RESEARCH ON LOCAL PROTECTION AGAINST PLASMA NITRIDING USING SPECIAL PAINTS WITH COPPER POWDERS AND MAGNESIA BINDING MATTER SISTEMS

Prof.PhD.eng. Marius BIBU, *Engineering Faculty, "Lucian Blaga" University of Sibiu*
Lecturer PhD. eng. Florin CIOFU, *Engineering Faculty, "Lucian Blaga" University of Sibiu*

ABSTRACT: *As a result of the investigations concerning the elaboration of efficient technologies for local protection of metallic pieces with isolated coats against plasma nitriding, two variants of special paints were elaborated. Those are based on lamella copper powder with a lime magnesia binding system, in which polystyrene was added in an organic solvent. The paper analyses the advantages as a result of the usage in a mixture of magnesium oxide with carbon tetrachloride, advantages as a result of the experiments done with selected types of paints (samples subjected to ionic nitriding in a period of 15 hours at a temperature of 530^{0}C). To check the efficiency of the protection of the elaborated paints, experiments were done comparatively on not protected metallic surfaces (steel 39MoAlCr15) and on metallic surfaces protected by protector films put in three variants of different thickness.*

KEYWORDS: plasma nitriding, special paints, magnesia binding

1. INTRODUCTION

As a result of the experimental researches regarding the elaboration of new more modern and more efficient technologies of local protection of the metallic parts (only on certain rigorous determined areas), with isolating layers against plasma nitriding, were practically realized two genuine alternatives of special paints used for this purpose, [1], [2]. These paints are based on copper lamellar powder (with a maximum granularity of 50 µm) in a mixture with a magnesium inorganic binding agent system (magnesium oxide), where was added polystyrene dissolved in an organic solvent (carbon tetrachloride). The obtained paints were noted V-1 respectively V-2 (when polystyrene was not used).

As a consequence of the observations noted after the experiments, a series of appreciations were made regarding the characteristics and the conduct of the special elaborated pastes or paints, with precise specifications on the binding systems and on inorganic and organic solvents used, that manifested or not positively during the applied thermal or thermo-chemical cycles.

The inorganic binding agents were during the made experiments the essential ceramic and refractory raw material that were the base for elaborating the proposed and analyzed protection pastes.

The solid powder and the solvent used determine the binding properties of the mixtures. Actually these are heterogeneous, solid-liquid systems the components of which interact physical-chemical forming a paste that can transform through (in certain conditions) in a resistant mass.

The nature of the processes that are the base for hardening the systems depends on the nature of the components used in the elaborated mixtures. The organic binding agents generally present a reduced thermal stability. The relative temperature of decomposition of these organic binding agents is pretty low, many times caused by the conditions of the gases releasing and the forming of the solid residues.

The elaborated mixtures and the afferent tests were made in a pretty large compositional range, including except these binding agents or systems of organic or inorganic binding agents the following components:

– refractory oxides, used for reducing the porosity and the forming of a very sure and compact physical barrier;

– metallic powders, for retaining the nitrogen atoms that may penetrate in the protection layer due to its porosity.

2. CHARACTERISTICS OF THE MAGNESIAN BINDING MATTER SYSTEMS AND OF MAGNESIUM OXIDE

After the experimental determinations were made, [1], [3], it came out that the magnesia binding matter systems**,** of thermo-resistant nature, present proportioning particularities, since their solid oxide compound represent at the same time the mass set.

As a consequence the liquid compound of the system (the salt solution) is dozed in a relatively small percentage (max.5%), and must be characterized by a refractoriness as good as possible, correlated with the used domain. For this purpose next to the sinterized magnesium (MgO) can also be used sinterized dolomite – $CaMg(CO_3)_2$, or a chrome-magnesium mixture. The liquid compound of the binding system can be in turn: magnesium chloride (MgCl2), magnesium sulphate (MgSO4), solution of sodium sulphate acid (NaHSO4), sulphuric acid (H_2SO_4), a concentrated mixture of $NaHSO_4$ and H_2SO_4.

