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Replacement of hard chrome : panorama of some candidate technologies

Electroless nickel-boron deposition

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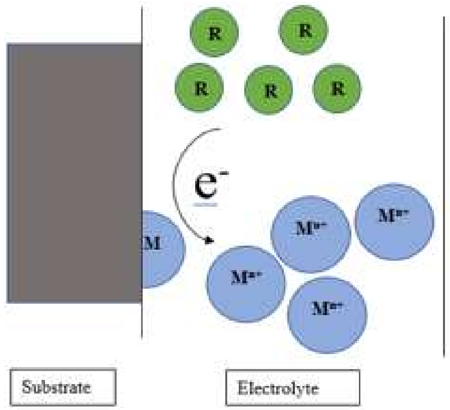
Electroless Nickel Deposition

- ✓ Discovered in 1946 by Brenner and Riddell
- ✓ No need for external current source
- ✓ No need for a conductive substrate
- ✓ Uniform deposits
- ✓ Excellent properties
- ✓ Appropriate for complex shapes

Theory of electroless nickel deposition

$$Reducing\ agent = Oxidized\ reducing\ agent + Ae^{-} \quad \text{Oxidation}$$

$$Ni^{+2} + 2e^{-} = \ Ni^{\circ} \quad \text{Reduction}$$

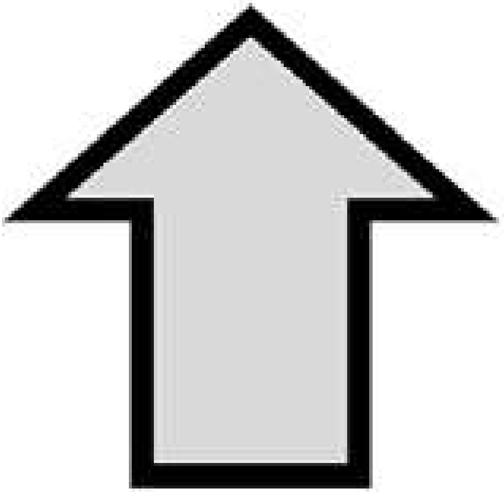


$$\Delta G^{\circ} = -\mathrm{n}\mathrm{F}\Delta E^{\circ}$$

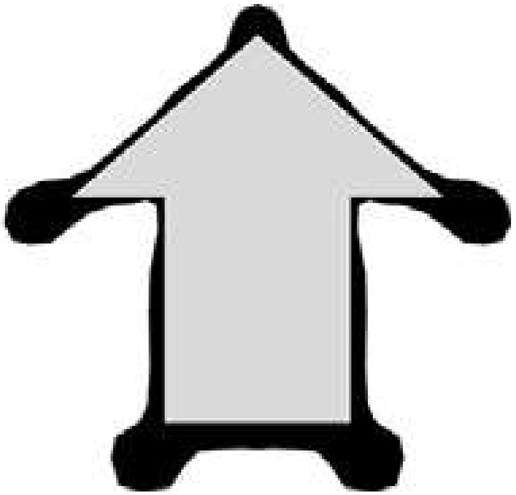
$E^{\circ} = E^{\circ}_{Ni/Ni^{+2}} - E^{\circ}_{reducing\ agent/oxidized\ reducing\ agent}$

