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SAPIENZA UNIVERSITÀ DI ROMA

INSTM- Italian Consortium on Materials Science and Technology

Ni-Cr NANO COMPOSITE COATING DEVELOPED VIA ELECTROLESS ROUTE: INFLUENCE OF DEPOSITION PARAMETERS

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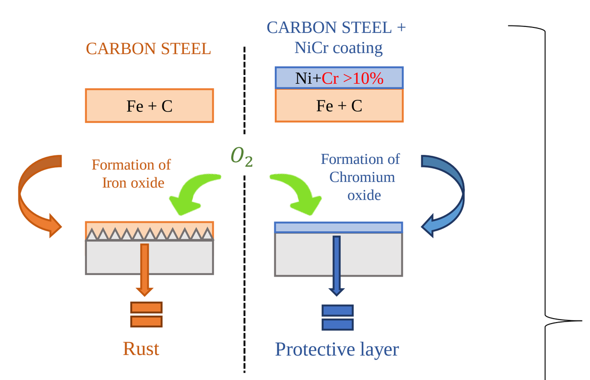
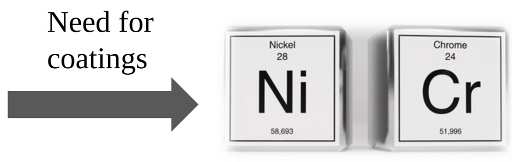
Introduction

Fields of application of NiCr coatings



- Carbon steel is harder than stainless steel and has high tensile strength but faces the risk of corroding.
- Stainless steel is more expensive than corrosion but is more expensive than steel and is also not hard.

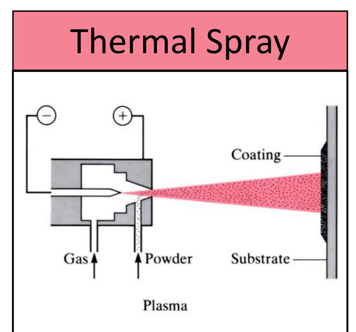
Need for coatings

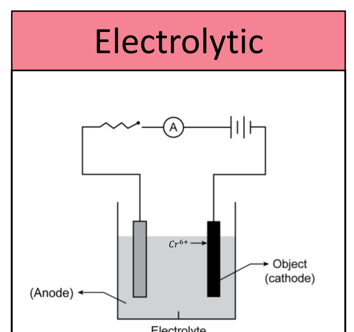


✓ NiCr coatings allow to confer anticorrosive properties while leaving the properties of the underlying steel unaltered.

- Conventional methods for making Ni-Cr coatings and their limitations.

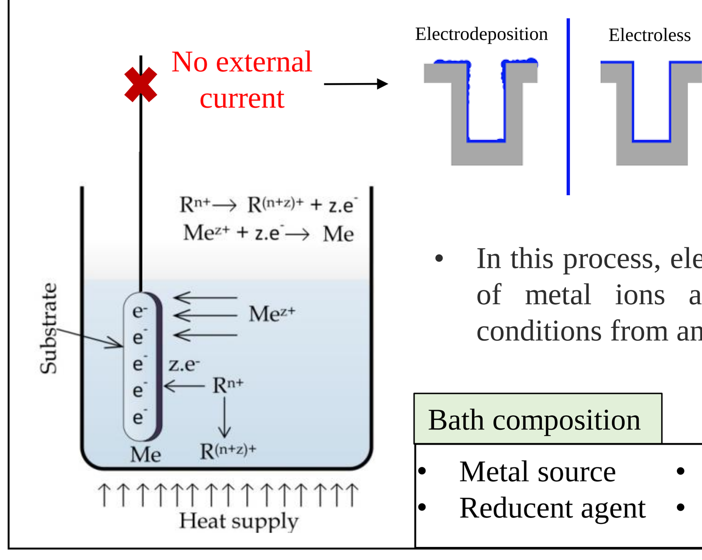
Thermal Spray	Electrolytic
✗ High energy intake	✗ Hesavalent chromium
✗ High flow rate and gas emissions	✗ Edge effect





ELECTROLESS METAL PLATING

- **Interesting new coating route**



✓ Homogen thickness
✓ Good adhesion
✓ Economic
✓ Compliant coating

- In this process, electrons used for the reduction of metal ions are released under specific conditions from an appropriate reducing agent.