The magnesia binding matter system were used for elaborating the refractory masses representing different reports between their solid compound, strictly compositional circumscribed, and the liquid compound with a wide compositional range, being signaled a series of particularities in their process of hardening and protection.

For hardening these refractory magnesia binding matter systems, the liquid compound (the salt solution) damps the solid compound grains; takes place an interaction with the forming of magnesium hydroxide – $Mg(OH)_2$. At the beginning the interaction products are of gel form.

The set grains ‘part that is not hydrated absorbs from the gel’s liquid and with time this one forms crystalline or crystalline-poly condensation structures. The nature of the formed phases essentially depends on the nature of the salt or the acid used.

So that the gels formed initially by interaction do not become hardened at the surface, it is necessary a quantity as small as possible of liquid (the sulphates are added as a solid powder).

Another way of using the magnesia binding matter systems is that in which with them are obtained protective mixtures with a thermo isolating (for this purpose were used relatively high proportions of salt solution $MgCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 7H_2O$). With better, but not convincing results, dolomite and calcium systems where were experimentally introduced chemical compounds like $MgCl_2$ or $CaCl_2$.

The hardening of these mixtures is based on the forming of magnesia hydrochlorides or on the crystallization of solutions of $Mg(OH)_2$ – magnesia salt. Another explanation regarding the hardening is that of forming not only of the $Mg(OH)_2$, of hydro-salts (the MgO interaction – magnesia salt), but also of their solid solutions with $Mg(OH)_2$, presenting resistant crystalline or crystalline-poly condensation structures.

From a large number of experimental tested mixtures [1], [3], very important results were obtained by using the magnesium oxide (MgO - magnesia).

This oxide considered alone (at the surrounding temperature or that of nitriding), either does not become hardened, or develops mechanical resistances relatively reduced. If it is used in mixture with organic solvents (for example carbon tetrachloride) and organic binding agents (for example polystyrene), at temperatures of thermo-chemical regime are obtained consolidated systems with good protective properties and mechanical resistance.

It was experimentally determined that the adding in a well established proportion of the technical magnesium oxide (preferably not in favor of the aluminum oxide) in the composition of the elaborated protective paints based on lamellar copper powder, compensate the deficiencies signaled by using other compounds.

The magnesium oxide, known as a refractory oxide with a very good conduct in the mixtures where was a compound, easily integrating in these, no matter if it was about the using of organic or inorganic solvents (alike the aluminum oxide – Al_2O_3, that manifested a very powerful tendency of precipitation). As a matter of fact, the presented characteristics for this oxide in Table 1 recommends it, compared with other oxides with refractory properties [7].

The systems that had in their composition the magnesium oxide were remarked because of the purity it presents (colorless crystals cubic shaped) and because of its stability at high temperatures (p.t.2800°C). The fact that it is one of the most stable oxides in the oxidant medium and very easy to obtain in a state of high purity, contributed to the outline of positive aspects regarding the conduct of protective mixtures where it was a compound (together with the solvents and organic binding agents mentioned before), and that were tested afterwards against the ionic nitriding.

3. CONCLUSIONS

In consequence, the magnesium oxide partially inserted between the very fine copper grains improves, due to its extremely high refractivity and to its powder state of aggregation, the resistance of the copper lamellae at the ionic nitriding regime.

This kind of set unit (protected mixture) that is formed in these conditions, stands much better on a longer period of time the ionic bombing, the cathode spraying and the thermochemical regime temperature, proper to the ionic nitriding process mentioned before [4].

