# Alternatives to coatings from Chromium VI baths

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Alternatives to coatings from Cr VI baths are presented for technologically advanced applications. The following possibilities are discussed: Ni-P and Ni-P+B<sub>4</sub>C coatings, Co-W and Co-W+B<sub>4</sub>C coatings and electrodeposition of chromium from Cr III baths. Alternative coatings show microhardness comparable to hard chromium, with mechanical properties that can be improved with thermal treatments. Some of the coatings investigated were subjected also to wear tests. Results demonstrated that wear resistance values of the deposits are comparable, or even higher, than those obtained with hard chromium. Promising results regarding the mechanical properties and wear resistance of the coatings were obtained by electrodepositing composite materials with Ni-P or Co-W matrices and dispersed microparticles of boron carbide B<sub>4</sub>C. The structure and composition of the films were characterized by XRD and SEM analysis; the mechanical properties of the deposits were studied by microindentation technique. Chromium electroplating using a Cr III electrolyte was used, but for electrowinning. A Cr III oxalate bath for hard chromium plating is presented. Formation of Cr II, inhibiting species and the Cr VI enrichment in the bath are considered as possible reactions giving difficulties yo maintain stable electrodeposition conditions.

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### Introduction

A most actual problem of the plating industry is the replacement of hexavalent chromium plating baths with less harmful electrolytes  $^{(1,2)}$  by maintaining, at the same time, the excellent properties characterising chromium coatings, such as high hardness (> 1000 HV), excellent wear resistance, oxidation resistance, and the low cost of the raw materials employed. Moreover, very thick coatings can be obtained and anodic pretreatments in the bath are possible with Cr VI electroplating.

Despite such properties, Cr VI electrolytes suffer of several drawbacks: expensive effluent treatment procedure, also related to the carcinogenic activity of Cr VI, poor throwing power and the need of high current densities with low faradic efficiencies, problems of adhesion to substrates and possible hydrogen embrittlement. Difficulties in the electrolyte control are also a consequence of the low amount of catalysing substances and of the build up of substances and impurities, i.e. Cr III, Cu, Zn, Fe and Al. A limited corrosion resistance of chromium steel parts, directly plated on steel, is closely related to the presence of micro-cracks in the coating.

Several alternative processes for chromium electroplating were proposed. None of them seems to be recognised as a valid substitute for chromium in most advanced applications. The process proposed should be different, depending on the specific application of the coatings.<sup>(3)</sup>

In this paper, results on Co-W and Ni-P layers or their composites with micrometric ceramic particles,<sup>(4,5)</sup> as valid alternatives for the replacement of chromium coatings in wear-resistant applications, will be presented.<sup>(6,7)</sup> Moreover the electrodeposition from Cr III electrolytes is considered. Results presented in this paper refer to preliminary experiments carried out with an oxalate based solution, which is a modification of that proposed by Polukarov et al <sup>(8)</sup>.

## Experimental

Deposits of Ni-P (P=9%) were chemically plated onto substrates of nitrided steel; electrodeposited composites of Ni-P (P=2%) with dispersed B<sub>4</sub>C particles were obtained onto copper, Co-W and Co-W+B<sub>4</sub>C coatings onto brass. For a detailed description of the electrochemical behaviour of the electrolyte solutions see Refs. (5-6).

Some Ni-P layers were subjected, immediately after deposition, to thermal treatment at 300°C in air, for 30 to 180 minutes. Some Co-W coatings were subjected to thermal treatment in vacuum, at temperatures in the range from 50 to 400°C. Experimental details can be found in Ref. 9.

Table 1 and Table 2 report electrolyte compositions and operating conditions employed for Co-W and Ni-P deposits.

Co-W			
Component	Concentration		
Cobalt sulphamate	0.1M		
Ammonium citrate	0.1M		
Glycine	0.1M		
Sodium tungstate	0.27M		
Sodium hypophosphite	0.1M		
Temperature	60°C		
pН	8.2		
deposition rate	10 µm/hour		

 Table 1. Co-W electrolyte composition and operating conditions.

