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POLYTECH MONS

Faculté Polytechnique

2ND CAPARICA CHRISTMAS CONFERENCE ON
SAMPLE TREATMENT
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# Morphological and microstructural observation of Duplex electroless coatings by TEM after sample selection by FIB.

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# Electroless nickel coatings?

**Reduction of nickel salts in aqueous solution, no external current** → **Constant thickness** → **All kinds of substrates** → **1946 (KaNiGen)**

**Deposition of metal (reduction)**

$Me_1^{n+} + ne^- \rightarrow Me_1$

- **Oxydation of a metal**: $Me_2 \rightarrow Me_2^{n+} + ne^-$
- **External current source**: $ne^-$
- **Oxydation of chemical agent**: $Red \rightarrow Ox + ne^-$

## Thermodynamic condition

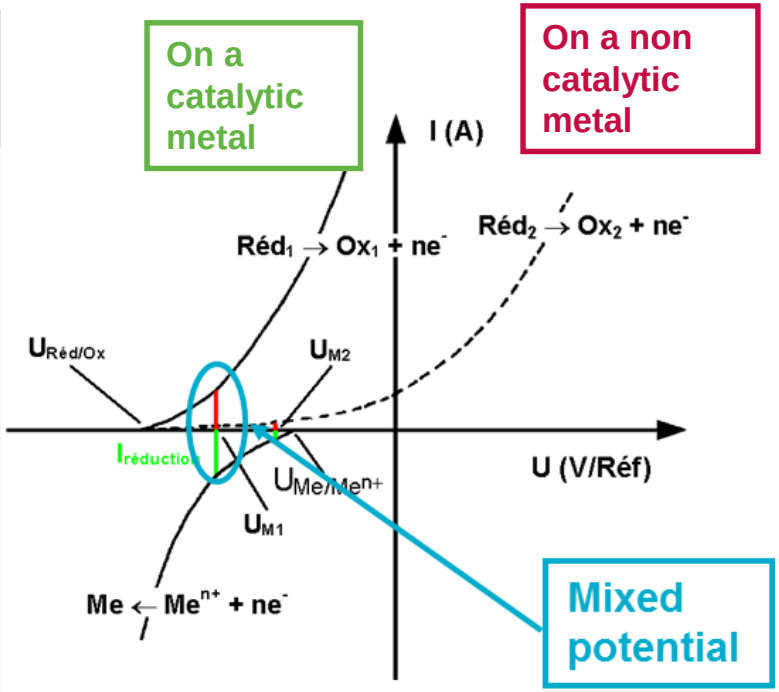
$Ni^{2+} + Red \rightarrow Ni + Ox$

- Spontaneous reaction possible only if $U_{Ni/Ni2+} - U_{Red/Ox} > 0$

➡ $U_{Ni/Ni2+} > U_{Red/Ox}$

## Kinetic condition

- Deposition occurs at mixed potential
- Catalytic activity: Plating rate influenced by over-potential
  - On the substrate
  - On the pre-deposited coating



# Electroless nickel coatings?

- Pure Nickel
  - Low-P (2-5 wt.% P)
  - Mid-P (6-9 % P)
  - High-P (10-13 % P)
- Binary alloys
  - **NiP** from $NaH_2PO_2$
  - **NiB** from $NaBH_4$ or DMAB
    - Ni-B-Pb / Ni-B-Tl (stabilizer)
    - B: 0.5 to 9 wt. %
- Ternary alloys
- Composites

## Applications

| | Ni-P (2-13 wt.%) | Ni-B (1-8 wt.%) |
|---|---|---|
| Hardness | 500-700 $hv_{100}$ | up to 900 $hv_{100}$ |
| Abrasion resistance | ++ (TWI: 24) | +++ (TWI: 11) |
| Adhesion (scratch tests) | **+++** | **+++** |
| Corrosion resistance | **+++** | **+** |
| +: fair | ++: good | +++: excellent |