Bath composition

- Metal source
- Reducent agent
- Ph buffer
- Complex agent
- Additives

Aim → **Alternative Ni-Cr coating obtained purely via electroless plating.**

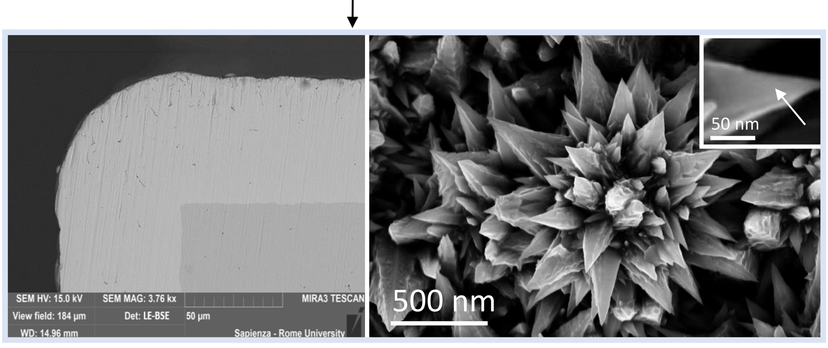
Electroless composite Ni-Cr

ELECTROLESS Ni-Cr-COMPOSITE COATING

✗ ELECTROLESS PURE Cr COATING

✓ ELECTROLESS PURE Ni COATING

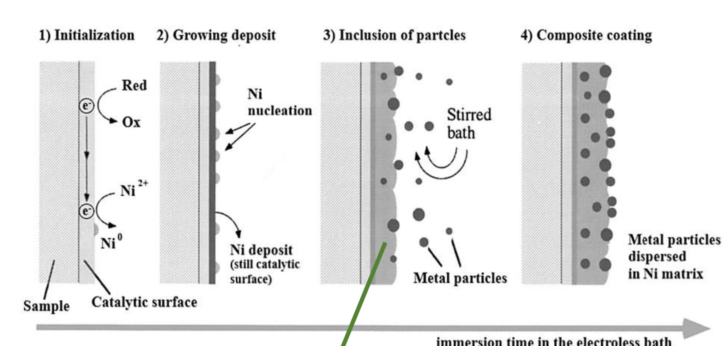
- No electroless-Cr bath is still available
- However, it is possible to use a Ni electroless bath to obtain a Ni-Cr composite coating

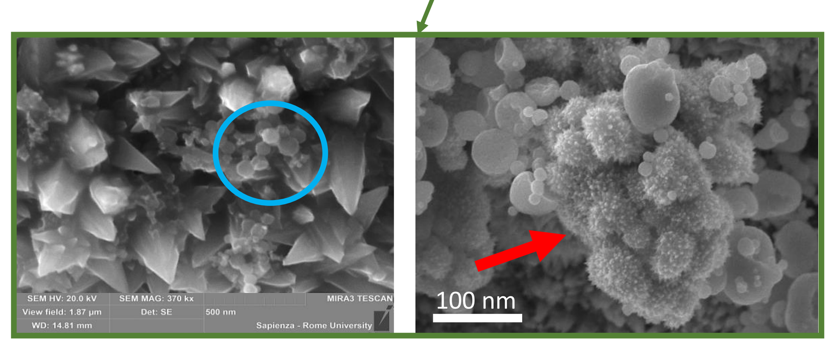


Typical cauliflower structure of the Ni coating for electroless plating using hydrazine as reducing agent.

✓ Autocatalytic process :

$$Ni^{2+} + N_2H_4 + 2OH^- \rightarrow Ni^0 + N_2 + 2H_2O + H_2$$

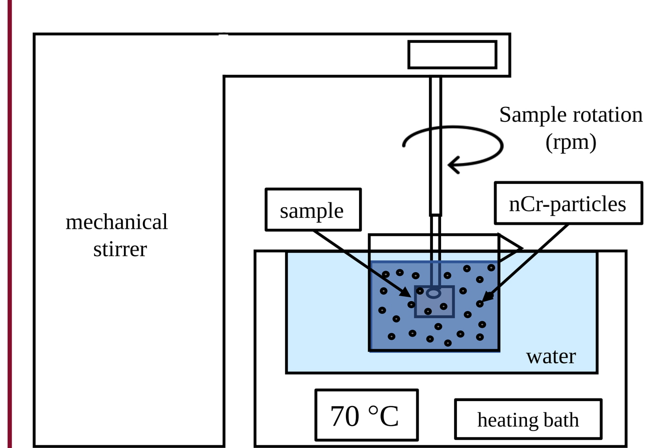


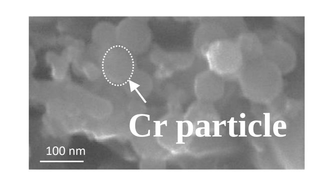


- A composite coating is obtained by adding to the reaction bath a dispersion of particles with a size typically in the order of 50-100 nm.
- Using nano particles of Cr, it is possible to include them in the Ni matrix enhanced by electroless and thus **obtaining a Ni-Cr coating purely via electroless plating.**
- Blue circle: Nano particles of Cr adsorbed on the growing Ni cauliflower structure.
- Red arrow: The adsorbed Cr particles are also a catalytic surface for the electroless reduction of Ni.

