ELCTRODEPOSITION OF TERNARY ALLOYS AND COMPOSITE COATINGS AS ALTERNATIVES TO HARD CHROMIUM.

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Abstract: Alternative coatings for hard chromium have been widely investigated in last years but until now no applicable process is adopted neither by military nor by industry, where special operating conditions are standard. Therefore, electroplating of hard chromium is still in use, using chromium six-valence solution, which is labeled as a material that might be banned in the near future.

We have investigated several chromium alternatives based on binary and ternary alloys, and composite coatings particles on hard steels. Coatings with a thickness of 10-200µm were obtained, from Ni based chemicals and with addition of several types of elements, W, Co and P, together with or without particles of SiC.

The coatings microhardness were measured in the range of 550-700 HV in the as- deposited form. In contrast to hard chromium, heating of these coatings to temperature between 250-500^{0}C caused the increase in microhardness to values of 900-1000 HV.

Optimal coatings were also tested for machinability and hydrogen embrittlement according to military specifications.

Several bath formulations and anodes types were studied, in order to get better control on coating composition and higher stability of the electrolyte. In the experiments of metal -ceramic composite coatings, different types of additives and bath agitation techniques were used in order to get homogenous dispersion of the particles in the coatings. This paper discusses major process parameters affecting coatings composition and morphology, the resulted mechanical characteristics and the probability for implementation of these deposition processes for industrial use.

Experimental :

Types of Coatings

- **Ternary :** Fe – Ni – C , Ni – W – V, Ni – W – B, **Ni – W – P, Ni – W – Co**
- **Composites :** Ni-Co -Al_2O_3, **Ni- P - SiC**
- **Substrates: High strength steels : 4340, 300 M, 15-5PH**

Measurements and Characterization:

Corrosion: Salt spray cabinet according to ASTM B117

Electrochemical measurements

Machining: were conducted using rod samples according to IAI standards. After machining the samples were examined for evidence of cracks and exfoliation.

Hydrogen embrittlement : were carried out according to ASTM F 519 on notch cylinders

Composition : EDS analysis, GDA

Morphology : SEM

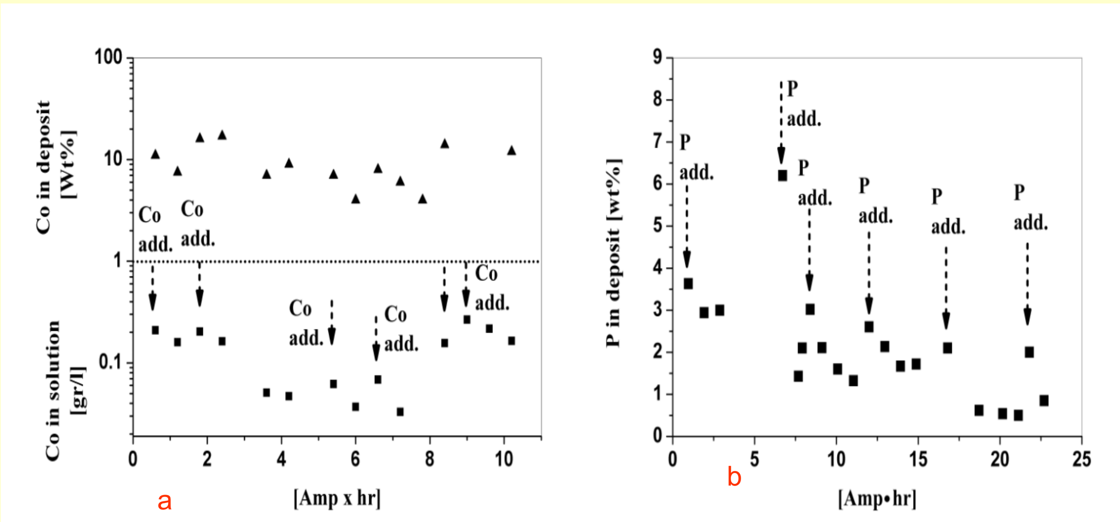
Microhardness: Measurement on deposit cross-sections, Vickers microhardness tester under 100-200gr.