# Electroless nickel coatings?

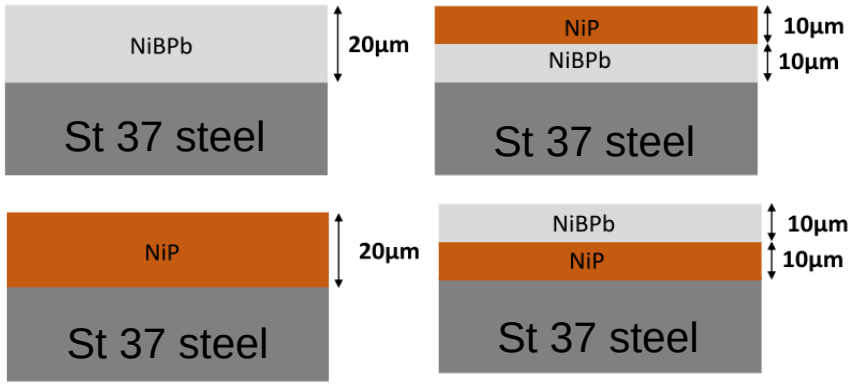
| Component | Role | Ni-B bath* | Ni-P bath |
|---|---|---|---|
| Metallic ions | Source of metal to be deposited | $NiCl_2 \cdot 6H_2O$ | Niklad ELV 808 A/B (Mc Dermid) |
| Reducing agent | Source of electrons | $NaBH_4$ | |
| Complexing agent | Complexes the metallic ions to<br>• increase the metallic ions solubility<br>• increase the stability by avoiding precipitation<br>BUT decreases the deposition current | $NH_2CH_2$<br>$CH_2NH_2$ | |
| Stabilizer | Regulate deposition speed by blocking a part of the catalytic sites | $PbWO_4$ | |
| pH adjuster | Regulates pH | NaOH | |

*F. DELAUNOIS, J.-P. PETITJEAN, P. LIENARD, M. JACOB-DULIERE, Autocatalytic electroless nickel-boron plating on light alloys, Surface and Coatings Technology 124 (2000), 201-209

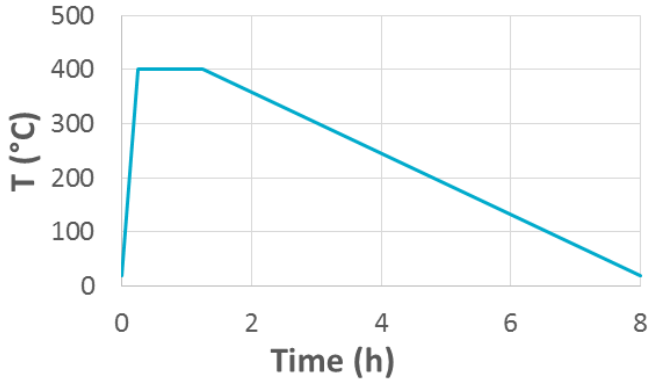
# Research question

**NiP better for corrosion** + **NiB better for wear and hardness** → **Combined (Duplex) coatings for optimised properties**