Experimental set up

- **Designed experimental plant**

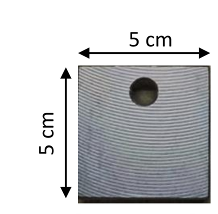




- Nano Cr particles coated with oleic acid. Average size 50-100 microns.

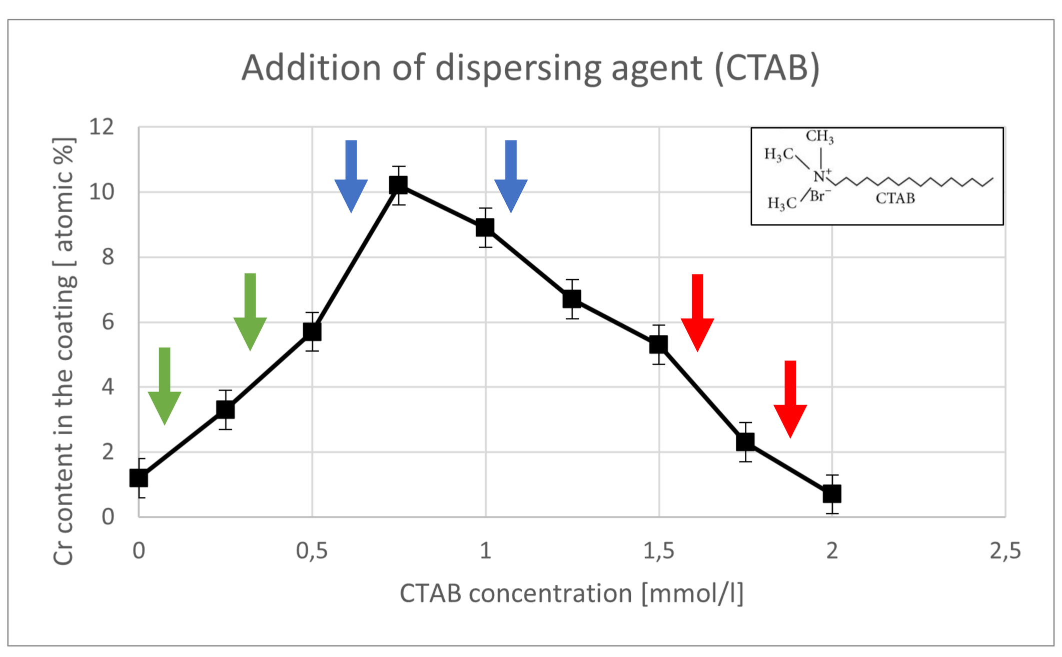
Steel-LF2: chemical composition

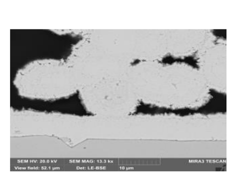
C %	Mn %	Si %	S %	P %	Cr %	Ni %
0.30 max	0.6/1.35	0.15/0.30	0.40 max	0.35 max	0.30 max	0.40 max



Samples: Steel-LF2

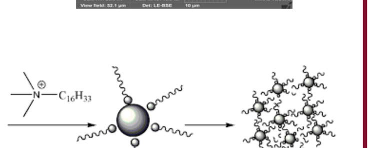
Deposition parameters





- Green arrow: agglomeration of the Cr particles

For CTAB concentrations lower than the critical micellar concentration (CMC), the particles tend to agglomerate, and the coating obtained is not homogeneous.