Adhesion: Bending of test panels made of steel 4130 SEM of cross-section

RESULTS

LONG –TERM OPERATION:

a. Co content in electrodeposited Ni-W-Co coatings and in the electrolyte during long -term operation of the bath. **b**. Phosphor content in Ni-W-P coatings, during long- term operation of the bath.(the arrow indicates addition of cobalt salt or hypophosphite)

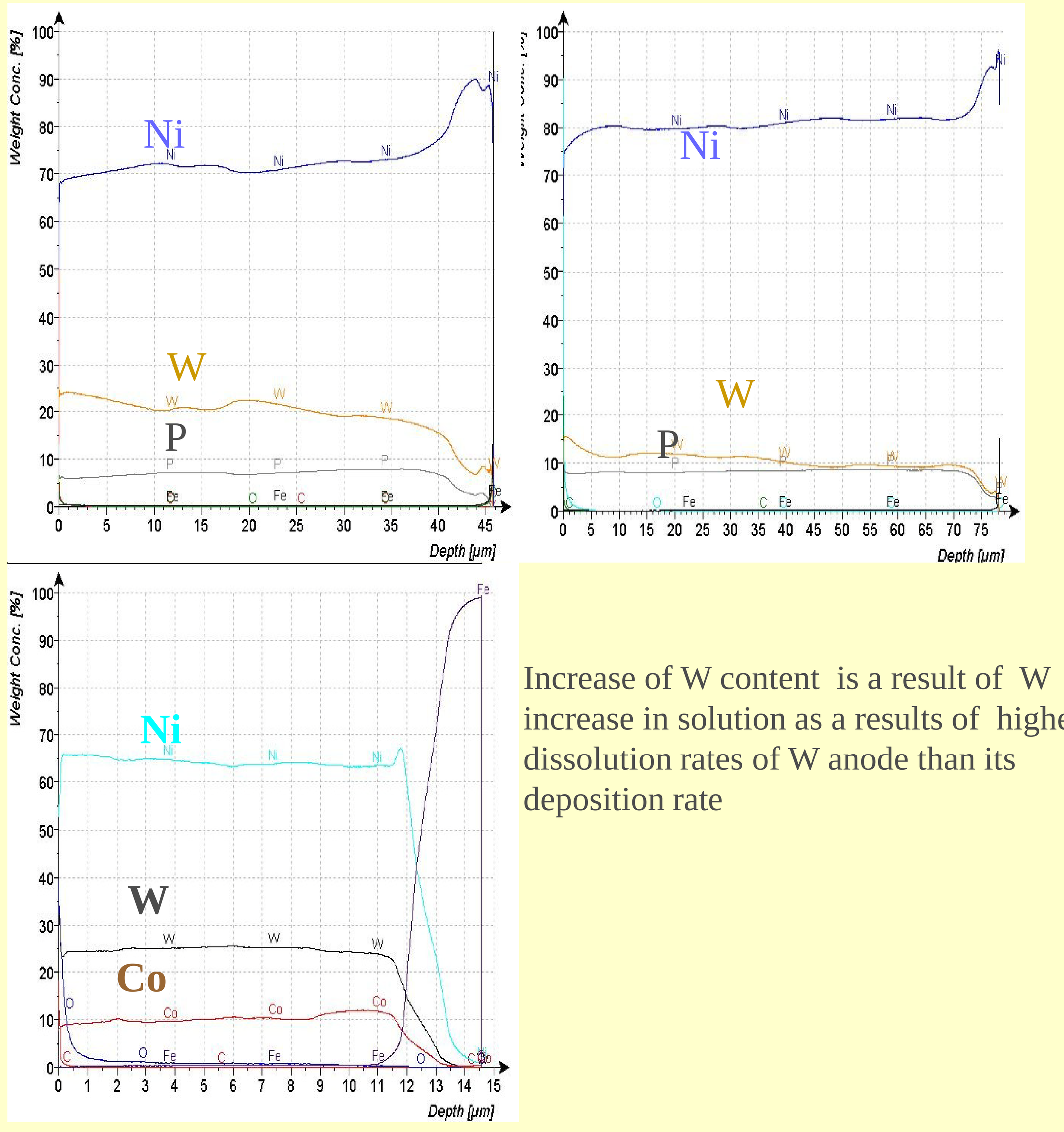


Controlled parameters: pH, Co/P content, W content, Ni content
Deposition at 3A/dm^2, pH 8.5-9, deposition rate : 0.2-0.3µm /min.

