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CONSIDERATIONS ON THE EFFECTS OF MAGNESIUM-BASED BINDERS IN THE SPECIAL PAINTS EMPLOYED FOR THE LOCAL PROTECTION OF STEEL PARTS AGAINST PLASMA NITRIDING

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ABSTRACT
This paper reflects some of the researches carried out by the authors with regard to the employment of special paints in the protection of certain areas of steel parts against the hardening effects induced by plasma nitriding (ionitriding). These researches have so far led to the development of two such paints (who have been patented), based on lamellar copper powder. In the paints' composition, an important role is played by the binder. The characteristics and effects of some possible binder systems are shown here, especially for the one that proved to be the most efficient – a binder based on magnesium oxide in a mixture with carbon tetrachloride and, in one variant, polystyrene.
Keywords: protection paints, plasma nitriding, magnesium-based binder

1. INTRODUCTION
The experimental researches carried out by the authors with regard to the elaboration of new technologies for the local protection of metallic parts with isolating layers against plasma nitriding led to the development of two variants of special paints used for this purpose, marked V-1 and V-2 [1, 2]. These paints are based on lamellar copper powder (with a maximum granularity of 50 μm) in a mixture with a magnesium-based inorganic binder (magnesium oxide), to which polystyrene dissolved in an organic solvent (carbon tetrachloride) was added.
The magnesium-based binders were the base for elaborating the analysed protection paints. The solid powder and the employed solvent determine the binding properties of the mixtures. Actually these are heterogeneous, solid-liquid systems, the components of which interact physically and chemically forming a paste that can turn (under certain conditions) into a rigid mass.
Inorganic, magnesium-based binders were preferred because organic binders generally present a reduced thermal stability, as their relative decomposition temperature is rather low.
A large range of various compositions for the elaborated mixtures were considered, which included, beneath the mentioned binders, also following components:
– refractory oxides, used for reducing the porosity and for the forming of a very safe and compact physical barrier;
– metallic powders, for retaining the nitrogen atoms that could penetrate the protection layer due to its porosity.

2. CHARACTERISTICS OF THE MAGNESIUM-BASED BINDERS
The magnesium-based binders have thermoresistant properties and can be sintered magnesium oxide (MgO), sintered dolomite - $CaMg(CO_3)_2$ - or a chrome-magnesium mixture. The liquid compound of the mixture is present in a relatively small percentage (maximal 5%), and displays a high refractoriness. It can be either