Table 2.	Ni-P	electrolyte	composition	and	operating
condition	s.				

Ni-P			
Component	Concentration		
Nickel sulphate	0.1M		
Sodium hypophosphite	0.3M		
Lactic acid	0.2M		
Acetic acid	0.2M		
Succinic acid	0.1M		
Glycolic acid	0.01M		
Ammonium fluoride	7 mM		
Temperature	85°C		
pН	4.5		
deposition rate	20 µm/hour		

In Table 3 the composition of Cr III bath is reported, with the operating conditions adopted for electrodeposition.

Cr III			
Component	Concentration		
Chromium sulphate	0.43 M		
Oxalic acid	0.12 M		
Magnesium sulphate	1.60 M		
Urea	2.26 M		
Methanol	136.36 ml/l		
j	$200 \text{ mA cm}^2$		
Т	30°C		

Table 3. Cr III electrolyte composition and operating conditions.

Vickers microhardness and elastic modulus of the deposits were obtained with a microindenter FISCHERSCOPE<sup>®</sup> H100, at different load values, from 5 mN to 250 mN. Coating compositions were obtained by EDS analysis and surface morphology was assessed with optical microscopy and SEM (Cambridge Stereoscan 360). Structure was controlled by taking XRD patterns (Philips PW 1830, PW3020).

Dry sliding friction and wear tests were carried out on both Co-W and Ni-P using a computercontrolled slider-on-cylinder tribometer. For experimental details see Ref. 10.

#### **Results and discussion**

Figure 1 and Figure 2 show microhardness and elastic modulus values obtained on Ni-P, with and without boron carbide microparticles, Co-W coatings and on hard chromium, as a reference. From the microhardness curves a decrease is observed at increasing applied load. The high hardness values for Ni-P and Co-W coatings, at very low applied load, might be related to the amorphous structure of Ni-P and Co-W layers and it is not observed with composite coatings, a possible consequence of the low phosphorus content of the deposit.



Figure 1. Microhardness of different coatings.



The elastic modulus was almost independent of the applied load for both hard chromium and Ni- $P+B_4C$  coatings, whilst the Ni-P and Co-W values show an increase at very low load. This behavior can be related to the hardness behavior. In all cases, the values obtained at high applied load were slightly lower than those for hard chromium.

Figure 3 and Figure 4 show the cross section morphology of Ni-P and Ni-P+B<sub>4</sub>C deposits.



Figure 3. SEM micrograph of Ni-P deposit (cross-section).



Figure 4. SEM micrograph of Ni-P+B<sub>4</sub>C deposit (cross-section).

It was possible to improve the mechanical properties of Ni-P and Ni-P+B<sub>4</sub>C coatings by thermal treatment (see Figure 5).



Figure 5. Hardness behaviour as a function of thermal treatment duration at 300°C for Ni-P and NiP+B<sub>4</sub>C coatings.

Thermal treatment at 300°C, for at least 1 hour, induces a transformation of the amorphous Ni-P structure towards a crystalline biphasic system, Ni-N<sub>b</sub>P. Hardness value is dependent on the annealing time. For instance, after a 200 min thermal treatment of Ni-P hardness increases from 500 HV up to 850 HV. In the case of Ni-P+B<sub>4</sub>C coating, hardness increases correspondingly from 600 HV to 1100 HV.

A similar treatment method was adopted for Co-W electrodeposits. Morphologies of Co-W without and with B<sub>4</sub>C particles are shown in Figure 6 and Figure 7, respectively.



Figure 6. SEM micrograph of Co-W deposit (cross-section).



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Figure 7. SEM micrograph of  $Co-W+B_4C$  deposit (cross-section).

Hardness of composite Co-W+B<sub>4</sub>C layers is higher than that of Co-W without particles (as shown in Figure 8). Hardness value of Co-W+B<sub>4</sub>C deposits is about 800 HV, with respect to 650 HV of Co-W deposits. An increase of the number of boron carbide particles incorporated in the deposit, which is related to that of particles in the electrolyte, improves the mechanical properties of Co-W composite layers. For instance, a B<sub>4</sub>C concentration of 4 g/l in the bath gives deposits of 780 HV, and 6 g/l corresponds to deposits of 810 HV.



