Fişa suspiciunii de plagiat / Sheet of plagiarism's suspicion	Indexat la: 83/06

Opera suspicionată (OS) Suspicious work	Opera autentică (OA) Authentic work

OS	Petrescu, D., Antonescu, L., "Experimental researches concerning the hardened coatings manufactured with the usage of the plasma stream thermal pulverization", *Proceedings of the 7th International Conference Coatings in Manufacturing Engineering*, Chalkidiki, Greece, *1-3 October 2008,*
OA	Jumate, N., "Cercetări asupra unor straturi superficiale obținute din aliaje amorfe pentru rezistență la uzură şi coroziune". Teză de doctorat. Universitatea tehnică, Cluj-Napoca, 2001.

Incidența minimă a suspiciunii / Minimum incidence of suspicion	
p.303:Figure 3	p.141:Fig.6.25
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EXPERIMENTAL RESEARCHES CONCERNING THE HARDENED COATINGS MANUFACTURED WITH THE USAGE OF THE PLASMA STREAM THERMAL PULVERIZATION

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ABSTRACT

In this paper is presented the methodology to analyze the hardened coatings with the usage of the optic and electronic micrographic and the results obtained after the specific mechanical testing achievements.

KEYWORDS: Plasma - Wear resistance - Hard coatings

1. INTRODUCTION

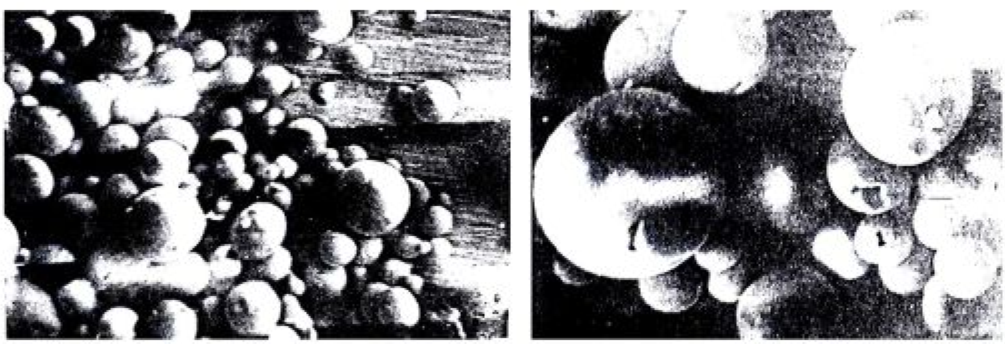
Mechanical parts replacement and/or removal out of the functional circuit, is generally caused by three main phenomena: wear, corrosion and fatigue. A characteristic of these three phenomena is the fact that they prime on the surface area, where the stress is more intense and more complex than the core /4, 5, 6/.

In order to obtain wear-resistant layers, hard materials are used, in powder form, or mixes of hard materials with matrix-forming components, usually applied with plasma-jets, or high-velocity flame.

Through thermal spraying, a new surface is formed by applying a new material layer on the part surface.

In the experimental tests, the material used was the powder by the NiCr-(FeSiCY) matrix, with a microstructure as described in Figure 1 /2/.

The chemical powder composition of the alloy materials in weight percents % gt is Ni 72%, Cr 16%, B 3,5%, Si 3%, Fe 4%, C 0,9%, Y 0,6%, and the fluidity of developed powders is 20,6 sec/50g. The fluidity value are determined using the Hallflow-meter, and they clearly show the effect of the shape and oxidation degree of particle surfaces, NiCr powder having a good fluidity as there are no oxides on the particles, and flow throught a calibrated hole.



a b

Figure 1: *Microstructure of the NiCr-(FeSiCY) powder a - powder microstructure (300:1); b - powder microstructure (800:1).*

This alloy type is recommended for punchers, slide valves, vent cones, mandrels, shafts working in corrosion conditions, at low temperatures and low static or dynamic stress.

The NiCr-(FeSiCY) alloy, applied through thermal spraying shows good anti-friction and shock resistant properties.

The NiCr-(FeSiCY) alloy has hard phases and can be used for layer application for recondition and preventive coating for parts. Adding boron and silicon to this hard alloy will help reduce the oxides, allowing autonomous flux properties to the alloy, facilitating the layer-sub layer metallurgic adherence, without the need of additional link layer when coating.