n= number of exchanged electrons

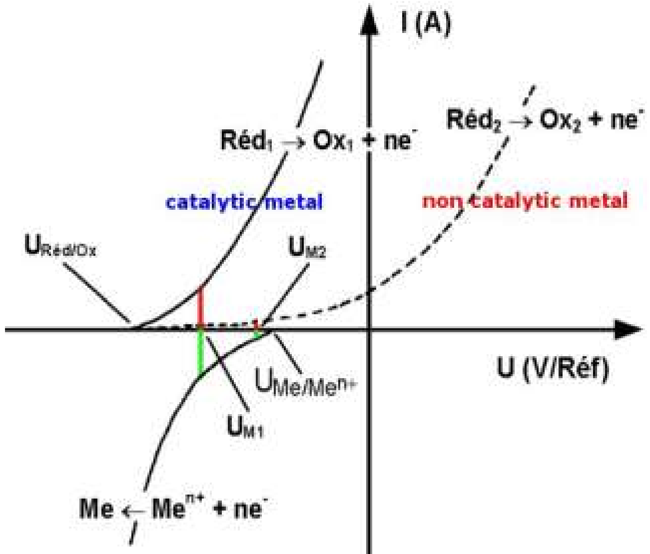
F= Faraday constant



Electroless plating

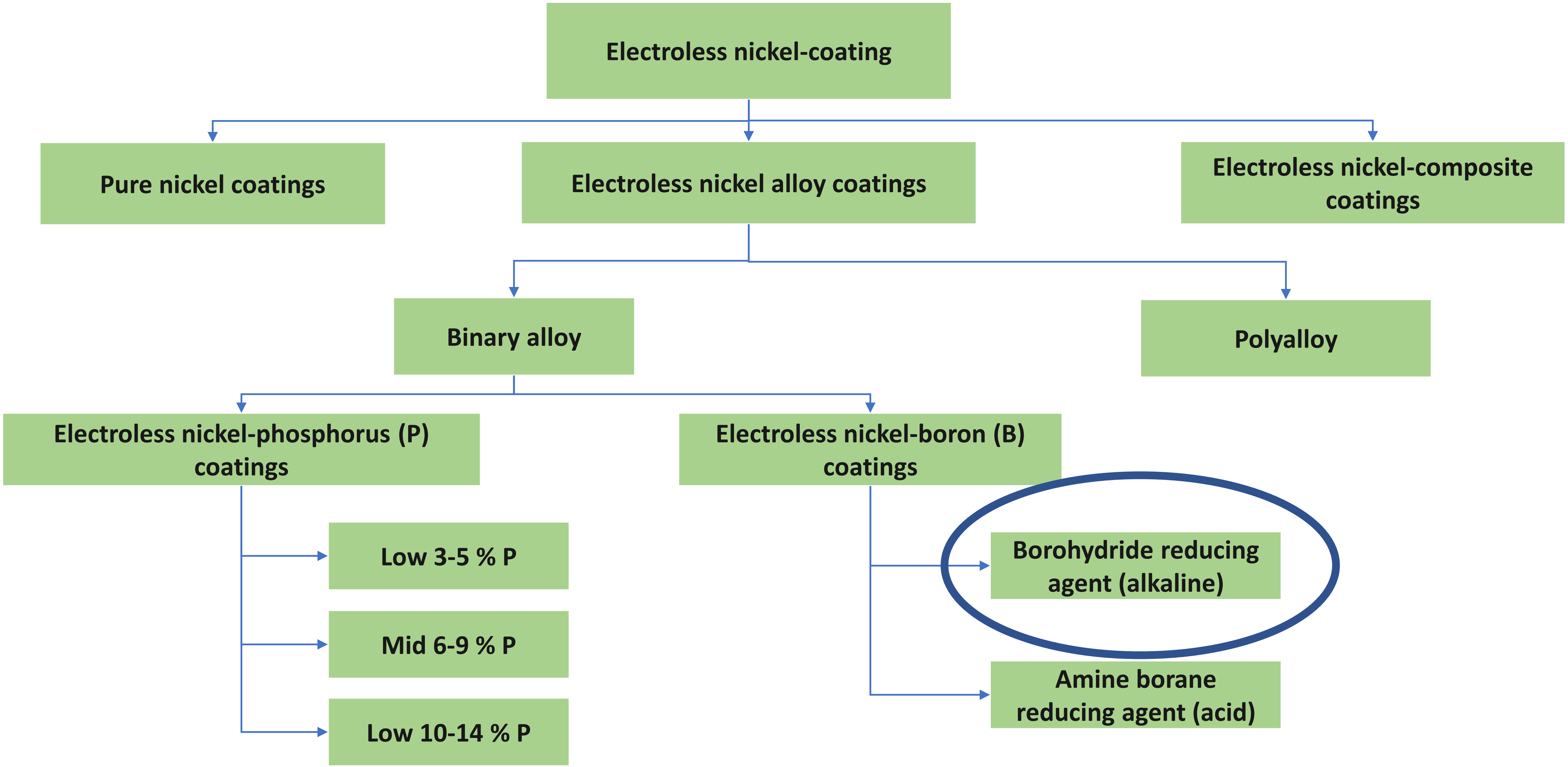


Electroplating



F. Delaunois

Electroless nickel-boron coatings classification



Electroless nickel-boron deposition bath and its parameters

Component	Function
Metallic salt (Nickel chloride or Nickel Sulfate)	Providing metallic ions
Reducing agent ($NaBH_4$ or DMAB)	Providing electrons
Complexing agent	• Regulating free metallic ions • Increasing the solubility of metallic ions • Preventing the precipitation of insoluble hydroxides • Modifying the equilibrium potential
Stabilizer	• Preventing the bath decomposition • Preventing the reduction reaction in the solution or the surfaces of the cell • Controlling of bath kinetic
pH adjuster	• Keeping the bath in the optimal working condition • Regulating the plating rate