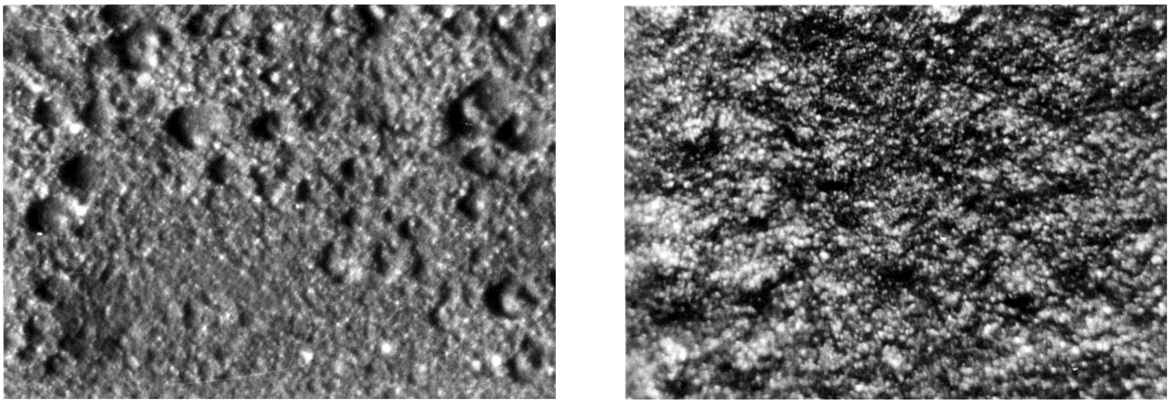
Table 1 **-** General properties of some refractory oxides used in protected mixtures at ionic nitriding

The Characteristic	Al_2O_3	BeO	MgO	TiO_2	ZrO_2	CaO	SiO_2
The crystalline form	Hexagonal	Hexagonal	Cubic	Square	Cubic	Cubic	-
The melting temperature [°C]	2050	2570	2800	1840	2700	2570	-
The specified mass [g/cm^3]	3.96...4	3.01...3.06	3.5...3.6	4.3	5.4...5.8	3.5...3.7	2.20
The mass thermal capacity [cal/g·grad]	0.2	0.5	0.27	0.18	0.10	0.18	0.176
The coeficient of thermal dilatation [10^{6}·i°C^{-1}] (20-1400°C)	7.3...8	8...9.5	13...14	7.5...8 600°C	10	13...13.7	0.54
The orientative thermal conductivity [kcal/m·h·grad] (20-1400°C)	4.7	14	4.9	3 1200°C	2	7.3 1100°C	1.2
The specific resistence [ohm·cm] - at 1200°C - at melting temperature	10^6 10^3	10^6 10^3	10^5 10^2	10^2 1	10^3 1	10^4	10^4

The resistence at traction [daN/mm^2] - at 20°C - at (...°C)	 26.5 1460°C	 11 1300°C	 2.2 1000°C	 - -	 15 1540°C	 - -	 - -
The compression resistence [daN/mm^2] - at 20°C - at (...°C)	 300 1600°C	 80 1600°C	 low low	 - -	 220 1500°C	 - -	 - -
Microhardness [daN/mm^2]	1750	-	-	-	900	400	-
The maximum used temperature - oxidant, [°C] - reducing, [°C]	 1980 1930	 2400 very good.	 2400 2000	 - -	 2500 2200	 2400 1400	 1200 -

Relating to the "superficial melting" phenomenon that may appear during “tougher” plasma nitriding regimes (more longer processes), it is mentioned that the magnesium oxide stops the hardening of the entire protective layer. The compactness that appears after the “melting” was accidentally signaled on isolated areas and not in the entire solid mass of the deposed pellicle on the metallic surfaces of the samples subdued afterwards to the plasma nitriding, [1], [2].

In what is concerned the further removal of the protective layers realized through the V-1 and V-2 special paints, at the end of the process, this is very easily realized, the magnesium oxide and the unmelted copper powder, from the depth of the layer making easy the removal without too many difficulties (by simple cleaning or brushing of the surfaces) [1].