Chrome (16%) increases the corrosion and oxidation resistance, boron and silicon have a pronounced effect on melting temperature decrease. Boron and carbon form together hard phases, increasing wear resistance. The novelty in this alloy is Yttrium, who decomposes water slowly, even in normal conditions, and with less-active non-metals forms compounds with a metallic character, with high melting points like borides, carbides, silicates. Yttrium has a low atomic radius (1,801Å) and can easily defuse, raising layer adherence and intensifying the mutual inter diffusion.

The NiCr-(FeSiCY) alloy has sphere-shaped particles, a shape that allows fluent flow through a calibrated orifice. The primal crystallizing structure is dendritic, formed of a solid solution matrix γ, based on nickel and various eutectics inter-dentritic crystallized, as shown in Figure 2 /2/.

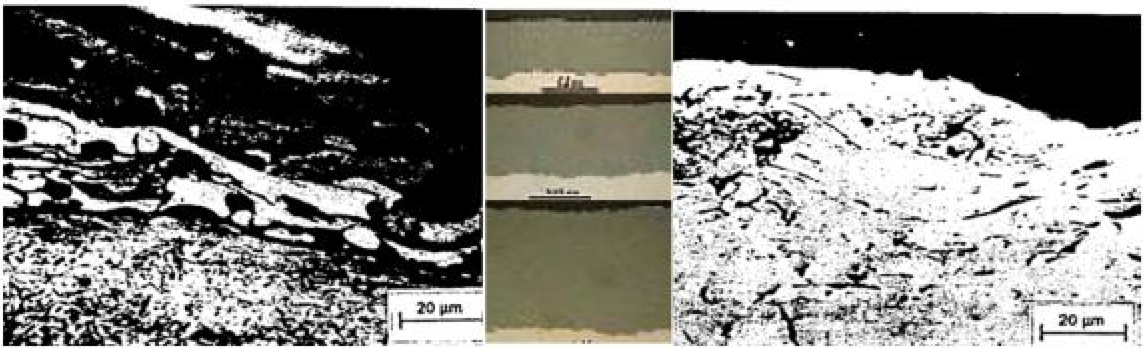


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Figure 2: *Layer of the powder, containing NiCr-(FeSiCY) a - optical microstructure; b - electronic microstructure*

2. EXPERIMENTAL RESEARCH REGARDING PULVERIZED LAYERS ADHERENCE USING THE NiCr-(FeSiCY) POWDER

Coating through thermal spray with the NiCr-(FeSiCY) alloy is a dynamic process and therefore there is no rigorous patterning of the coating process. There is no unanimous standardization accepted for the coating devices, and the layer characteristics, so there aren't any reference elements regarding the layer, also due to the impossibility of the total reproduction of the layers obtained through this procedure.

In the figure 3 canes see the shows of the meta/stable layers with an amorphous structure, applied through plasma/jet thermal spraying and NiCr powders as following: sample 16 – steel sub – layer, sample 29 – brass sub – layer, sample 35 – copper sub - layer, sample 37 - aluminum.

Judging by the dislocation theory, the material hardening is determined by the brake on the dislocation movement by the internal barriers, as grain limits, etc.

On amorphous materials, the stress limit coincides with the break limit, because the plastic deformation phenomenon is missing due to the lack of crystalline grains to stop the dislocation movement /7,8/.

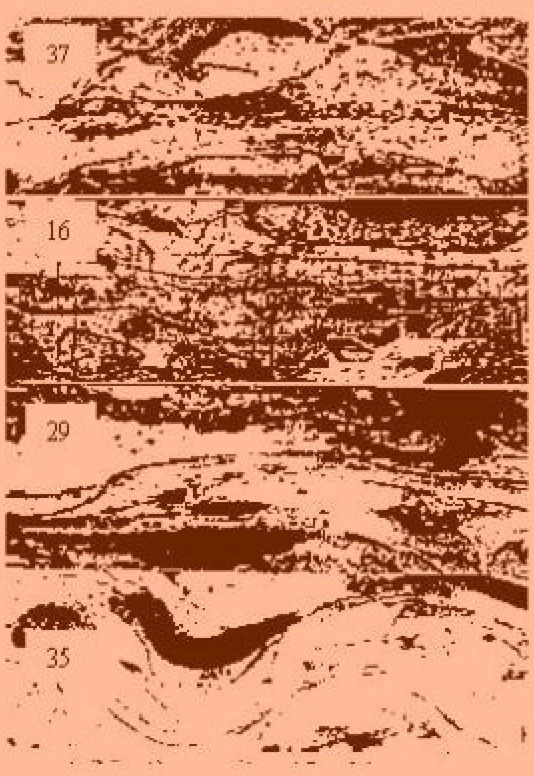

Figure 3: Plasma-jet thermal coatings using NiCr powder.