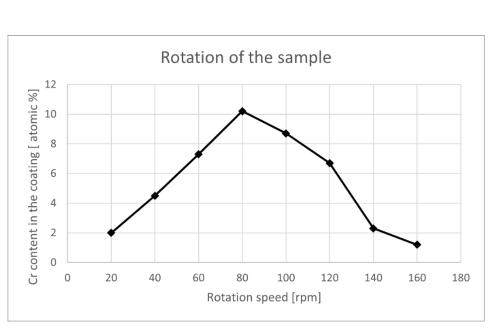


- Blue arrow: micellar aggregation

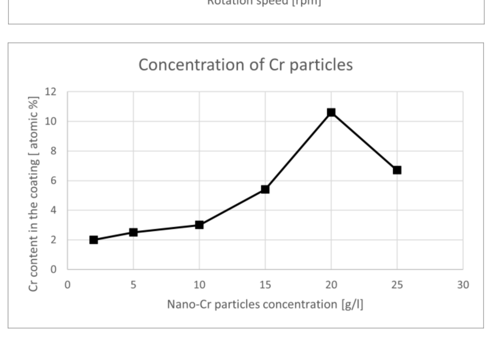
Once the critical micellar concentration (CMC) is reached, the Cr particles are well dispersed in the deposition bath

- Red arrow: foaming due to agitation

Beyond the CMC value of the CTAB, the progressive increase in the stirring speed leads to the formation of foam. The particles remain included in the formed foam.

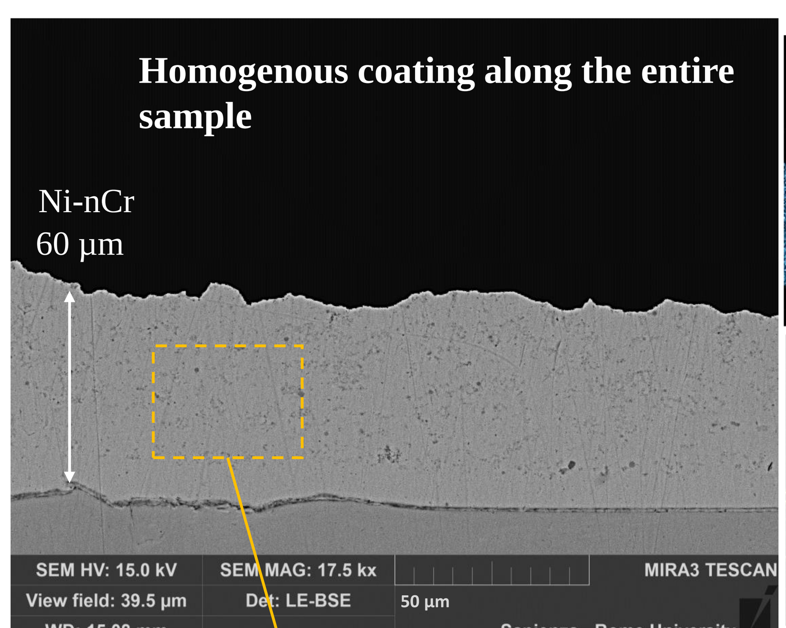


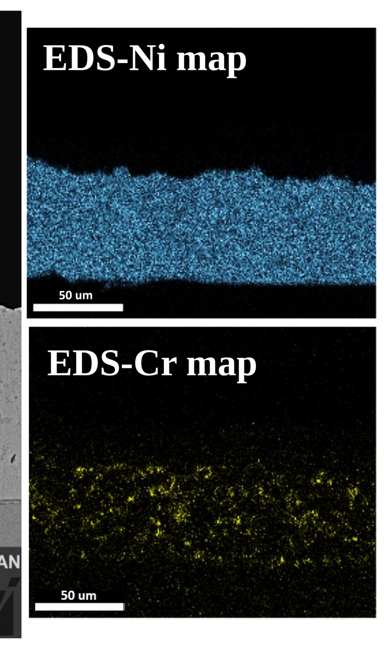
- The **rotation speed of the sample** determines the dispersion of the particles in the deposition bath and the adsorption equilibrium of the latter on the sample surface. The optimal value is 80 rpm.

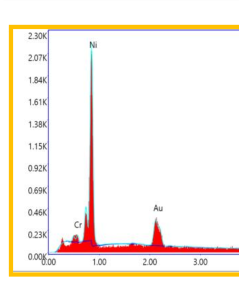


- The concentration of Cr in the coating is directly proportional to their **concentration in the deposition bath**. The limit value is around 20 g / l, beyond which they tend to deposit on the bottom of the deposition bath and reactivity is compromised.