Deposition Rate of the investigated coatings

Coating	Current Density A/dm^2	Current Efficiency, %	Deposition Rate, µm/min	Time for 50µm Deposition, Min.
NiP (Sulphate)	3-10	70-85	0.4-1.7	125-29
NiP (Sulphamate)	3-20	95-99	0.5-3.9	100-13
Ni-W-P	3-5	60-80	0.2-0.3	250-167
Ni-W-Co	3	55-70	0.2-0.3	250-167
Cr	16-60	13-20	0.16-0.97	312-52

Coatings Composition –GDA Depth Profile



Increase of W content is a result of W increase in solution as a results of higher dissolution rates of W anode than its deposition rate

Microhardness of Ni-W-Co coatings

Coating content Wt%		Microhardness, HV			
W	Co	As deposit	250°C	500°C	750°C
26	6	550-580	630-640	825-835	420-460
33	8	540-550	730-750	850-900	300-430
34	13	600-725		960-1050	
30	14	640-650	740	930-940	600-610
27	16	640			
Hard Chrome		800-1050	950	600-700	200

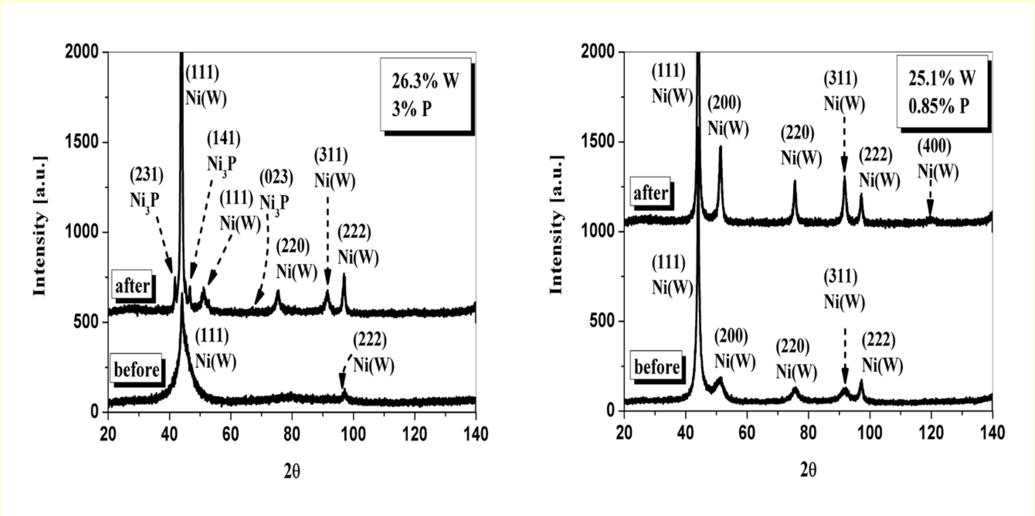
Microhardness of Ni-W-P coatings

Coating content Wt%		Microhardness, HV			
W	P	As deposit	250°C	500°C	750°C
26	0.1	575	704	850	422
24	3	630	750	1020	760
11	4	740	820	900	570
6	7	580	680	940	750
Hard Chrome		800-1050	950	600-700	200

