY

The main theme of the thesis is the **material degradation** as a major event determining the variation of *product quality* throughout its *life cycle (l.c.)*. In other words, the *objective-dialectical correlation* between degradation and quality has been investigated.

It should be noted at the outset that there are currently no papers in which a metallurgical engineer deals with the material degradation based on a *theory of degradation*, based in its turn on new methodologies and paradigms.

a) New notions have been defined, as follows:

- Technological degradation;
- Use degradation;
- Process degradation;
- Early degradation;
- Complex degradation.

♦ It is a *complex degradation*, because it involves two kinds of materials: the melted steel subjected to continuous casting (C.C.) and the ceramic materials of the refractory lining, as a construction element of the continuous casting plants (C.C.P.).

♦ The *fundamental phenomena* occurring in the process are *phenomena of interaction between the two materials*, with degrading (destructive) and early degradation effects, materialized in:

- *Generation of inclusions*, which adversely affect the steel quality;
- *Reduction of* ceramic lining *durability* due to the formation of compounds with inferior properties than those of the primary manufacturing materials.

b) The fact that the theory of material degradation must be based on new paradigms is certainly justified:

∗ Performant use and degradation – *Contrary unitary processes* carried out during the life cycle of materials;

∗ Degradation of materials – *ecological process* of generating polluting secondary materials;

∗ Interdependence between degradation and the *function of durable (sustainable) material*.

Chapter II
THE CURRENT STATE OF KNOWLEDGE ABOUT THE MATERIAL DEGRADATION PHENOMENA AT CONTINUOUS CASTING

➢ It is carried out an own analysis of the influence of inclusions found in the steel structure, using the characteristic elements of a new scientific branch, known as *Inclusion Engineering*, based on certain technologies for obtaining the *designed inclusions*.

➢ It is studied the *negative influence* of inclusions on the quality of metallic materials.

➢ It is analysed the possible *positive influence* of the inclusions on the quality of processes and materials.

➢ It is analysed the degradation of refractory ceramic materials found in the C.C.P. linings, as a source of *exogenous inclusions* generation.

Chapter III
RESEARCH OBJECTIVES AND PLAN. RESEARCH METHODOLOGY. EXPERIMENTATION LOCATIONS AND EQUIPMENT

a) Research directions and objectives

This summary presents selectively the following issues:

❖ For this paper, the research will be placed in the wider area of knowledge about degradation, i.e. in the field of *double interest for degradation*, which means the sphere of interaction between the two areas: steel and ceramic material.

❖ The paper will *mainly deal with the phenomena related to exogenous inclusions*. This is because the author found that currently the metallurgists' attention is *mainly focused on the endogenous inclusions*.

❖ A situation like the previous one must show that the metallurgist engineer must schedule researches in *convergence areas*, such as the *metallic material - ceramic material area.*

b) The technological area of placing the researches

Description of the C.C.P. construction and operation

c) Materials under investigation

The degradation interactions occur on two material vectors: molten steel and ceramic material of the tundish refractory lining.

c.1) Steel (S)

Three steel grades have been subjected to research (Table 3.1).

Table 3.1

Steel type	Symbol	Chemical composition								
		C %	Si %	Mn %	P %	S %	Al %	Ti %	Nb %	Cr %
Low carbon steel	L.C.S.	0.0550	0.003	0.178	0.0090	0.0160	0.041	-	-	-
Very low carbon steel	V.L.C.S.	0.0018	0.005	0.090	0.0066	0.0071	0.040	0.046	-	-
Bubbled steel	B.S.	0.033	0.316	1.530	0.0075	0.0006	0.035	0.012	0.045	0.166

c.2) Ceramic mixtures investigated (C.M.)

c.2.1) Chemical compositions

The ceramic mixtures (C.M.) were prepared using materials whose compositions are shown in the Table 3.2.

Table 3.2

Name	Symbol	Composition				
		MgO %	CaO %	SiO_2 %	Fe_2O_3 %	Al_2O_3 %
Pure magnesia	P.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 magnesia	M.S.M.C.M.	66	1	26.7	5.1	0.6
Magnesium lime	M.L.C.M.	80.4	14	1	4	0.6

c.2.2) **Mineralogical characterization**

To assess the chemical-mineralogical degradation of the C.M. components, it becomes necessary to know the initial state of the components.