The model that describes the best the amorphous state is Bernal – Scott. This model shows that in amorphous state, the atoms are densely and randomly paired (random dense packing) in an amorphous state, featuring mostly short-distance order, so that the atoms can't align in ordered crystal structures on a long distance.

The short distance order is on a short field of 10...20 Å, being determined by geometrical restraints, due to atom size and their chemical links.

The amorphous phase ratio depends on the nature of the sub-layer material, as shown in Table 1.

Table 1: Amorphous phase ratio determined through X-ray diffraction.

Sample Number	Sub-layer type	Amorphous phase ratio %	Crystalline phase ratio %
16	Steel	18,8	81,2
35	Copper	52,8	47,2
29	Brass	85,9	14,1
37	Aluminum	48,0	52,0

The ratio of the amorphous phase on the plasma-jet applied NiCr powder was between 18,8% and 85,9% on the applied layers.

In order to obtain layers of the NiCr powder able to form 100% amorphous phases, the cooling speed must be increased, increasing the roughness of the alloy, due to the alloy degree increase, in order to disable the boride and carbide formation, those being dissolved in acid solution.

The firms who manufacture the equipments and powders used in thermal coating have their own norms, the customer depending on the supplier. One of the important characteristics on thermal coating is the layer-sub layer adherence. The most used destructive methods to eliminate adherence are the mechanical methods, such as:

- determination of adherence through shearing test;
- determination of adherence through traction test;
- determination of adherence through bending test;

Because the layers applied through plasma-jet thermal spraying at atmospheric pressure, quickly cooled, had a small thickness (15 - 300μm) the adherence determination was made through traction and bending tests.

- Determination of adherence through shearing test is done, using the formula:

$$\sigma_f = \frac{F}{A}, \quad \left[\frac{N}{mm^2}\right] \qquad (1)$$

Where: F is the maximum force on layer break/shearing of the thermal powder zone, in [N];
A - shearing area, in [mm^2].

The weight loading speed being 20 N/s /1, 2, 3/ in accordance to SREN 657:2005.

- Determination of adherence through traction test is done, using the formula:

$$\sigma_t = \frac{F_t}{S}, \quad \left[\frac{N}{mm^2}\right] \qquad (2)$$

Where: F_t is the traction force (perpendicular on the layer surface) where the layer breaking takes place.
S - thermal powdered surface of the sample, in [mm^2].

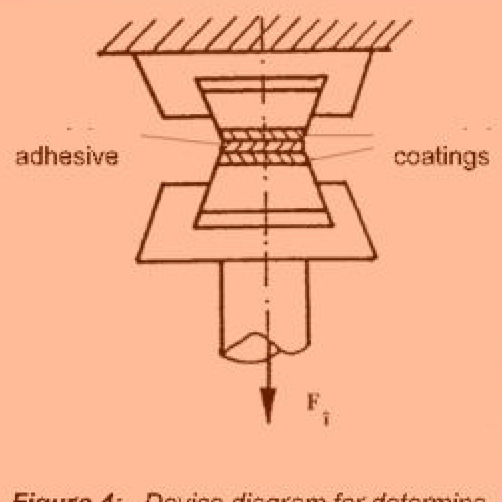

Figure 4: Device diagram for determination of adherence on traction.

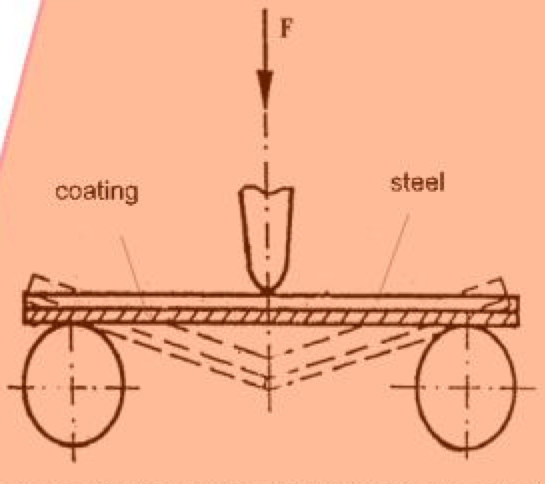

Figure 5: Device diagram for determination of adherence on bending.