## Electroless nickel deposition




## Heat treatment



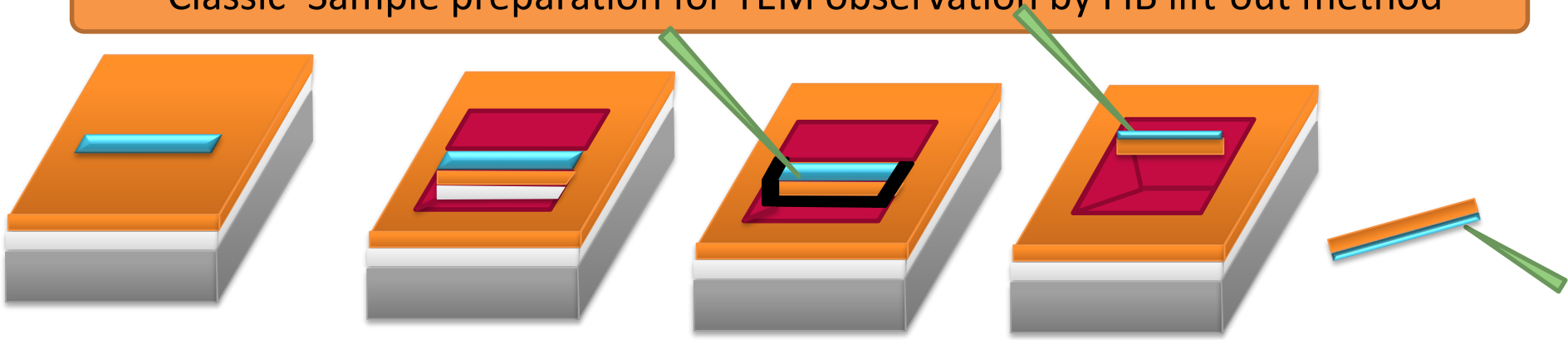

| Properties of Duplex coatings | As plated | | | | Heat treated | | | |
|---|---|---|---|---|---|---|---|---|
| | NiB | NiP | NiP/NiB | NiB/NiP | NiB | NiP | NiP/NiB | NiB/NiP |
| Hardness | 1 | 4 | 2 | 3 | 4 | 1 | 3 | 2 |
| Abrasion | 3 | 4 | 1 | 2 | 1 | 4 | 2 | 3 |
| Wear | 1 | 4 | 2 | 3 | 2 | 1 | 4 | 3 |
| Scratch resistance | 1 | 3 | 2 | 4 | 1 | 3 | 2 | 4 |

**?**

**Influence of structure/interfaces on properties**

# Experimental

‘Classic’ Sample preparation for TEM observation by FIB lift-out method



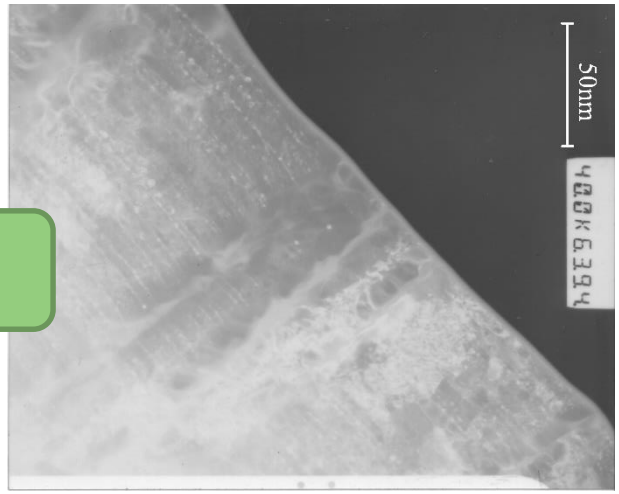
Observation of the sample by SEM and deposition of protective layer

FIB milling

Lift out

Thinning by ion milling

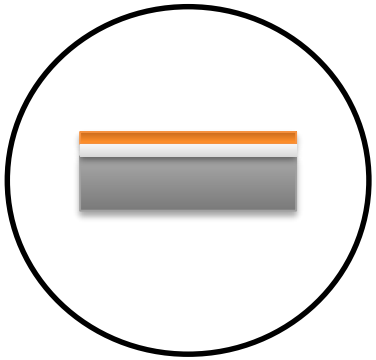
Results



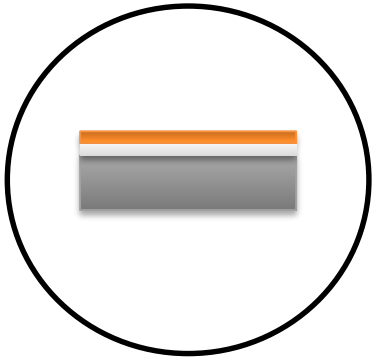

- No access to interface
- Information only about top layer

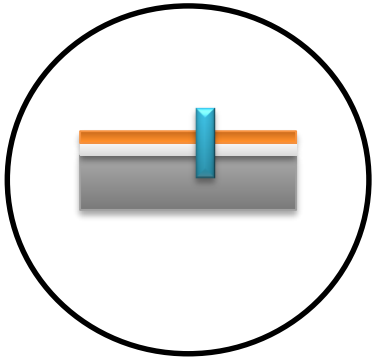
# Experimental

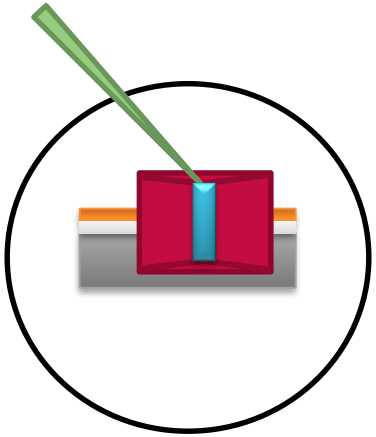
Alternate method, based on area selection lift out method