$D = F(T, pH, C_{Ni+2}, C_{Red}, C_{ORed}, O/V, K, B, S, n_1...)$

D= Deposition rate

T= Temperature

pH= solution pH

C Ni^{+2}= Concentration of nickel ions in the solution

CRed = Concentration of reducing agent

CORed= Concentration of spent reducing agent

O/V= Bath load

K= type and concentration of complexant

B= type and concentration of accelerator

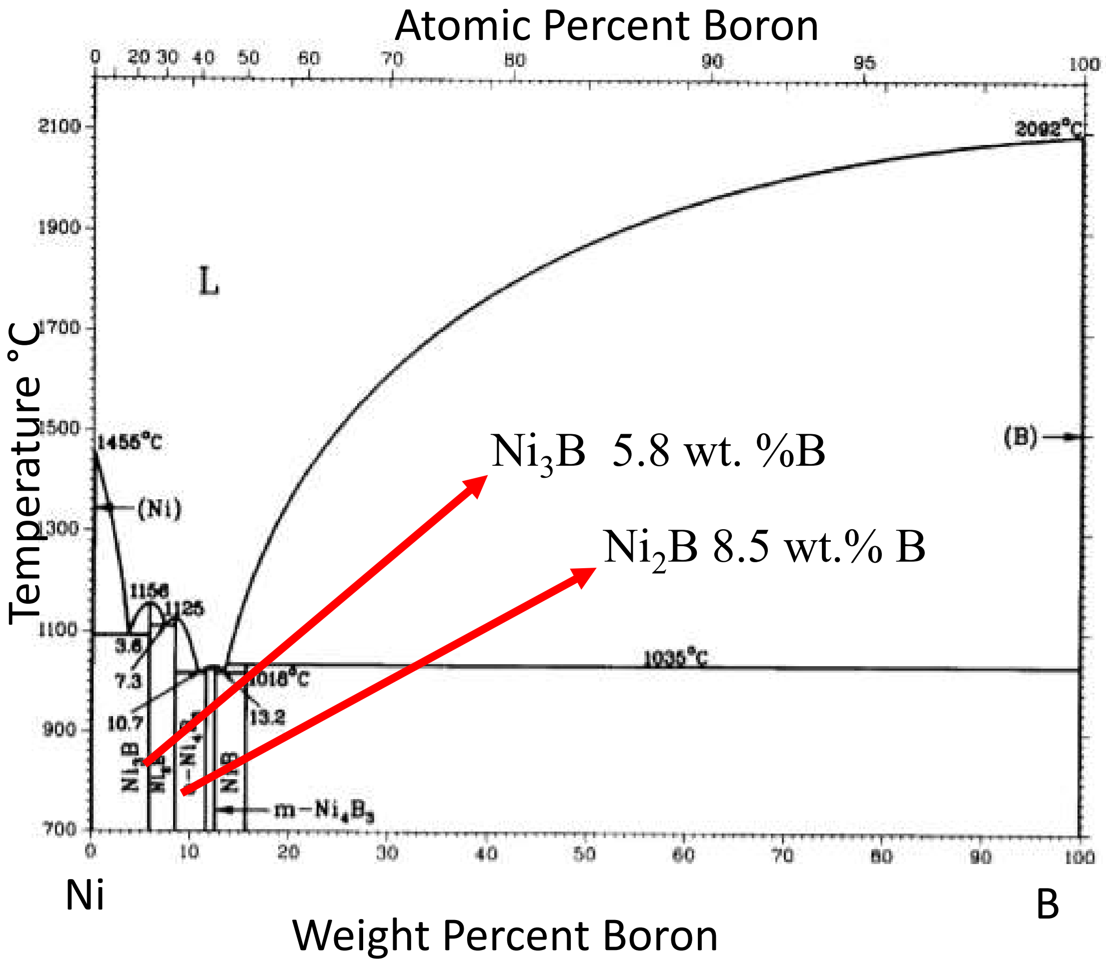
S= type and concentration stabilizer

n1= other factors such as agitation, the extent of bath contamination

Electroless nickel-boron deposits properties

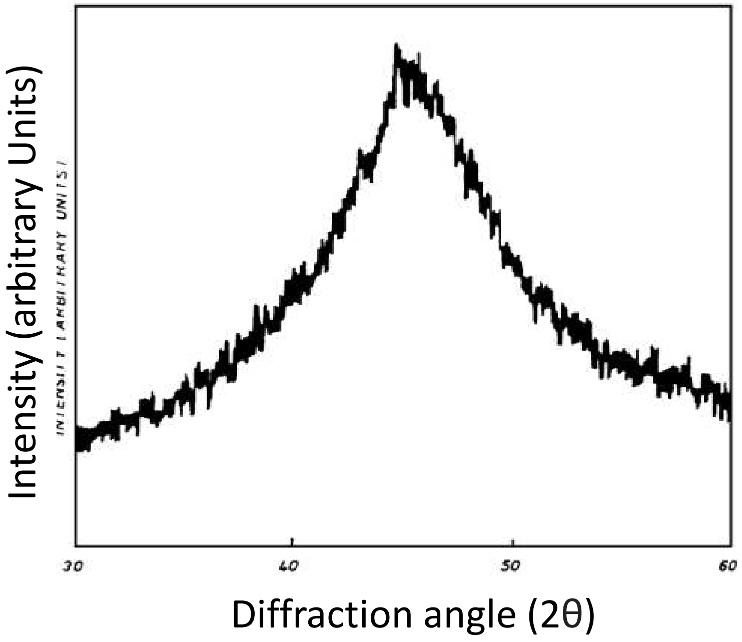