Figure 8. Hardness profile as a function of thermal treatment temperature (Co-W and Co-W+B<sub>4</sub>C at two different concentrations).

Figure 8 shows that thermal treatment improves the mechanical properties of Co-W deposits. For such materials, it was difficult to assess from XRD patterns a phase change.<sup>(6)</sup> We have shown,<sup>(6)</sup> by varying the amount of phosphorus in the deposits, that hardness increase can be related to segregation of finely dispersed phosphides of high hardness.

Table 4 reports the friction coefficients (against DLC) of different coatings compared to that of hard chromium layers.

Coefficient of friction		
Coating	Value	
Hard chromium	0.2	
Co-W	0.2	
Co-W annealed	0.1	
Ni-P	0.6	
Ni-P annealed	0.4	
Ni-P+B <sub>4</sub> C	0.53	
Ni-P+B <sub>4</sub> C annealed	0.68	

# Table 4. Coefficient of friction of different type of coatings.

Electrodeposition of chromium from trivalent baths is an attractive alternative to Cr VI baths for several reasons. Most important is the presence of trivalent chromium less harmful than hexavalent chromium.



Figure 9. XRD pattern of Cr deposit from oxalate bath (S: substrate; Cr: chromium).

Gabe enumerated the following advantages in using Cr III baths in comparison to Cr VI ones, better faradic efficiency, less corrosive and hazardous solutions, easier effluent treatment, possible solution regeneration and possible use of soluble anodes for solution replenishment <sup>(11)</sup>.

The deposits obtained in this work with the reported solution had a typical carbon content of about 2-4 at%. The carbon is present in form of chromium carbide. XRD pattern of Figure 9 shows reflections attributable to chromium carbide.

The intense hydrogen evolution is related to the low faradic efficiency for Cr reduction, as shown in Figure 10 where a decrease of the faradic efficiency  $\Phi$ , with of the deposition time, is shown.



Figure 10. Faradic efficiency as a function of deposition time.

This behavior can be related to the slow kinetic reactions involving Cr II and Cr III species, changing the solution speciation during the electrodeposition process.



Figure 11. Cross section of a Cr deposit (45 min of deposition).

Figure 11 shows the cross section of a fractured chromium sample, electrodeposited in 45 min in the operation conditions reported in Table 3. Coating thickness is about 10  $\mu$ m. The deposit is made of fine filamentary crystals of cross section diameter <100  $\mu$ m. This fibrous structure can account for the high hardness of these deposits: 900-1100 HV, increasing further after thermal treatment.



Figure 12. Faradic efficiency as a function of electrolyte pH (deposition time 15 min).

Faradic efficiency is also strongly dependent on pH, with values noticeably increasing when the pH is 1-2. Lower pH favors intense hydrogen gas evolution, whilst at higher pH the formation of chromium hydroxide or basic salts could explain the strong efficiency decrease to almost negligible values. Highest values attained of faradic efficiency were 25-30%.

Temperature and current density play an important role. The faradic efficiency increases by decreasing the electrolyte temperature, and by increasing the current density (see Figure 13 and Figure 14).



Figure 13. Faradic efficiency as a function of deposition temperature (deposition time 15 min).



Figure 14. Faradic efficiency as a function of deposition current density (deposition time 15 min).

#### Conclusions

Different alternatives to hard chromium are proposed, according to the specific coating application.

Thick coatings of Co-W and Co-W+B<sub>4</sub>C with uniform properties through the film thickness were obtained by electrodeposition. Such deposits show good mechanical properties: high microhardness, high fracture toughness, low internal stresses and high adhesion, even onto HSS steel. Moreover good wear resistance properties and low friction coefficients were observed in dry sliding conditions. Co-W deposition baths show some difficulties concerning the reproducibility (at the laboratory scale) and expensive metals are employed. Such coatings might be particularly devised for technologically advanced applications, e.g. in a high temperature environment, when low friction coefficient is required.