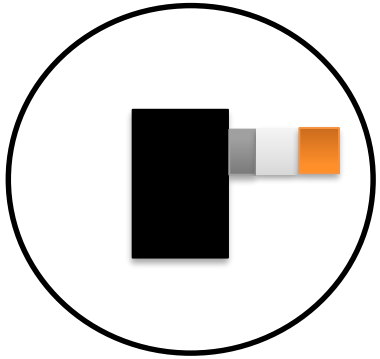


Initial sample: embedded and polished cross section









Detection of zone of interest by SEM

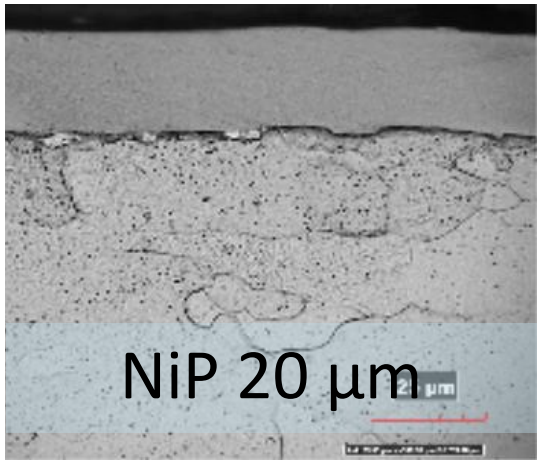
Deposition of protective layer on zone

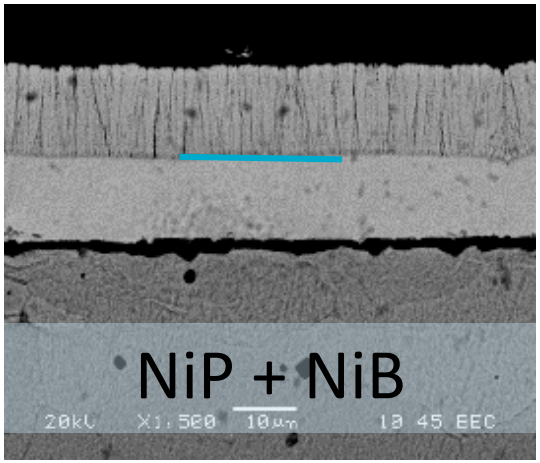
FIB milling and lift out

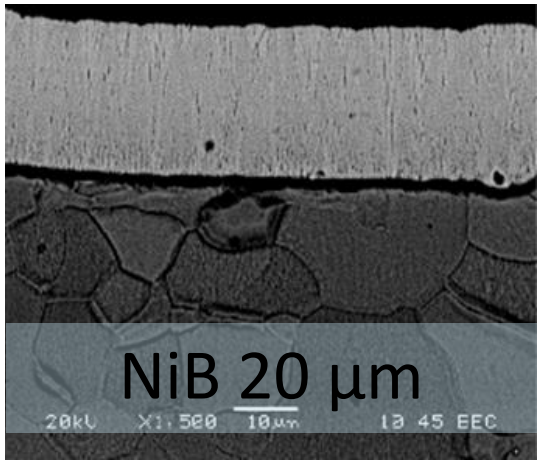
Thinning by ion milling

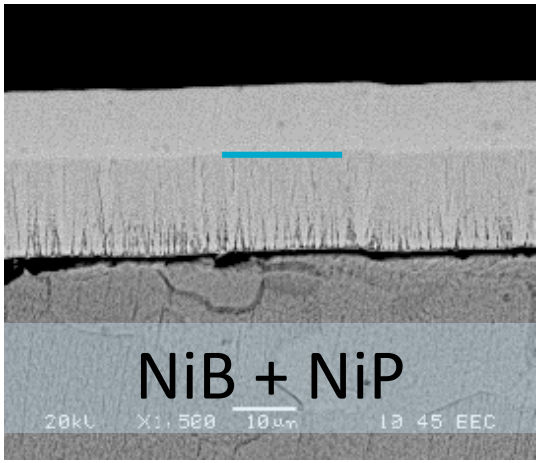
# Preliminary sample characterization

As plated samples



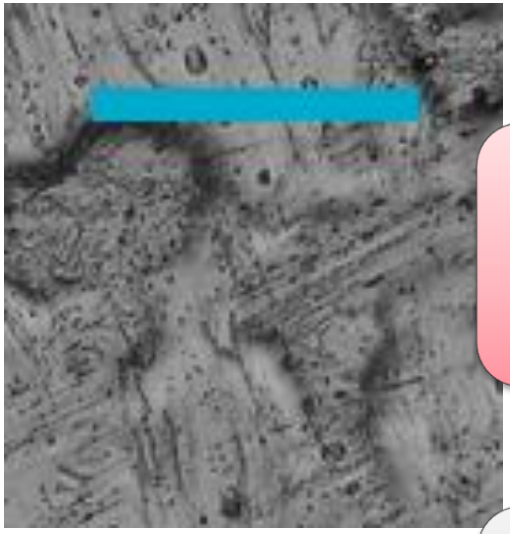

- **Chemistry (atomic %), by GDOES:**
  - NiB: 6.5 – 7.5% B + 1-1.5% Pb
  - NiP: 7.5 - 9.5 % P
  - Balance Ni