As deposited NiCr coating





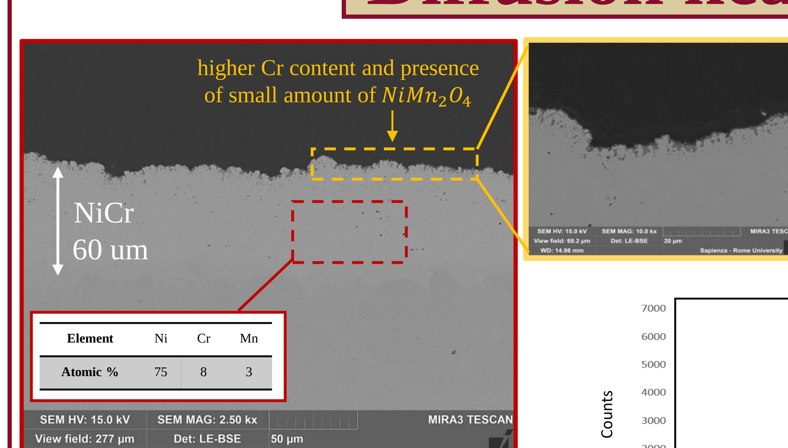


Element	Atomic %
Ni	90
Cr	10

- **As coated NiCr coating**

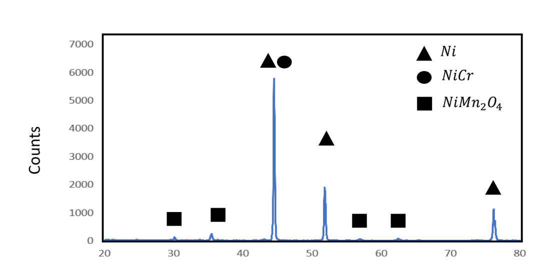
The atomic % of Cr in the coating is around 10. The distribution of the particles is homogeneous throughout the coating. The thickness of 60 µm was obtained after 6 h of deposition at 70 ° C with the deposition parameters described above.

Diffusion heat treatment



Element	Ni	Cr	Mn
Atomic %	75	8	3

The diffusion process was carried out in Ar atmosphere at 900 ° C for a total of 4 hours.

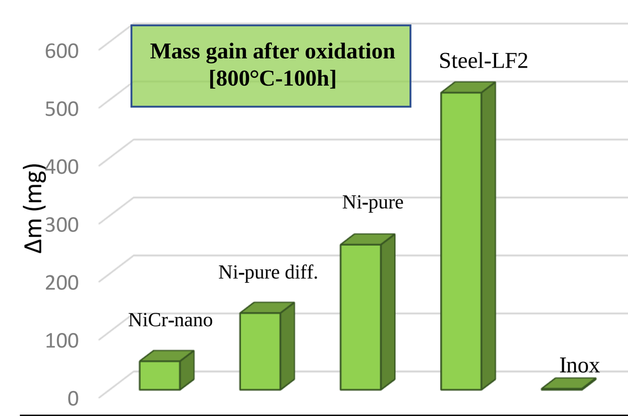


- **Diffuse NiCr coating**

The diffusion of the nano particles in the Ni matrix is complete, with the formation of NiCr. In addition, trace amounts of Mn are present in the coating, originating from the substrate

- XRD analysis confirms the presence of NiCr phase. It also shows the presence of small amount of nickel manganite phase ($NiMn_2O_4$) formed by the diffusion of Mn from the substrate towards the coating.

Heat treatment



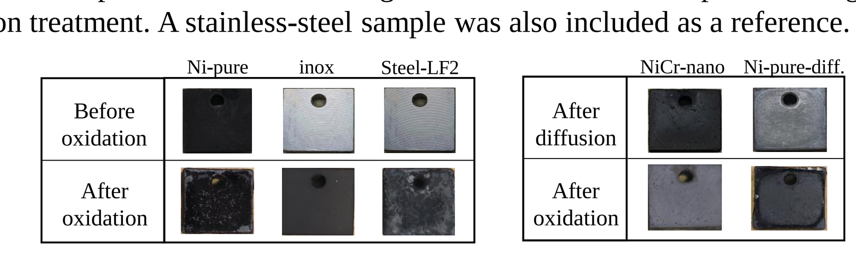
Sample	NiCr-nano	Ni-pure-diff.	Ni-pure	Steel-LF2	Inox steel
Mass gain (mg)	49,1	132,2	250,1	512,3	1,7