XRD of Ni-W-P COATING

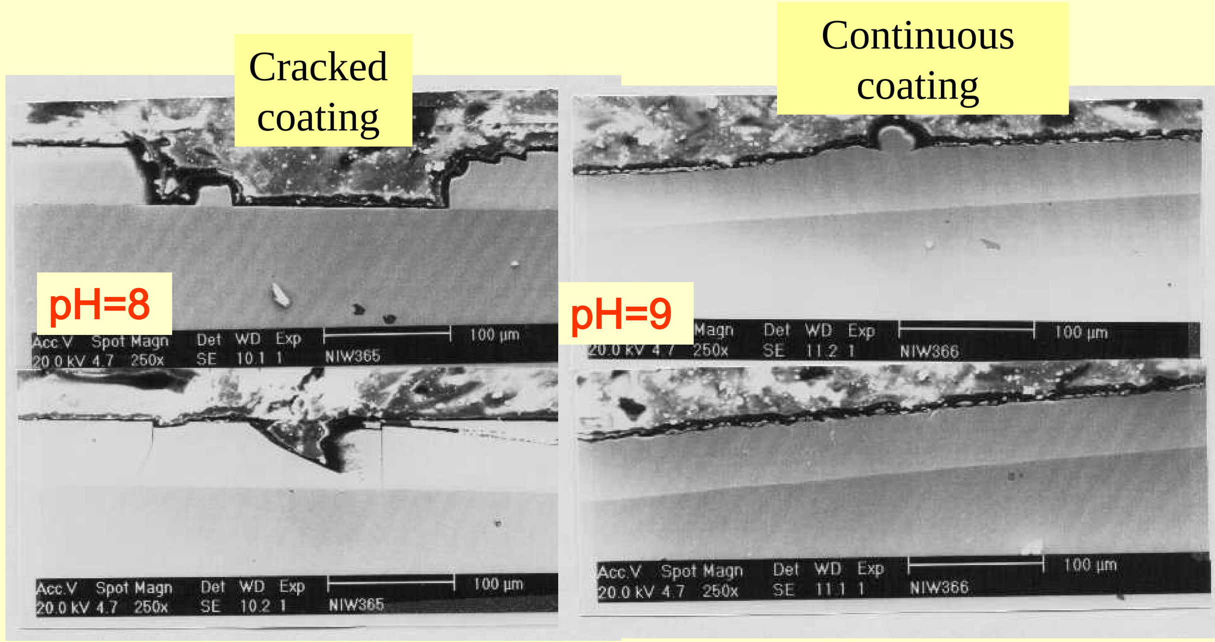
Effect of Heat treatment , 500^{o}C, 1Hr