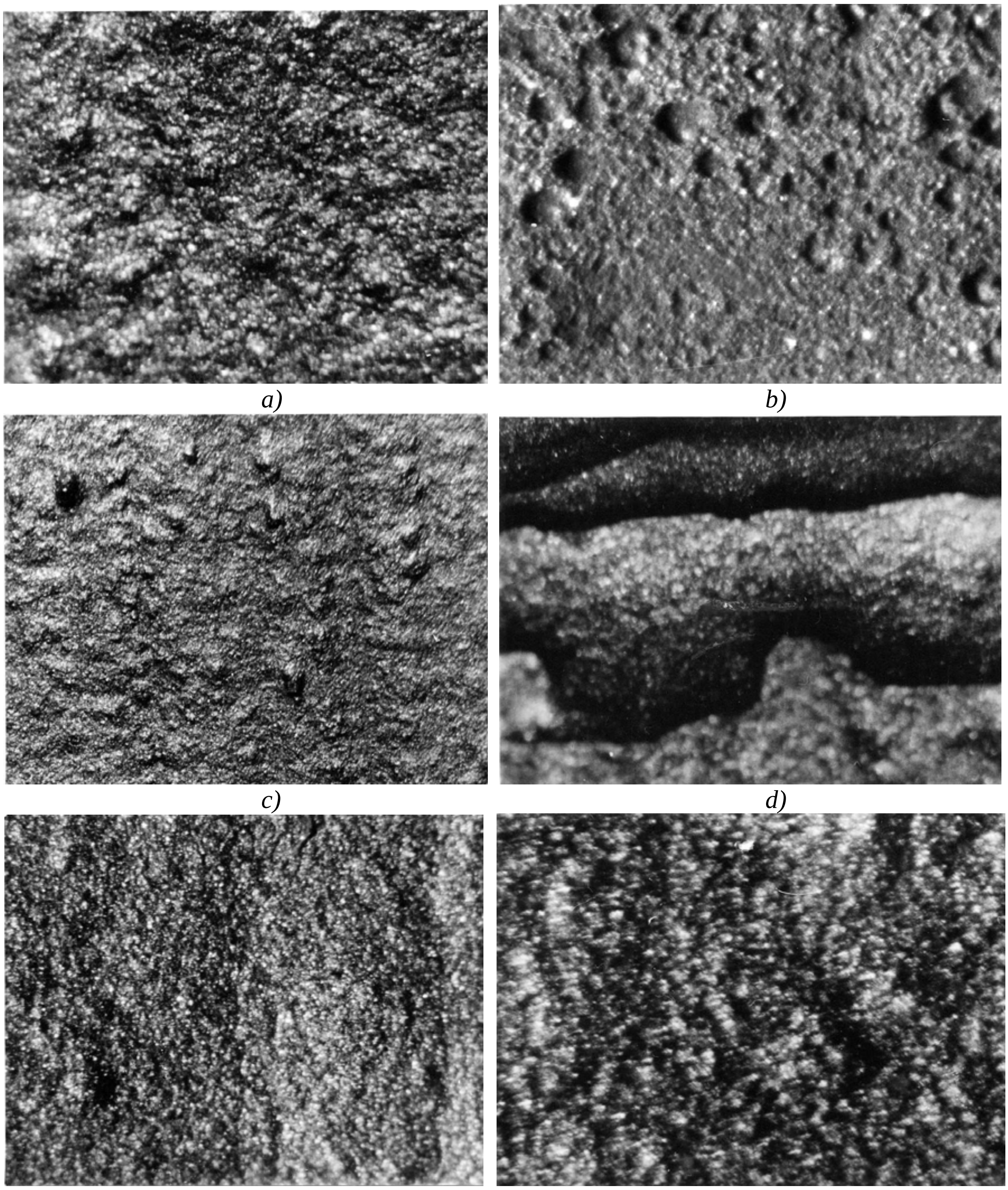
magnesium chloride (MgCl2), magnesium sulphate (MgSO4), a solution of sodium sulphate acid (NaHSO4), sulphuric acid (H_2SO_4), or a concentrated mixture of $NaHSO_4$ and H_2SO_4.
For hardening these refractory magnesium-based binders, the liquid compound (the salt solution) damps the solid compound grains; an interaction takes place, leading to the forming of magnesium hydroxide – $Mg(OH)_2$. At the beginning, the interaction products are of gel type. The set grains' part that is not hydrated absorbs from the gel's liquid and with time it forms crystalline or crystalline-polycondensation structures. The nature of the formed phases essentially depends on the nature of the salt or the acid used.
The researches have shown that magnesium oxide, if used alone (at room temperature or at nitriding temperature), either does not become hardened, or presents relatively reduced mechanical strength. If it is used in mixture with organic solvents (for example carbon tetrachloride) and organic binding agents (for example polystyrene), consolidated systems with good protective properties and mechanical strength result.
It was experimentally determined that adding magnesium oxide in a well-established proportion in the composition of the elaborated protective paints based on lamellar copper powder, compensates the deficiencies that appeared with using other compounds.
The magnesium oxide, is known as a refractory oxide with a very good conduct in the mixtures where it was a compound, easily integrating in these, no matter if it was about the using of organic or inorganic solvents (unlike aluminium oxide, that displayed a very powerful tendency towards precipitation). As a matter of fact, the presented characteristics for this oxide in table 1 recommends it, compared with other oxides with refractory properties.

Table 1 General properties of some refractory oxides used in protection paints against ionic nitriding

Characteristic	Al_2O_3	BeO	MgO	TiO_2	ZrO_2	CaO	SiO_2
1	2	3	4	5	6	7	8
Melting temperature: [ºC]	2050	2570	2800	1840	2700	2570	-
Specific mass [kg/m^3]	3960-4000	3010-3060	3500-3600	4300	5400-5800	3500-3700	2.20
Thermal expansion coefficient [$10^6 \cdot$ ºC^{-1}] (20-1400ºC)	7.3...8	8...9.5	13...14	7.5...8	10	13...13.7	0.54
Specific electrical resistance [$\Omega \cdot$ cm] (at 1200ºC)	10^6	10^6	10^5	10^2	10^3	10^4	10^4
Tensile strength [N/mm^2] (at 20ºC)	265	110	22	-	150	-	-
Compression strength [N/mm^2] (at 20ºC)	3000	800	low	-	220	-	-
Microhardness: [daN/mm^2]	1750	-	-	-	900	400	-
The maximum temperature for employment:							
- oxidant, [°C]	1980	2400	2400	-	2500	2400	1200
- reducer, [°C]	1930	very good	2000	-	2200	1400	-