1. Chemistry, structure and morphology

Chemistry



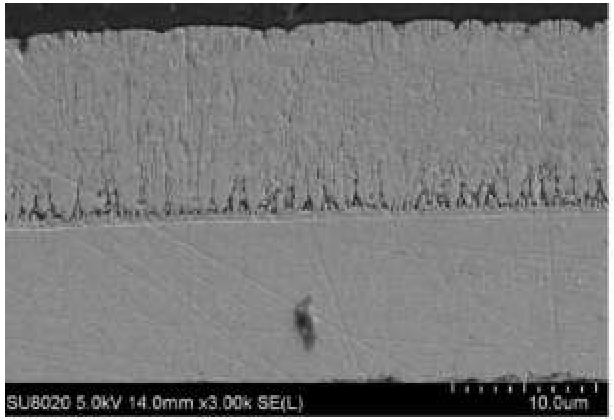
H. Okamoto

Structure

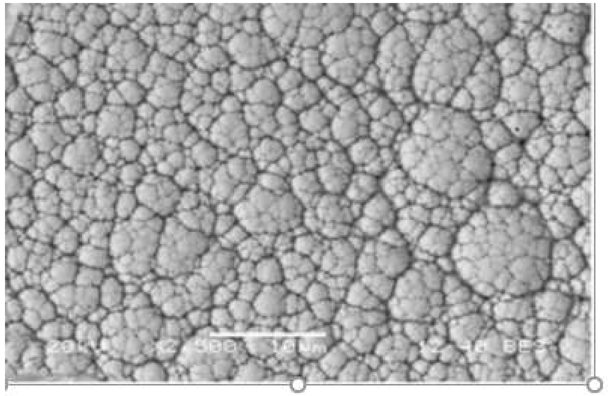


K. Krishnaveni, T. S. N. Sankara Narayanan, and S. K. Seshadri

Cross-section morphology



Surface morphology



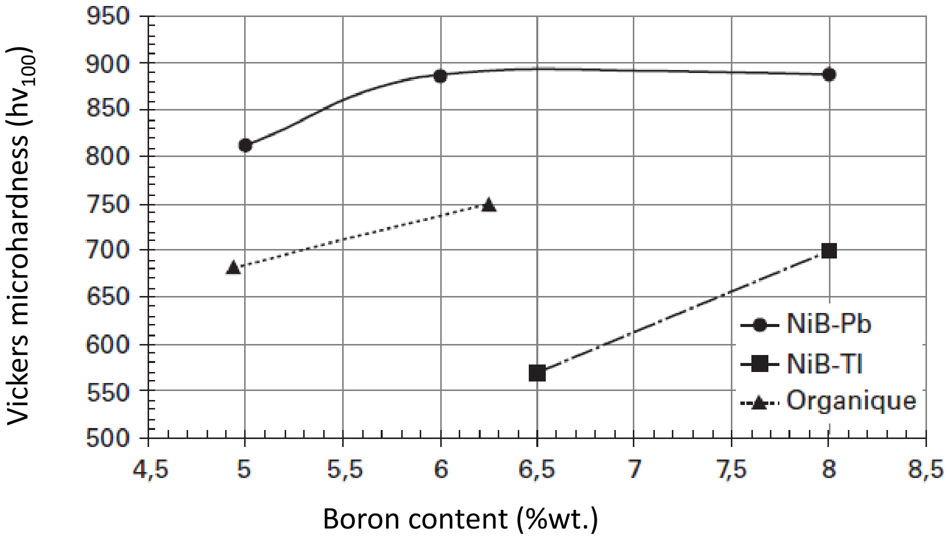
V. Vitry, A. F. Kanta, and F. Delaunois,

Electroless nickel-boron deposit properties

2. Mechanical properties

Properties	Value
Hardness hv_{100}	500 to 950
Young's modulus GPa	190
Tensile strength Mpa	110
Ductility	Lower than ENP
Internal stress	Tensile
Fatigue life	