a b

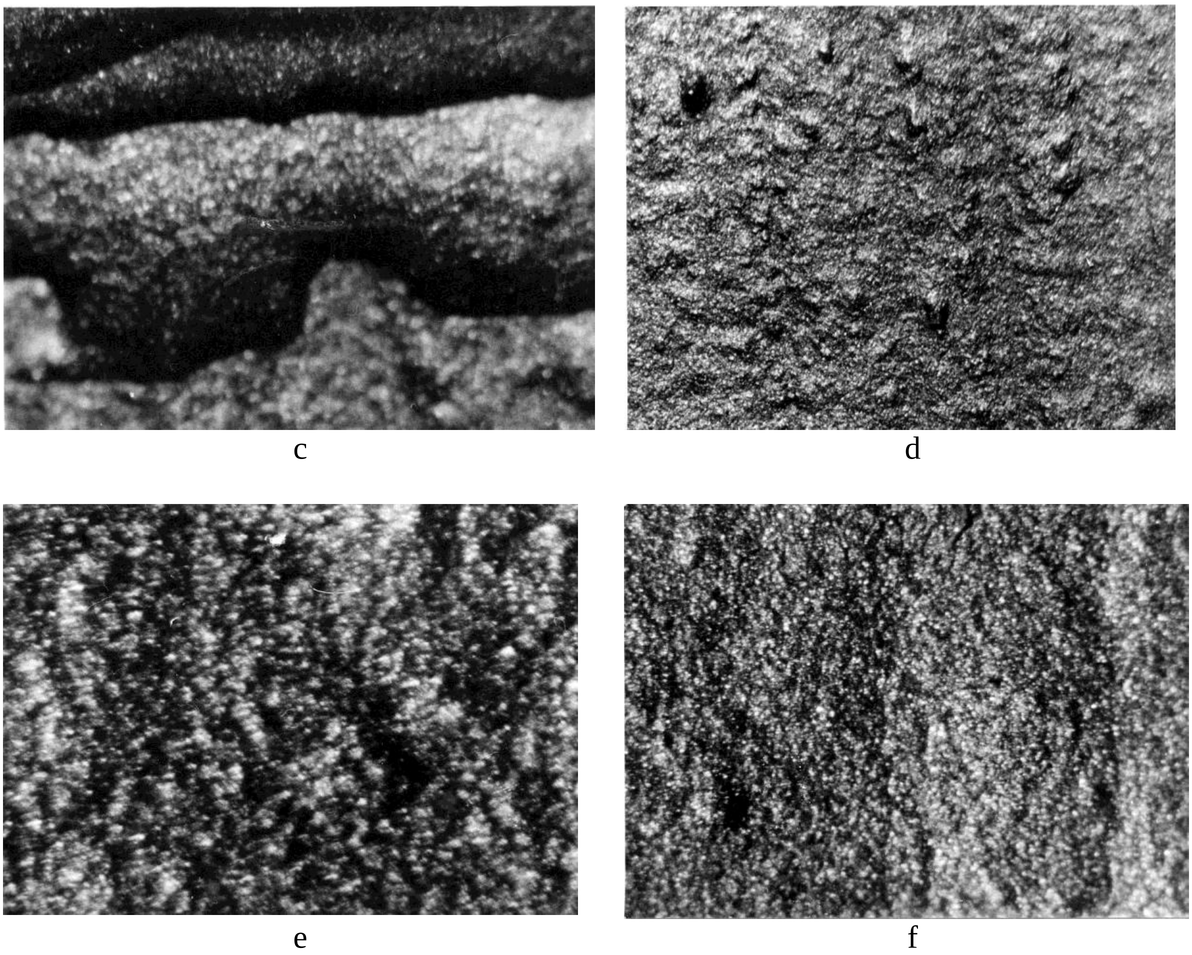


Fig.1. The surfaces appearance (x10) of protection paints based on lamellar copper powder in mixture with magnesium oxide and polystyrene dissolved in carbon tetrachloride, on steel samples 39MoAlCr15, ionic nitrided - 15 hours/530°C