As a second alternative Ni-P and Ni-P+B<sub>4</sub>C (with low Ni content) coatings were investigated. Such layers can show mechanical properties comparable with those of chromium layers in the case of composites. Ni-P+B<sub>4</sub>C are particularly suitable as wear resistant layers for normal temperature applications. Low roughness is achievable by proper finishing of the Ni-P and Ni-P+B<sub>4</sub>C surfaces. Electrochemical Ni-P+B<sub>4</sub>C is a less expensive option than hard chromium, and also with respect to Co-W alloys. They show very high corrosion resistance in normal environments and high electrodeposition efficiency. Disadvantages are due to the operation difficulty for the obtainment of uniform composite layers. In particular, a careful control of the hydrodynamic conditions during deposition must be realized, with good bath stirring, optimal dispersion of the ceramic microparticles and uniform impinging of them onto the plating surface.

The electrodeposition from trivalent chromium baths is a most interesting alternative to hard chromium from Cr VI baths, if a proper bath control is achieved. Chromium III baths are still under development and utilized only for decorative applications; a mature technological level was not gained to implement trivalent chromium electrolytes in commercial operations. We studied the behavior of Cr III oxalate baths, containing organic substances such as methanol, giving carbon codeposition and possible carbides in the deposit.

Results are quite encouraging, but further investigations are needed in order to have a better understanding of the solution chemistry and the discharge mechanism.

Problems are related to:

- 1) the difficulty to obtain high current efficiency at low deposition current densities;
- 2) time inhibition of the surface on which deposition occurs, related in part to the control of Cr II species and to their time control;
- 3) the difficulty to extend good results obtained depositing onto steel to other substrates.

The need of Cr II species at the surface can be explained with reference to the Normality-Inertia parameter, recently introduced to quantify the Piontelli classification on electrokinetic behavior of elements in aqueous solutions.<sup>(12)</sup>

Electrokinetic behavior of metals in aqueous solutions can be related to the relative values of the different enthalpic contributions to a Born Haber cycle representing the metal ion discharge at the cathode.

The cathodic deposition reaction of a metal can be described with a Born Haber cycle having the following steps:

- dehydration with transfer of the metal ion from the aqueous solution to the gas phase, with enthalpic contribution  $\Delta h^{\circ}_{hydr}$ ;
- neutralization (deionization) with discharge of the ionic gas species, with enthalpic contribution  $\Delta h^{\circ}_{ion}$ ;
- crystallization (deatomization) with transfer of the neutral gas species to the solid phase, with enthalpic contribution  $\Delta h^{\circ}_{at}$ .

The total enthalpic change with respect to the discharge cell reaction of the galvanic chain M /  $\epsilon_M \parallel \epsilon_H$  / NHE is given taking account of the cycle by:

$$\Delta h^{\circ}_{cel} = \Delta h^{\circ}_{hydr} + \Delta h^{\circ}_{ion} + \Delta h^{\circ}_{at}$$

Minimizing the interliquid contact  $\varepsilon_M \| \varepsilon_H$  voltage and assuming a constant value for the reference semicell contribution  $K_{NHE}$ , we obtain:

 $E^{\circ} = -(\Delta h^{\circ}_{hydr} + \Delta h^{\circ}_{ion} + \Delta h^{\circ}_{at} - T\Delta s^{\circ}_{cel})/(zF) + K_{NHE}$ 

where  $T\Delta s^{\circ}_{cel}$  is the very limited contribution given by the standard entropy change for the cell reaction (from  $\Delta g^{\circ}_{cel} = \Delta h^{\circ}_{cel} - T\Delta s^{\circ}_{cel}$ ).