Hardness evolution with boron content



Hardness value

Reference	Hardness	Coating composition	Substrate
Vitry et al., 2008	854 hv_{100}	6 wt. %B	Al with Ni-P protective layer
Vitry et al., 2011	891 hk_{25}	6 wt. %B-1 wt. % Pb	Mild steel
Dervos et al., 2004	1000 hv_{100}	5 wt. % B	Carbon steel
Oraon et al., 2008	1171 hv_{100}		
Pal et al.,	7.5 GPa	6 wt. %B -1 wt.% Pb	Mild steel
Correa et al., 2012	616 hv_{50}		AZ91D Mg alloy
Yunacti et al., 2021	933 hv_{50} 886 hk_{50} 11.6 GPa	4 wt.% B	Mild steel

3. Tribological properties

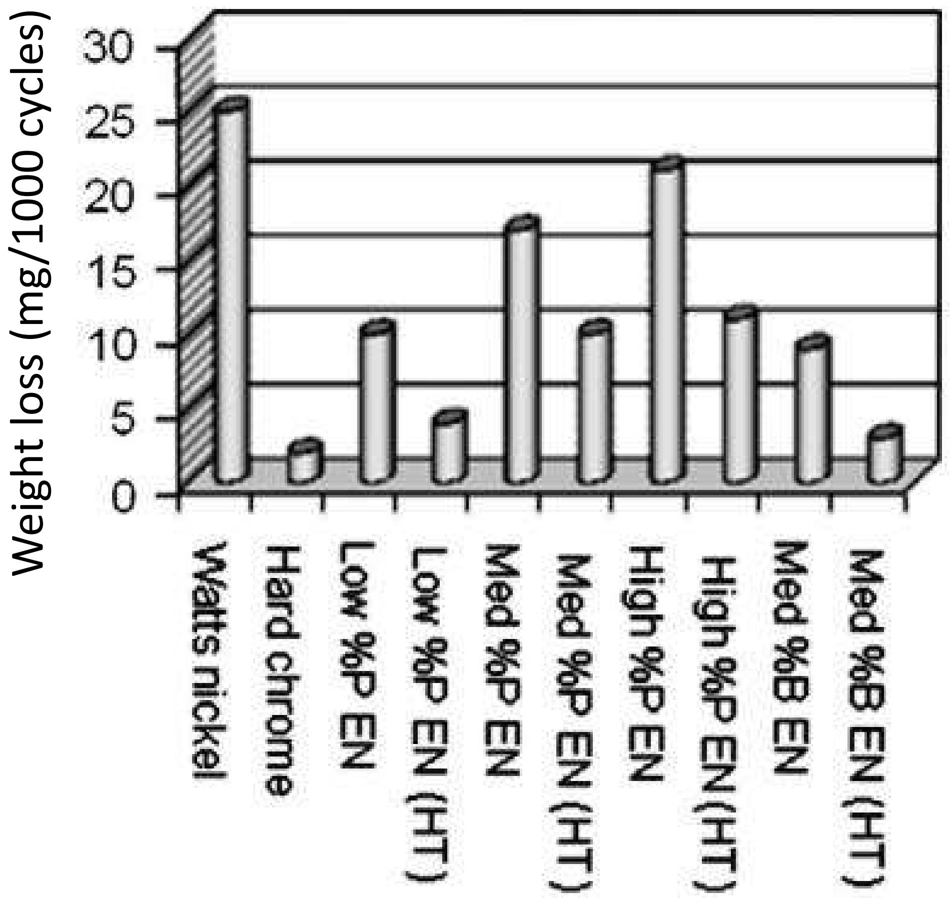
Wear and adhesion comparison

Deposit	Wear rate kg/N*m	Taber Wear Index (CS-17)	Critical load (N)
Electroless nickel-phosphorus	4.6*10^-10	31	25
Electroless nickel-boron	2.5-10^-10	36	14

Better tribological properties

- High hardness
- Cauliflower-like surface morpgology
- Columnar structure
- B content in deposit