The device diagram for determination of adherence on traction is showed in Figure 4.

Determination of adherence through bending test is done using the device shown in Figure 5.

We determine the force formed on the first fissure of the applied layer, the arrow s, and bending angle α .

The adhesive used on traction adherence determination is of the "bisonite" type, with a maximum break resistance of 16000 Pa.

On the bending adherence determination (Figure 5) square-section samples were used, made of OLC 45, with the following dimensions: 140 x 10 x 10 mm.

The distance between holders was l = 120 mm, their diameter was D = 30 mm, and the bend radius of the part was s = 15 mm. The load is made using a force F, making a unitary effort on bending of $10\left[\frac{N}{m^2 \cdot s}\right]$, until the first fissure appears.

Table 2 shows the results of experimental measurements for traction and bending tests, the results spreading on a large interval.

Table 2: Experimental values for the traction and bending tests on the applied layers.

Traction Adherence	S, in mm^2	99.8	101,1	98,2	99,2	99,4	98,8	100,2	100,1	99,6	98,6
	F_t, in N	110	420	280	560	460	360	480	480	360	480
	σ_t, in Pa	1,1 x10^6	4,6 x10^6	3,8 x10^6	5,6 x10^6	4,6 x10^6	3,6 x10^6	4,8 x10^6	4,6 x10^6	2,6 x10^6	4,8 x10^6
Bending Adherence	F, in N	2600	3000	3100	3600	3200	3600	3500	3600	3200	3600
	s, in mm	4,0	8,6	9,8	11,6	10,2	7,4	12,6	12,0	12,6	8,8
	α, in deg	7,8	16,6	18,6	20,8	19,6	21,6	19,8	14,6	22,6	26,0

The causes that can affect the coatings adherence are:

- Thermal spray done at low temperature, so that for a quick cool for an amorphous structure, the temperature of the sub layer being, therefore the mutual diffusion between the thermal coating - sub layer is low.
- The sanding of the sub layer was made, willingly, for a low roughness in order to allow flattening/radial expansion of the fine particles in fluid form, therefore the mechanical adherence of the particles on the sub layer is low.
- The anti-adherence forces of the sub layer, generated by the residual tensions due to rapid cooling of the particles aren't compensated by the low roughness of the sub layer.
- The thermal spray coating adherence is for the most part a mechanical adherence and less of a metallurgic or diffusive adherence.
- The applied layer adherence for the bending test was made measuring the arrow s and the bending angle α , until the first fissure is made.

The layers obtained through plasma-jet spray are thin, therefore being subject to bending, surpassing the elastic deforming. The force F is the pressure force until the first fissure appears (Table 2). The arrow s and bending angle α where the first fissures appear in the coating are the measurement for the lamellar cohesion of the coating and not the measurement for the adhesion of the layer powdered on the sub layer.

The final conclusion is that the adherence is good enough for the thermal sprayed coatings to be mechanically processed, and they can be used to recondition/preventive cover parts that work in mild exploitation conditions of the current production.