The ratio of the enthalpic contribution for the whole process  $\Delta h^{\circ}_{cel}$  with respect to the enthalpic contribution for transfer from the aqueous solution to the metallic gas atom  $\Delta h^{\circ}_{ion} + \Delta h^{\circ}_{hydr}$ , corrected mutiplying by the ratio  $\Delta h^{\circ}_{ion,H}$ , which takes into account the relative importance of the ion valence state, gives the parameter of Normality-Inertia:

 $\mathbf{P_{NI}} = [\Delta h^{\circ}_{cel} / (\Delta h^{\circ}_{ion} + \Delta h^{\circ}_{hydr})] * (\Delta h^{\circ}_{ion} / \Delta h^{\circ}_{ion,H})$ 

Elements with a high  $P_{NI}$  value are inert metals, according to the Piontelli classification, whilst those with low  $P_{NI}$  value are normal metals in the same classification.

There is no relationship between the electromotive force of the standard reaction and the  $P_{\rm NI}$  value. Among most electronegative metals Ti, Al and Be have high  $P_{\rm NI}$  values, whilst Mg and Mn have more limited values.

From data reported in Table 5 we observe that metals easily passivated and not deposited from aqueous solutions have  $P_{NI}$  values greater than  $P_{NI,H}$ ; this is the case of Al and Ti, but also Cr III has a similar behavior. Cr II has a  $P_{NI}$  value lower than  $P_{NI,H}$  giving a possible justification to the need of Cr II species at the cathodic interface where discharge reactions occurs, while if only Cr III is present at the surface the discharge could be inhibited.

Electrodic	<b>D</b> h <sup>°</sup> at	<b>D</b> h <sup>°</sup> ion	<b>D</b> h <sup>°</sup> <sub>hydr</sub>	<b>E</b> °( <b>V</b> )	P <sub>NI</sub>
reaction	/zF	/zF	/zF		
$H_2 = 2H^+ + 2e^-$	2,2591	13,6626	-11,3075	0,0000	1,959
$Al=Al^{3+}+3e^{-}$	1,1390	17,8066	-16,1659	-1,676	2,208
$Ti=Ti^{3+}+3e^{-}$	1,3733	16,0882	-14,2291	-1,21	2,047
$Mn=Mn^{2+}+2e^{-1}$	1,4546	11,5992	-9,5836	-1,18	1,462
$Cr=Cr^{2+}+2e^{-}$	2,0599	11,6951	-10,0321	-0,9017	1,916
$Cr=Cr^{3+}+3e^{-}$	1,3733	18,1393	-15,7655	-0,743	2,096
$Fe=Fe^{2+}+2e^{-}$	2,1573	12,1050	-10,1275	-0,47	1,853

 Table 5 - Born-Haber cycle enthalpic contribution for metal electrodic reactions

 in aqueous solution, standard electromotive force and Normality–Inertia parameter

## References

- 1) J. H. Lindsay, Plat.&Surf.Fin. 82, 19 (1995).
- 2) S. R. Schaschameyer, Proc. Cong. Hard Chromium Plating 1995, 4 (1995).
- 3) M.El-Sharift, Trans IMF 75, B143 (1997).
- 4) B. Bozzini, P. L. Cavallotti, G. Giovannelli, *Praktische Metall*. <u>33</u>, 130 (1996).
- 5) B. Bozzini, M. Boniardi, Zeit.Metalk.de, 88, 493 (1997).
- 6) P. L. Cavallotti, N. Lecis, L. Gobbato, *Oberflaeche-Polysurfaces* **2**, 10 (2001).
- 7) A. Krohn, C.W. Bohn, *Plating* 58, 237 (1971).
- 8) Y.M. Polukarov, V.A. Safonov, A.A. Edigaryan, L.N. Vykhodtseva, Prot. Met. 37, 447 (2001).
- 9) M. Bestetti, L. Gobbato, N. Lecis, P.L. Cavallotti, *Proc. Euromat 2001*, Rimini, June 10-14, 2001 (2001).
- 10) L. Nobili, P.L. Cavallotti, G. De Ponti, D. Colombo, Metallurgia Italiana. XC, 49 (1998).
- 11) D. Gabe, *Proc. Int. Seminar on Hexavalent Chromium in the metal finishing industry 2002*, AIFM, Milan, 8<sup>th</sup> March 2002.
- 12) P.L.Cavallotti, B.Bozzini, L.Nobili; G.Zangari, *Electrochim.Acta*, **39**, 1123(1994).