Abrasive wear comparison



J. Sudagar, J. Lian, and W. Sha

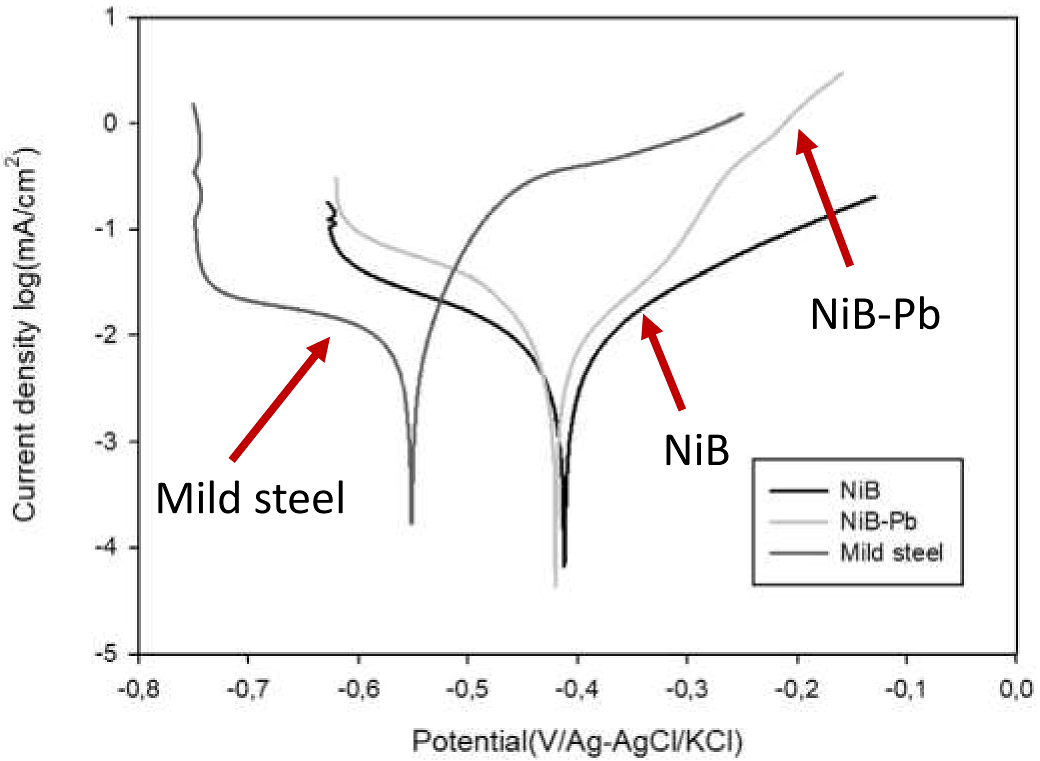
Electroless nickel-boron deposit properties

4. Corrosion, electrical and physical properties

Parameters impact corrosion properties

- Composition of the coating
- Homogeneity of elemental distribution throughout the deposit
- Surface morphology of the deposit
- Microstructure of the deposit
- The test medium
- The presence of impurities in the deposit
- The nature of the substrate
- Presence of pores and pits

Polarization curves



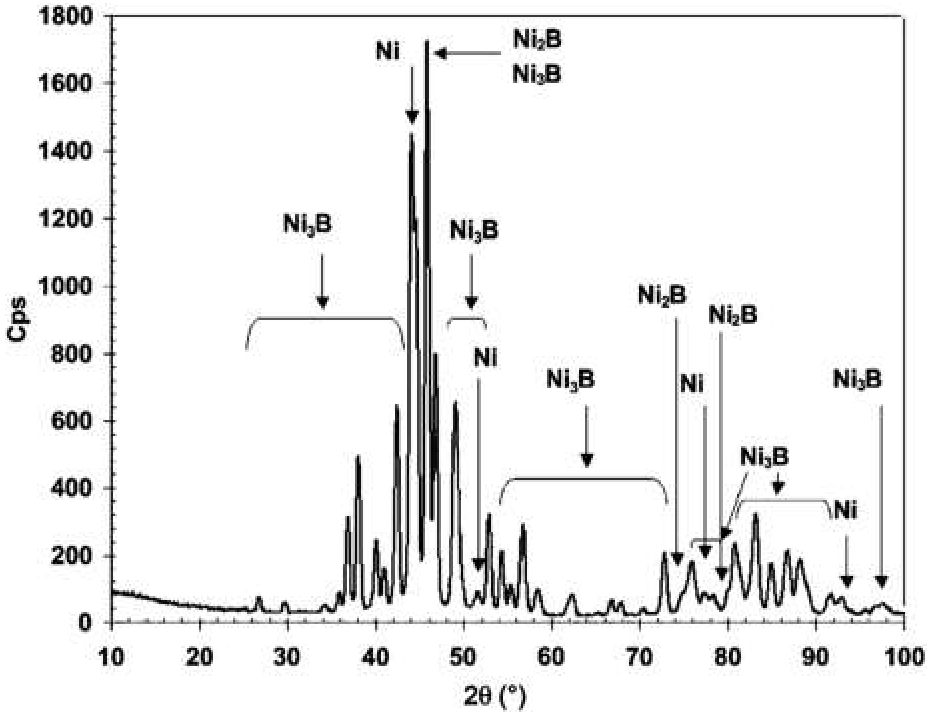
Bonin, L.; Castro, C.C.; Vitry, V.; Hantson, A.L.; Delaunois, F.