The structural constituents were identified using the microscopy. The Figure 3.8 is presented as an example.

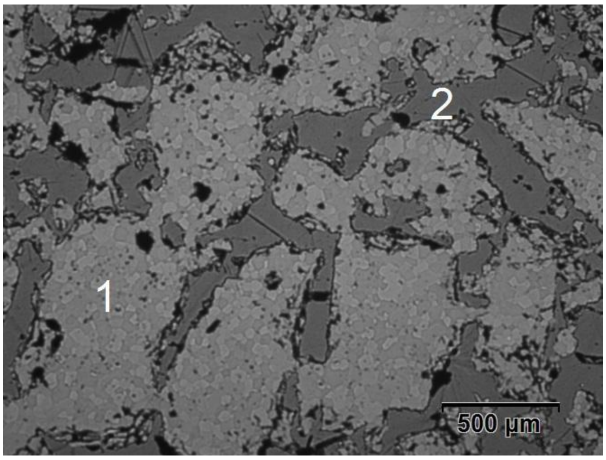

Fig. 3.8. *Structure of P.M.C.M.*
1 – periclase; 2 – pore filled with preparation resin.

d) The research infrastructure

d.1) Research locations

The experiments were conducted at:

– Voest Alpine Linz Research Centre;
– Research & Eco-Metallurgical Expertise Centre, Bucharest.

d.2) Research structures

Twelve experiments resulted from the combination of steel with the ceramic mixtures (E_1 – E12).

Chapter IV
CONTRIBUTIONS TO THE EXPERIMENTAL KNOWLEDGE OF MATERIAL DEGRADATION AT THE CONTINUOUS CASTING OF STEEL
4.1. OWN SCHEMATIZATION OF THE STEEL – CERAMIC MATERIAL INTERACTION PHENOMENA

a) Own interpretation of the interaction phenomena

It has been proposed an own interpretation of the interaction processes that determine the degradation of steel due to inclusions, and the C.M. degradation due to its use.

b) Content and purpose of experiments:

– Experimental research to characterize the material degradation processes at the continuous casting of steel;

– Physical-chemical-mineralogical changes occurred at the degradation of ceramic materials included in the refractory linings of the technological plants;

– Experimental results.

For all 12 experimental situations (E_1 - E_{12}), I aimed to find the following indicators:

– Chemical changes;
– Structural changes;

- Penetration depth, a_p, of the steel into the refractory mass;
- Steel cooling rate, v_r, in the ceramic mixture;
- Degree of chemical-structural degradation, g_d.

c) Research results

The thesis presents the measurement results, the photographic aspects of microscopy analysis (Figures 4.2 - 4.17) and the tables showing the chemical analyses.

For example, the Figures 4.3 and 4.4 are presented in this summary.

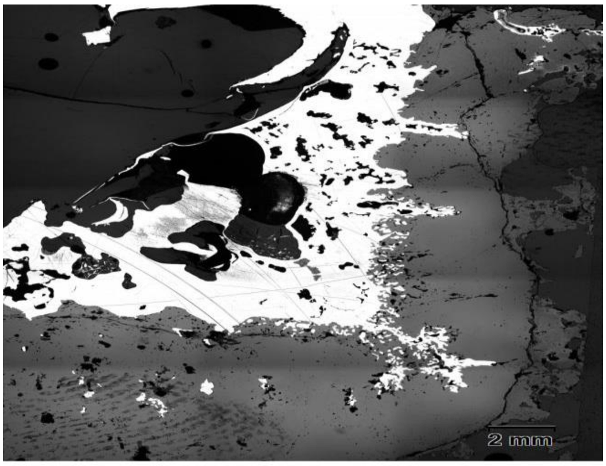

Fig.4.3. *Case of P.M.C.M. - V.L.C.S interaction:* 1 - steel; 2 – penetrated ceramic mixture