3. CONCLUSIONS

1. The alloy system for the NiCr-(FeSiCY) is destined for punchers, slide valves, vent cones, mandrels, shafts working in corrosion conditions, at low temperatures and low static or dynamic stress. This alloy, applied through thermal spraying, shows good anti-friction and shock resistant properties. Because the alloy has rough phases, it can be used for reconditioning layers application and preventive part cover.
2. On this plenary rough alloy NiCr-(FeSiCY), adding boron and silicon reduces oxides, allowing good autonomous flux properties, facilitating the metallurgic layer-sub layer adherence, without the need for additional link layers. Chrome (16%) increases the corrosion and oxidation resistance, while boron and silicon have a pronounced effect in melting point reduction. Boron and Carbon form hard phases, increasing wear resistance. The novelty on this alloy is Yttrium, which decomposes water slowly, even in normal conditions, and with less active non-metals forms compounds with metallic character, with a high melting point, like borides, carbides, silicates. Yttrium has a low atomic radius (1,801 Å) therefore it can easily defuse, increasing adherence on the applied layers and intensifying the mutual layer - sub layer inter-diffusion.
3. The fluidity of the NiCr powder is very good, because the NiCr alloy grains are 95% spherical, have no oxides on their surface, and look as formed by crystal grains.
4. On fast hardening, the cooling speed can't be measured directly, but only through it's effect – the microstructure of the thermal sprayed layers.
5. In order to obtain layers of the NiCr powder able to form 100% amorphous phases, the cooling speed must be increased, increasing the roughness of the alloy, due to the alloy degree increase, in order to disable the boride and carbide formation, those being dissolved in acid solution.
6. The NiCr-(FeSiCY) alloy has a spherical particle shape, allowing a fluent flow through a calibrated orifice. The main crystallization structure is dendrites, formed of a solid solution matrix γ nickel-based and various eutectics inter-dendrites crystallized.
7. The powder particle of the NiCr-(FeSiCY) alloy has a solid solution Ni - α and the eutectic with dispersed particles of Chrome Boride (4000HV) and Chrome and Yttrium Carbides (2500HV).The powder grains have a very fine microstructure due to formation rapid cooling.
8. The adherence values for the coatings of the NiCr-(FeSiCY) alloy on traction tests spread through a wide interval. The causes that affect coating adhesion could be: thermal spray done at low temperature, so that for a quick cool for an amorphous; structure, the temperature of the sub layer being $T_{ss} < 200^{\circ}C$, therefore the mutual diffusion between the thermal coating - sub layer is low.
9. The sanding of the sub layer was made, willingly, for a low roughness in order to allow flattening/radial expansion of the fine particles in fluid form, therefore the mechanical adherence of the particles on the sub layer is low.
10. The anti-adherence forces of the sub layer, generated by the residual tensions due to rapid cooling of the particles aren't compensated by the low roughness of the sub layer.The thermal spray coating adherence is for the most part a mechanical adherence and less of a metallurgic or diffusive adherence.
11. Adherence on the applied layer on the bending test was made measuring the arrow s and the bending angle α, until the first fissures form in the thermal sprayed layer. The layers made using plasma-jet thermal spraying are very thin, therefore being subject to bending, surpassing the elastic deforming. The force F is the pressure force until the first fissure appears. The arrow s and the bending angle α, where the first fissures appear in the thermal sprayed layer are the measurement of the lamellar cohesion of the coating and not the measurement of the adhesion of the sprayed layer on the sub layer.
12. The adherence of the thermal sprayed layer on the sub layer, analyzed on traction tests is higher in the amorphous structured layers compared to the ceramic layers.
13. The final conclusion is that the adherence is good enough for the layers to be mechanically processed and they can be used to recondition/preventive cover parts that work in mild exploitation conditions in the current production.

4. REFERENCES

1. Moskowitz, L.,M., Klar, E., Structure-Property Relationship in Flame Sprayed Nickel Base Powder Coatings, Int. Powder Metallurgy Conference, 22-27 June, Washington D.C., 1980, pg. 1-21.
2. Petrescu Doina – Research regarding thermal spraying, with applications for reconditioning and preventive cover on parts, PhD Thesis, April, 2008.
3. Smith, M.,F., a.o. – A Comparison of Technique for the Metallographic Preparation of thermal Sprayed Samples, Proc. of the Fourth National Thermal Spray Conference, 4 -10 May, Pittsburg, USA, 1991, pg. 97-104.
4. Smith, R., W., Apelian, A. – Thermal Plasma Materials Processing-Applications and Opportunities, Plasma Chemistry and Plasma Processing, Vol. 9, No. 1 Supplement, 1989, pg. 1355-1655.
5. Smith, R.,W., Apelian, D. – Melting phenomena of several nickel base alloy in a plasma jet operation at low pressure, Mat. Res. Soc. Symp. Proc., Vol. 98, 1987, pg. 88 -99.
6. Smith, R.,W., Apelian, D. – Plasma spray consolidation of materials, Pure & Appl. Chem., Vol. 62, No. 10, 1990, pg. 1825-1832.
7. Calka, A., ş.a. – Thermal properties of nanocrystalline and amorphous Fe-B alloy made by mechanical alloying, Materials Science and Engineering, A 133, 1991, pg. 555-559.
8. Surinach, M.,- Investigation cristalliyation and thermal stability of $Fe_{78}B_{22-x}Si_x$ Metallic Glasses, Rapidly Quenched Metals, Elsevier Science Publishers, BV, 1985, pg. 323-326.