5. Physical properties

Properties	Value
Melting point	1170 °C
Density	8.25 g/cm^3
Coefficient of thermal expansion	12.1 mm/m °C
Electrical resistivity	89-ohm cm

Effect of heat treatment on electroless nickel-boron deposit

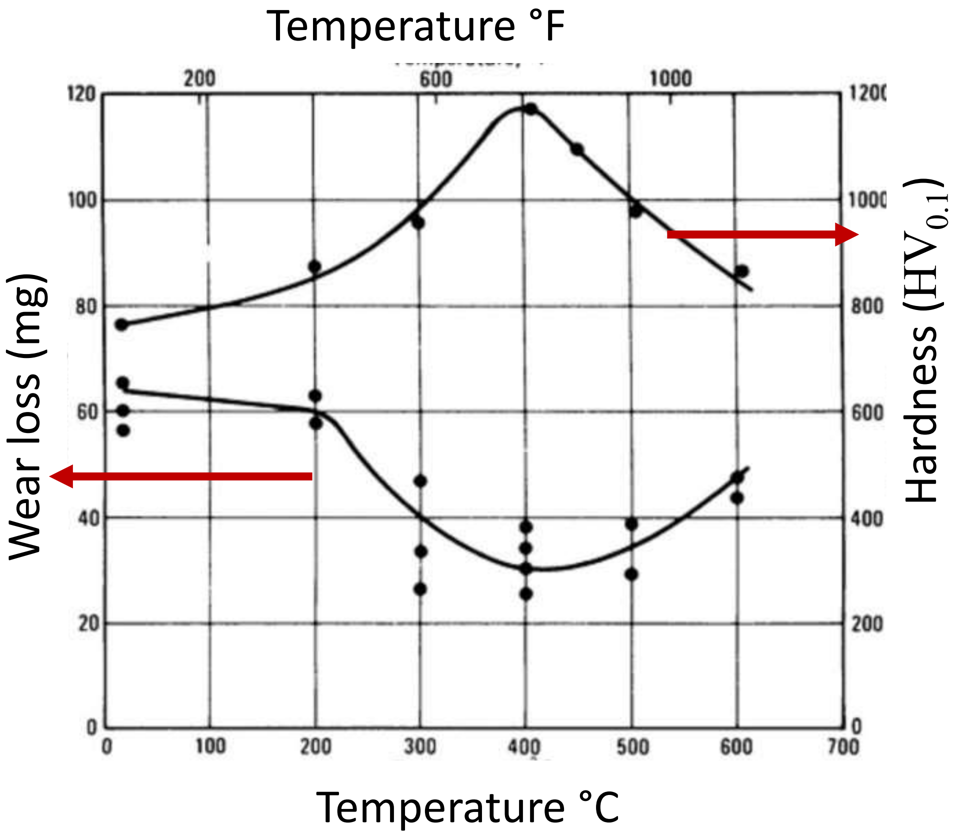
Structure



M.Anik, E. K.

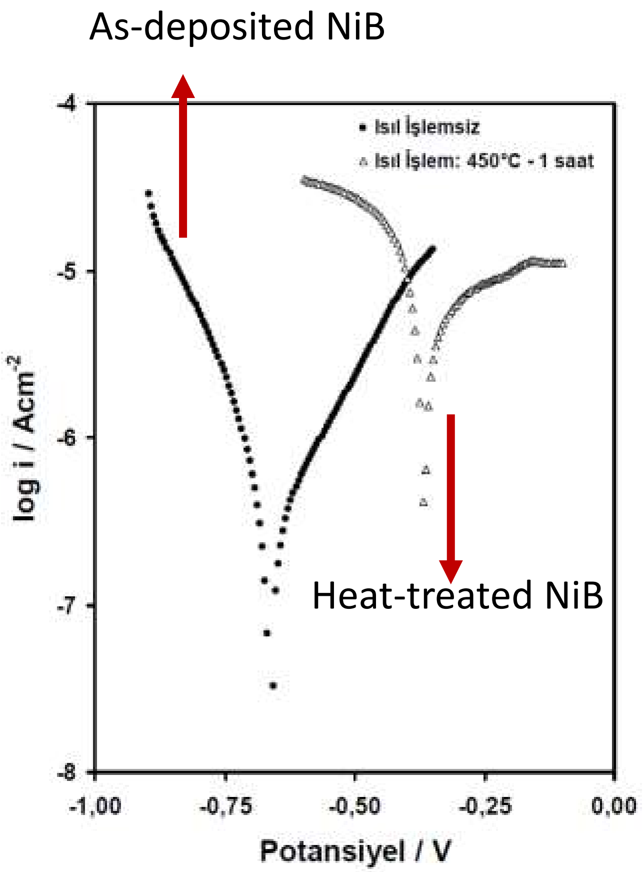
- Change in the microstructure
- Increase in the hardness
- Grain boundary and dislocation formation
- New phases

Hardness and wear loss



Abee, L.