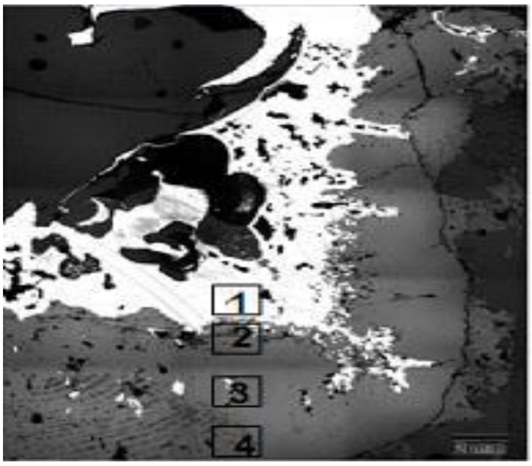

Fig.4.4*. Areas subjected to microscopic analysis*

b) Data processing. Interpretation of results

The *tabular processing* and *graphic processing* of the correlations have been performed, as follows:

- (MgO degradation degree versus the depth of penetration, a_p);
- (Depth of penetration versus the type of ceramic mixture);
- (Depth of penetration versus the conductivity coefficient (a_c) of the ceramic mixture, using the calculated values).

The data processing results are shown in the Tables 4.1-4.4 and Figures 4.6, 4.18, and 4.19.

For example, in this summary is shown the diagram presented in Figure 4.6.

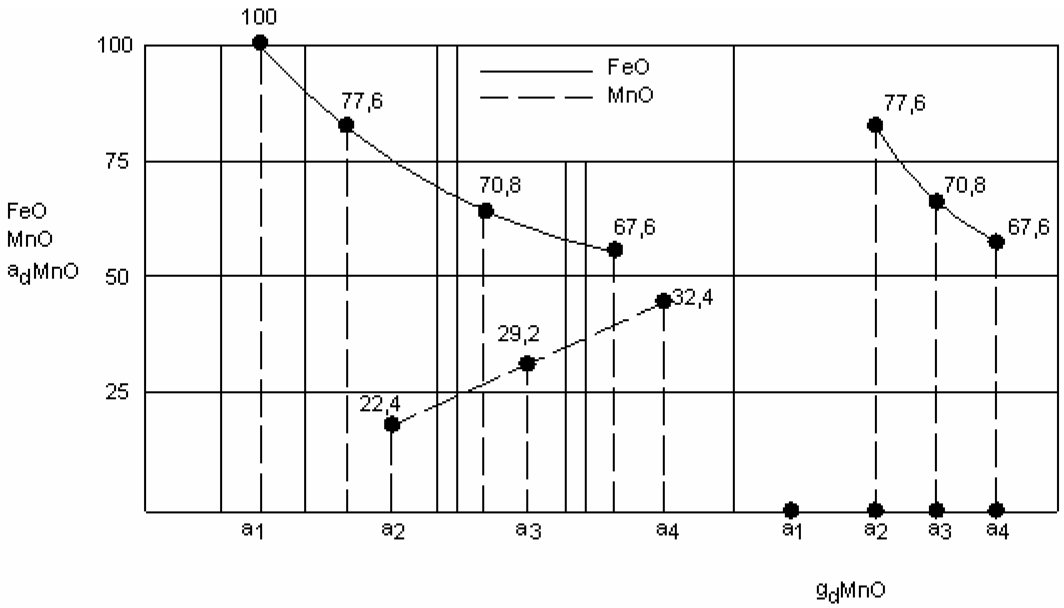

Fig.4.6. *The dynamics of the chemical-mineralogical changes*

e) Generation of exogenous inclusions in the processes of early degradation of steels at C.C.

Two possible situations have been investigated (metal inclusions and non-metallic inclusions), for various steel-C.M. experimental combinatorial situations.

e.1) Generation of metal inclusions

The following situations have been investigated:

- The possibility of nickel droplets formation;
- The possibility of silicon droplets generation, for:
  - The case of low-silica magnesia in contact with low carbon steel;
  - The case of low-silica magnesia in contact with very low carbon steel;
  - The case of low-silica magnesia in contact with bubbled steel.

The thesis presents the measurement results, as well as the results of the structural (Figures 4.20 -4.24) and chemical analyses.

For example, this summary presents the case of nickel droplets formation (Figures 4.20 and 4.21).