Effect of P content

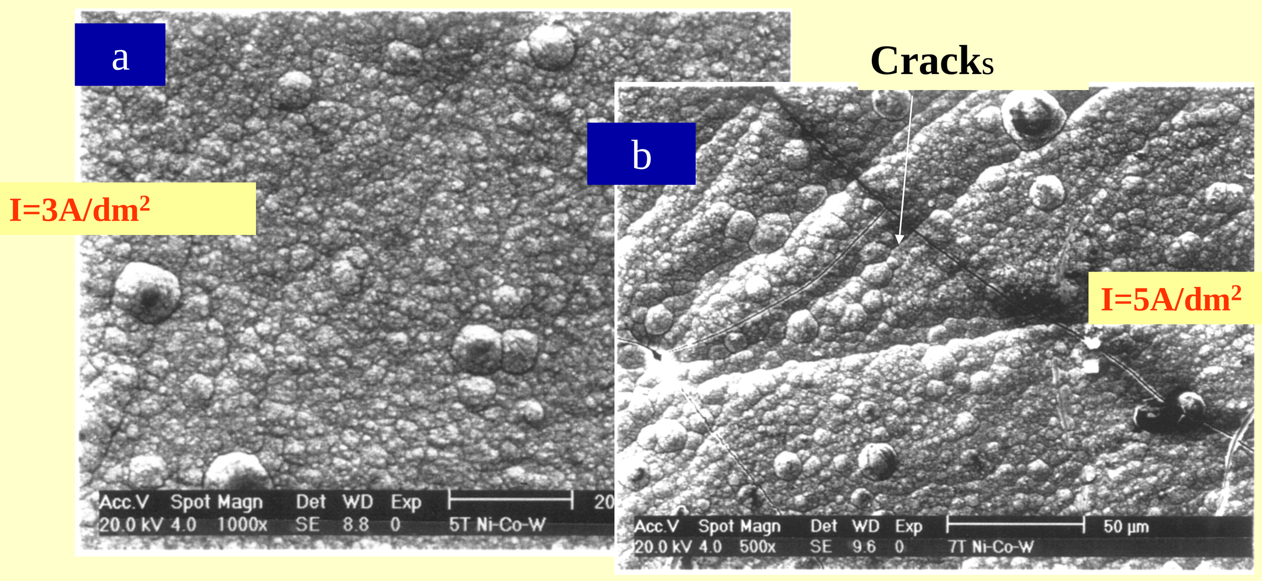


- As-Deposited: The crystallographic structure changes from amorphous to crystalline as the P content reduced from 3% to 0.85%.
- The XRD peaks of the as-deposited coatings belonged to face-centered–cubic solid solution of Ni-W , where nickel is the solvent and tungsten the solute.
- Precipitation of Ni_3P phase was found after heat treatment at 500^{o}C of coating with 3%P.
- After heat treatment at 500^{o}C, the diffraction peaks become sharper indicating the crystallization of Ni-W solid solution