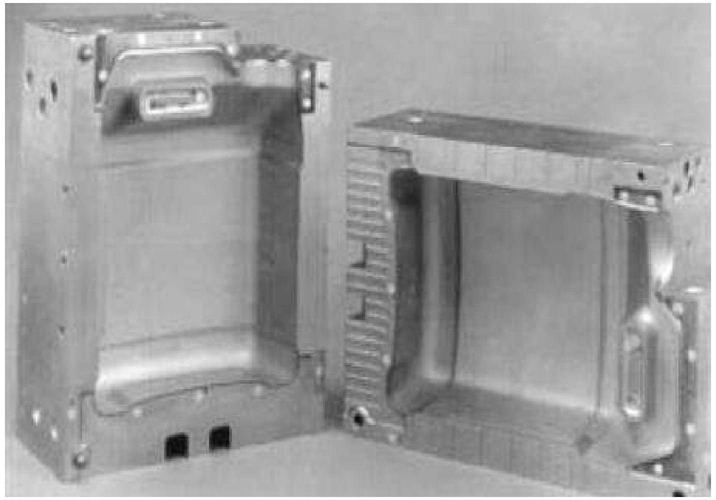
Polarization curves



Anık, M.; Körpe, E.; Baksan, B.

Electroless nickel-boron deposit applications

- ❖Machinery construction, textile machinery
- ❖Chemical and plastic
- ❖Automobile
- ❖Mining
- ❖Oil and gas
- ❖Electrical and Electronics
- ❖Aerospace



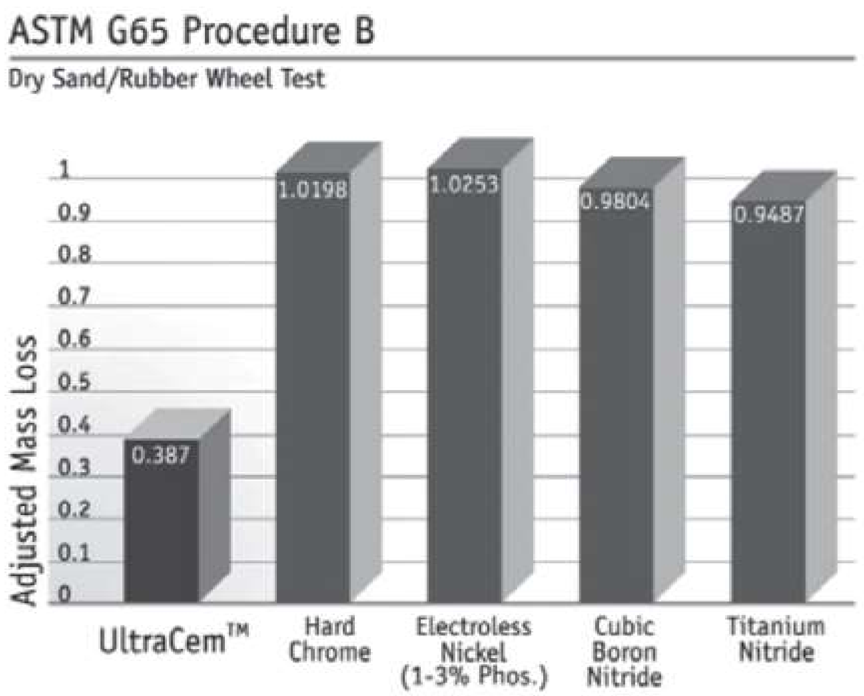



S. Avcioglu,

R. Parkinson,

Comparison electroless nickel-boron and hard chrome coatings

References	Deposit	Nanoindentation hardness (Oliver-Pharr)	Young modulus	Vickers hardness	Force
Gawne et Ma (1988) [22]	Hard chrome as-deposited			1100-560 $HV_{0.1}$	
	Heat-treated at 400° C			840 $HV_{0.1}$	
	Heat-treated at 600° C			470 $HV_{0.1}$	
Simao et Aspinwall (1999) [99]	Hard chrome			1100-750 $HV_{0.025}$	
Almotairi et al. (2016) [103]	Hard chrome	9 ±1.5 GPa	290±67	8.5 GPa	
Montagne et al. (2019) [84]	ENB as-deposited	10±1	191±9		
	ENB heat-treated	15.2±0.9	256±6		
Vitry et Bonin (2017) [68]	ENB as-deposited			850 $HV_{0.1}$	
	ENB heat-treated			1100-1200 $HV_{0.1}$	



Conclusion

- ✓ Uniform deposit is obtained even on complex shape;
- ✓ Bath composition and process parameters have strong impact on deposit properties;
- ✓ ENB deposits properties significantly depends on bath chemistry;
- ✓ ENB deposits have cauli-flower like surface morphology and columnar cross-section;
- ✓ Hardness of ENB deposit is close to the one of hard chrome and higher than ENP;
- ✓ ENB deposit has superior wear resistance;
- ✓ Heat treatment importantly enhance hardness and and wear resistance of ENB deposits;
- ✓ ENB deposits are used in many industries for various applications;

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