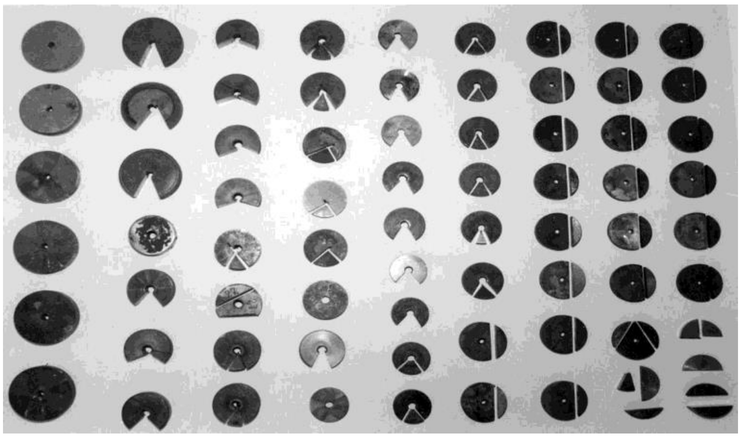


Fig.2. A general view of the steel test pieces 39MoAlCr15 initially protected (with different mixtures based on copper powder), ionic nitrided (15 / 30 hours at 530ºC), cleaned, and finally sectioned for determining the macrodurity HV 0,1

As well were checked the protection alternatives with pellicle double systems, [1], that supposed the necessity of the existence of an intermediate layer little adherent (formed only from magnesium oxide), to allow an easier removal of the external protective layer after the ionic nitriding. As for this stage of the experiments made, the results were mostly unsteady, being signaled at the samples side areas (especially at edges etc.) pretty high values of the macrodurities HV 0,1 experimentally measured (values between 700...1100 HV 0,1) [5, 6].

In figure 1 is presented for exemplification the aspect of some protective layers surfaces based on lamellar copper powder in mixture with magnesium oxide and polystyrene dissolved in carbon tetrachloride (alternatives of the isolating paints V-1 and V-2, [1]. The images realized after the plasma nitriding (for 15 hours at 530°C temperature) of the samples protected with these compositional mixtures specially elaborated for stopping the nitrogen diffusion in the parts external metallic layers

As well the figure 2 presents a general view of the steel test pieces 39MoAlCr15 initially protected with different mixtures specially isolated based on lamellar copper powder, ionic nitrided (15/30 hours at 530^0C temperature), cleaned and finally sectioned for determining the macro-hardness HV 0.1 [1].

REFERENCES

[1] **Bibu M.,** *Researches regarding the working out of local protection technologies at plasma thermochemical treatments*, Doctor's degree thesis, "Lucian Blaga" University of Sibiu, Faculty of Engineering, Sibiu, Romania, 1998

[2] **Bibu, M.,** *The Chemical Composition's Influence of the Special Protective Paints Based on Copper Lamellar Powder on Protected Metallic Surfaces' Structure at Ionic Nitriding*, 12th Romanian International Conference on Chemistry and Chemical Engineering (CIChICh – 2001), Faculty of Industrial Chemistry, "Politehnica" University of Bucharest, Romania, 2001, pp. 184-191.

[3]. **Bibu, M.,** *The influence of special protective paints based on copper lamellar powder on the metallic protected surface's at ionic nitriding*, 12th Romanian International Conference on Chemistry and Chemical Engineering, Faculty of Industrial Chemistry, "Politehnica" University of Bucharest, Romania, 2001, pp. 192-199.

[4] **Du, H., -** *"A New Thermodynamic Evaluation of Fe-N and Fe-N-C Phase Diagrams*", Material Research Center, Royal Institute of Technology, Stockholm, TRITA-MAC-0511, Sweden, 1993, pp. 89-96.

[5] **Vermeşan G., Deac V.,** *Bazele tehnologice ale nitrurării ionice*, Editura Universităţii din Sibiu, 1992.,

[6] **Titu, M.,** *Contribuţii cu privire la modificarea transferului substanţial la prelucrarea dimensională prin eroziune electrică cu câmpuri coercitive*. Teză de doctorat, Sibiu, 1998.

[7] **Alin Nioaţă** - *Researches regarding the optimization of thermal treatment depending on hardness for maraging 300 ste*el — Metalurgija, 52 (2) (april-june 2013) pp. 231-234, ISSN 0543-5846