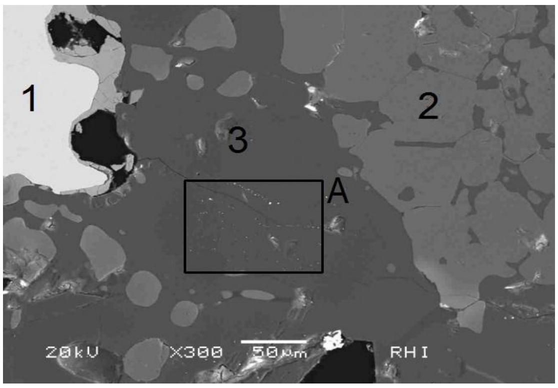

Fig.4.20. *Experiment for searching the Ni formation:*
1 - Iron; 2 - Macerated magnesia; 3 - Olivine

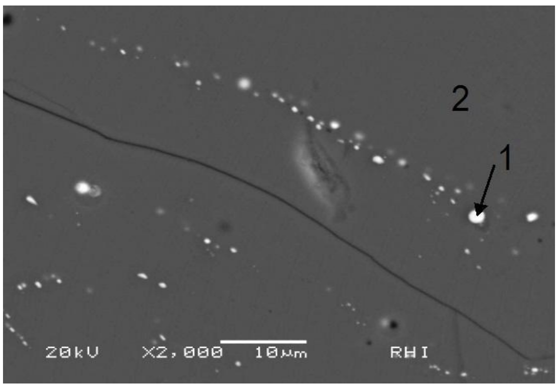

Fig.4.21. *Detail "A" of Figure 4.20:*
1 - Droplets of ferronickel; 2 - Olivine

e.2) Generation of non-metallic inclusions

The generation of non-metallic inclusions has been investigated for:

- Iron oxide in the contact surface;
- Iron oxide in periclase crystals;
- Sulphides;
- Multi-oxide inclusions;
- Inclusions transferred from the ceramic mixture into the metallic melt.

The thesis presents the results of measurements and structural & chemical analyses (Figures 4.25 - 4.71; Tables 4.6 - 4.11).

For example, this summary presents:

- The formation of iron oxide in the contact surface (Figure 4.25);
- EDX analysis for a removable inclusion, selecting the case of interaction between low-silica magnesia and very low carbon steel (Figure 4.44).

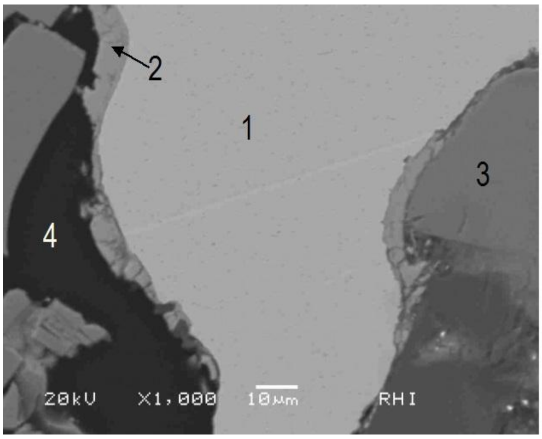

Fig.4.25. *Situation at the interaction between low-silica magnesia and low carbon steel:*
1 - Metallic iron;
2 - FeO;
3 - Magnesium-wüstite;
4 - Preparation pasta

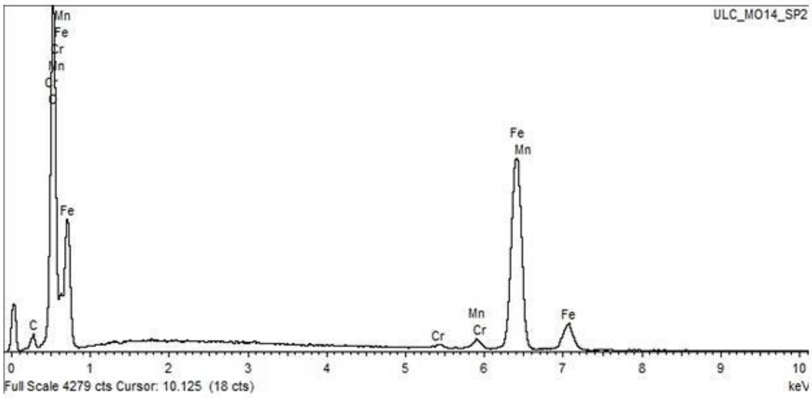

Fig.4.44. *EDX analysis for SP2.*

Chapter V
OWN CONTRIBUTIONS TO ENRICHING THE KNOWLEDGE HERITAGE ABOUT THE DEGRADATION OF MATERIALS

In this summary, the issues below are selectively presented:

a) Launching on the knowledge market of the research on material degradation at continuous casting is itself a novelty initiative, because, by *early degradation*, a material degradation begins in the early stages of its life cycle.