The systems that had in their composition magnesium oxide were remarked because of the purity it presents (cubic shaped, colourless crystals) and because of its stability at high temperatures (its melting point is at 2800°C). The fact that it is one of the most stable oxides in oxidant environments and very easy to obtain in a state of high purity, contributed to the outline of positive aspects regarding the conduct of protective mixtures of which it was a compound (together with the solvents and organic binding agents mentioned before) and which were tested afterwards against the effects of plasma nitriding.
Regarding the "superficial melting" phenomenon that may appear during "tougher" plasma nitriding regimes (longer process durations), it is mentioned that the magnesium oxide stops the hardening of the entire protective layer. The compactness that can appear after the “melting” was identified only on

isolated areas and not in the entire solid mass of the deposed film on the metallic surfaces of the samples subjected to plasma nitriding [1, 2].
Figure 1 presents, as an example, the aspect of some surfaces covered with protective layers 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). The samples were nitrided for 15 hours at 530°C.



a) *b)* *c)* *d)* *e)* *f)*

Fig.1 The surface 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, plasma nitrided for 15 hours at 530°C.

Figure 2 presents a general view of the test samples made of the steel grade 39MoAlCr15 protected with different protective mixtures based on lamellar copper powder, ionic The samples were nitrided for 15 hours at 530°C, cleaned and cut for determining the HV 0.1 microhardness.

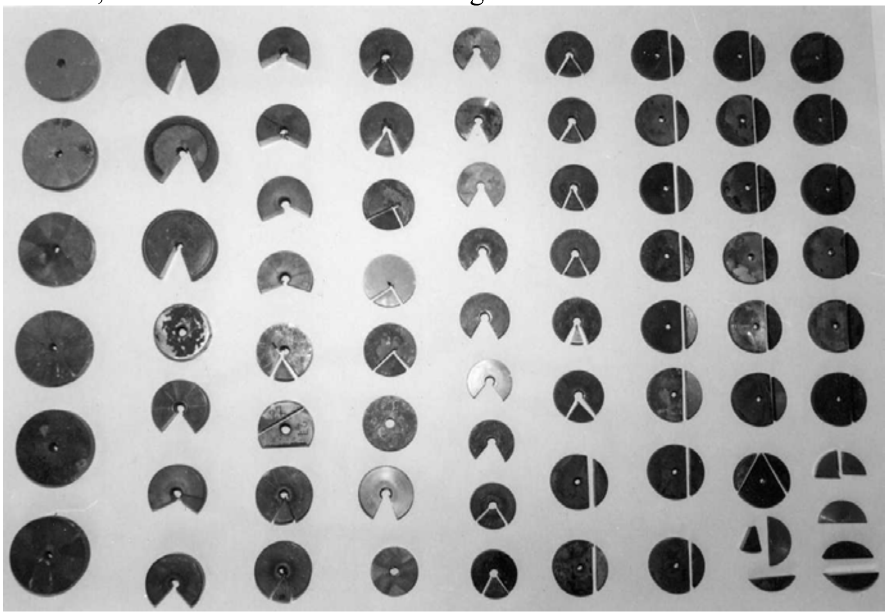


Fig.2 Overview of the test samples made of 39MoAlCr15 protected with different protective mixtures based on lamellar copper powder, ionic The samples were nitrided for 15 hours at 530℃, cleaned and cut for determining the HV 0.1 microhardness.

3. CONCLUSIONS

The researches carried out by the authors with regard to the usage of magnesium-based binders in the composition of special paints used for the local protection of metallic parts against the effects of ionitriding have shown that the magnesium oxide partially inserted between the very fine copper grains improves, due to its extremely high refractoriness and to its powder state of aggregation, the resistance of the copper lamellae during the nitriding process.

This protective mixture withstands much better and for a longer period of time the ionic bombardment, the cathode spraying and the thermochemical regime temperature, characteristic for the ionic nitriding process mentioned before.

Concerning the removal of the protective layers realised through the V-1 and V-2 special paints at the end of the plasma nitriding process, this is very easily realised, the magnesium oxide and the unmolten copper powder making the removal easy (by simple cleaning or brushing of the surfaces).

4. REFERENCES

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