- **Oxidation tests parameters**

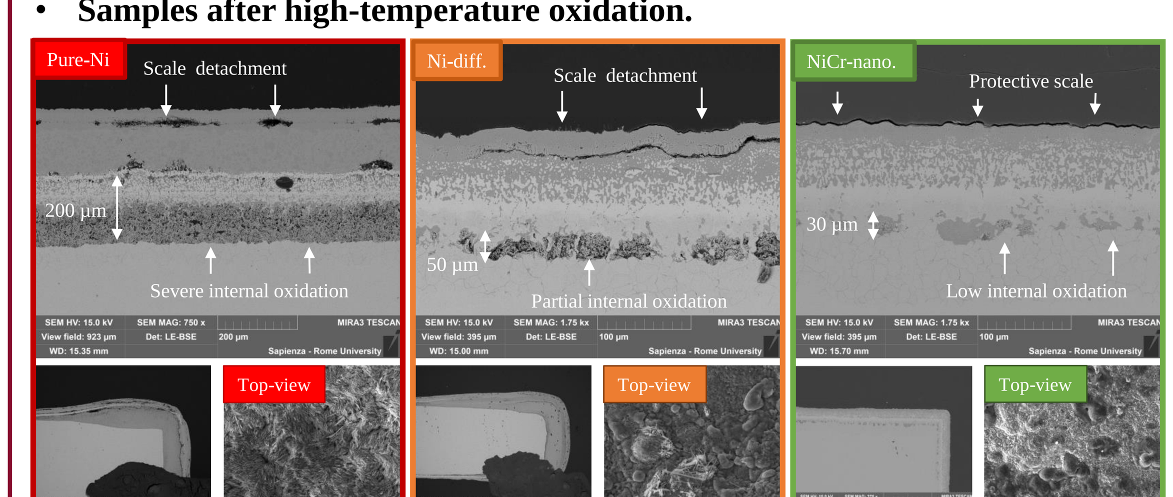
Parameters	Isothermal oxidation
Furnace	Muffle
Atmosphere	Air
Temperature (°C)	800
Time (h)	100
Heating rate(°C/min)	10
Cooling rate(°C/min)	10

- **High temperature oxidation test**

The obtained NiCr coating was compared in oxidation with the bare substrate, an electroless Ni-pure as coated coating and an electroless Ni-pure coating after the diffusion treatment. A stainless-steel sample was also included as a reference.



- **Samples after high-temperature oxidation.**



- **As coated NiCr coating**

The sample coated only with Ni shows severe internal oxidation with detachment of the oxide scale, which is unprotective. The Ni-coated sample that has undergone diffusion heat treatment shows partial internal oxidation but also exhibits significant oxide scale detachment. The sample coated with NiCr, on the other hand, shows a low degree of internal oxidation and especially the formation of a protective oxide scale. This scale is continuous throughout the sample and does not show any detachment. In contrast, in the Ni-coated samples, the oxide profile is highly irregular, and the edges appear to have sustained heavy oxidative stress.

Conclusion

- **Good deposition efficiecies** and the preliminary results of **high-temperature oxidation** suggest that the studied coating are a good alternative to produce NiCr coatings.

- Studying the influence of deposition parameters, it was possible to obtain a starting point for an experimental set up for the deposition of NiCr electroless coatings. The possibility of including metal particles in metal matrix for electroless plating is a step forward in composite coatings obtained for electroless plating. The fundamental parameters for this type of coating technique are:
  - **Addition of dispersing agents:** by adding surfactants such as CTAB to the reaction bath, these enable greater dispersion of the particles in solution and influence the adsorption equilibrium of the particles on the growing coating. The concentration of these is a key parameter for a good inclusion of the particles in the coating.
  - **Rotation speed of the sample and particles concentration:** the optimal values of these parameters have been studied to obtain the maximum yield in terms of Cr content in the coating.

- The high-temperature diffusion process on NiCr coatings obtained by electroless plating shows the formation of a homogeneous NiCr phase over the entire sample. The coating layer, however, was not able to block the diffusion of elements from the substrate. towards the coating surface .
- Comparison of the high-temperature oxidative stress behaviour of the obtained NiCr coating and the substrate as such, shows a substantial protective effect of the NiCr coating. The post-oxidation weight gain is ten times lower for the electroless NiCr-coated sample than for the LF2 substrate used.
- The formation of a protective oxide layer in NiCr-coated specimens is homogenous along the entire surface and near the edges. The coating also significantly reduces internal oxidation and there are no detachments or cracks.

➢ Future prospects:

- The partial presence of mixed oxides in the protective scale suggests that the Cr content in the coating needs to be increased. Further investigations into the deposition parameters and the high-temperature diffusion process are needed to improve the protective properties of electroless-plated NiCr coatings.