b) Using an *own schematization*, the melting steel - ceramic material interaction processes are *originally* interpreted, according to the recent bibliographic information.

d) *An original pilot model was designed and built*, represented by a crucible lined with the ceramic materials under investigation, in which the desired steel grades were melted.

e) Methods and equipment of the latest generation, found in the laboratories of two prestigious institutions, were used to investigate the steel-ceramic material interactions.

j) The study of C.M. *coefficient of thermal conductivity (a)* influence on the penetration depth was proposed and conducted for the first time.

l) Regarding the influence of inclusions on the steel degradation, this thesis is one of the first extensive papers applying elements of a new technological-scientific field, known as *inclusions engineering.*

m) Depending on the chemical composition of the steel, some droplets of Ni can appear in the C.M. mass, but not droplets of Si.

n) Regarding the exogenous inclusions decanted into the steel, it was found that:

- The inclusions are in small amounts, being included in the MgO particles;
- It is possible to appear *multi-oxide (multi-element) inclusions*, in whose generation all the steel chemistry elements (Ca-Al-Fe-Mg_Si-Ti-Cr-Mn-B-Na-K) are involved;
- The chemical composition of some detected inclusions included FeS and MnS;
- The SEM analyses revealed the diffusion of Fe in the form of FeO in periclase grains, resulting magnesium-wüstite, but there were no droplets of Si or other metals, neither in the steel nor in the ceramic mixture.

p) The SEM analysis of steel, for knowing the possibilities of metal droplet generation, shown that there were no such phenomena for Si, Mn and Mg.

r) The research on the possibilities of generating metal in the ceramic mixture L.S.M. has also shown that:

- The iron oxide (FeO) forms constituents in periclase, but not in olivine;
- There is no possibility of silicon diffusion in periclase, because it was found only in olivine;
- The magnesium concentration in magnesium-wüstite is higher than in olivine.

Chapter VI
FINAL CONCLUSIONS

a) The paper was designed and developed on the coordinates of two *modern concepts (models) of socio-economic evolution:*

- Durable (sustainable) development;
- Global knowledge.

c) In the area of convergence between the natural-ecological system *(environmental engineering)* and the technological system (*material engineering*), the author aimed to investigate the process of **material degradation** as a *phenomenon* of processes, materials and products *quality alteration*.

e) Thus, the author undertook to investigate the *technological degradation.* According to her classification, as opposed to the *use degradation,* the terms "technological degradation" or *"technological process degradation"* means, in the author's view, the *early degradation* of material starting in the manufacturing phase of the life cycle.

f) New aspects of *material degradation theory* are presented and operationalized.

g) The author demonstrates that the study of material degradation should become a major priority for expanding the *global knowledge*, which in the PhD thesis is manifested by knowledge in the intersystem convergence area found between the technological system (metallic materials engineering) and the natural-ecological system (environmental engineering with regard to the transformation of primary materials into wastes or residues caused by degradation).

Chapter VII
THE NEED FOR FURTHER RESEARCH

a) In terms of complex degradation, it becomes necessary to set up joint teams of metallurgical researchers in the field of steel making & casting and ceramics researchers in the field of refractory ceramic material manufacture.

e) It becomes necessary to know the possibilities for optimizing the process parameters in terms of the a_p value. This is proposed because the microscopic research has shown two contradictory processes:

- On the one hand, reactions in the FeO-MnO-SiO_2 system that lead to the occurrence of low melting temperature constituents, but,
- On the other hand, the formation of magnesium-wüstite, which is a dense material and, therefore, it can block the continuous penetration.

f) In a context similar to the above, it would become important to study the processes also in case of changing the ceramic mixtures preparation technology. Thus, the increase C.M. tamping degree may have two effects:

- Lower porosity, and thus lower physical penetration, but also
- Lower amount of air in pores and, therefore, lower amount of FeO, which is leading to the need of lower amount of magnesium-wüstite as a penetration blocking agent.

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