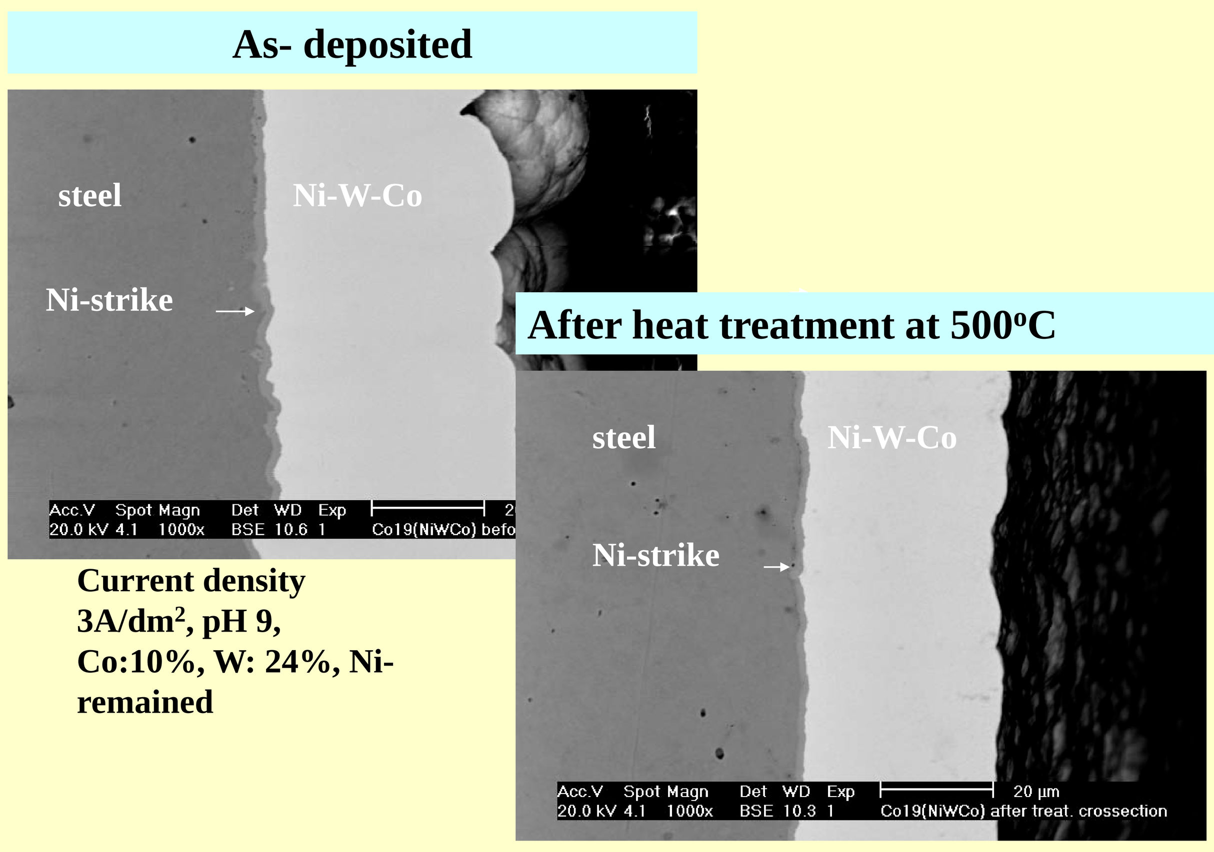
Ni-W-P : Effect of pH



Ni-W-Co coatings- Effect of Current Density

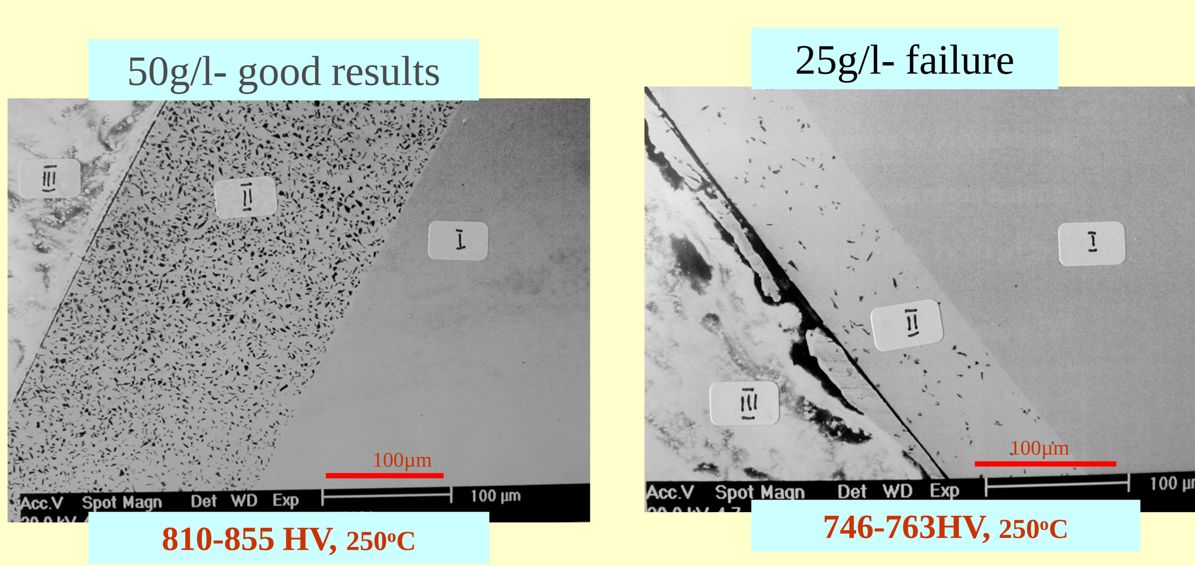


Ni-W-Co : EFFECT of HEAT TREATMENT



Current density 3A/dm^2, pH 9, Co:10%, W: 24%, Ni- remained

Ni-P- SiC: Effect of Particles Content on Machining test



The good results of machining test were obtained for the coating deposit in the presence of 50g/l irrespective of current density in the range of 3-10A/dm^2

SUMMARY

- Ternary alloy coatings Ni-W-P and Ni-W-Co and NiP-SiC coatings were studies as alternatives to hard chromium coating.
- Coating composition of the ternary alloy was found to be sensitive to the change of element concentration in the bath, therefore there was a need to control very carefully bath composition at long-term operation.
- Ternary Ni-W-P and Ni-W-Co coating with thickness of above 50µm, with good adhesion and without cracks could be obtained.
- NiP-SiC coatings with thickness of 100-300µm and good machinability were deposited.
- Heat treatment of Ni-W-Co and Ni-W- P coatings resulted in increasing hardness to about 1000HV after heat treatment at 500^{o}C, which can be attributed to precipitation of Ni_3P.
- In contrast, the microhardness of Cr coatings decreased after heat treatment. The microhardness of NiP-SiC coatings achieved values close to hard chromium after heat treatment at 250^{o}C.