| | Ni | P | B | Pb |
|---|---|---|---|---|
| Ni-B/Ni-P | 91,39 | 9,14 | 6,72 | 1,21 |
| Ni-P/Ni-B | 90,01 | 7,79 | 7,18 | 1,47 |
| Ni-B | 91,99 | | 6,66 | 1,11 |
| Ni-P | 92,06 | 7,78 | | |

- **Morphology**
  - Clear delimitation of the various layers
  - ENB columnar – ENP featureless
  - No apparent influence of interface on growth.

# Preliminary sample characterization

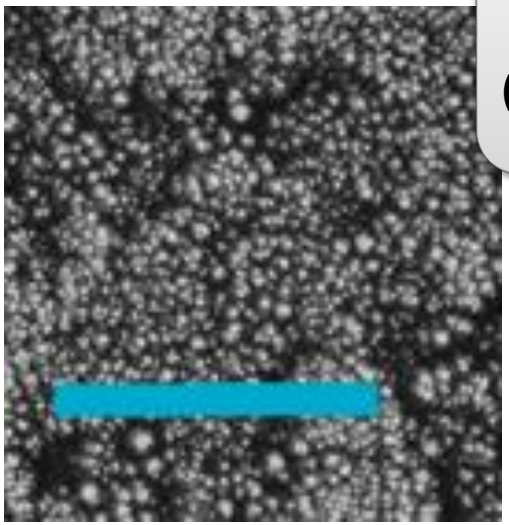
As plated samples



**NiP**

**(planar)**

**+**



**NiB**

**(cauliflower-like)**

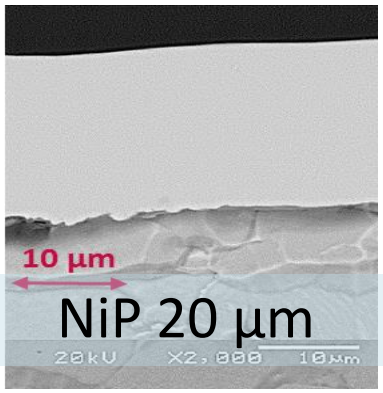
**100µm**

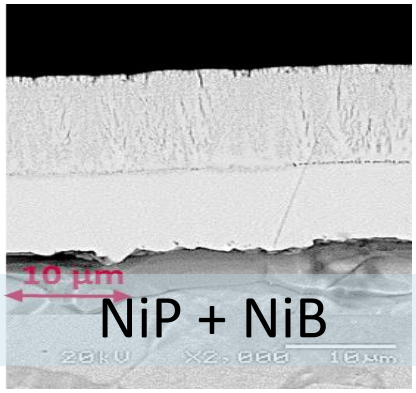
**Duplex**

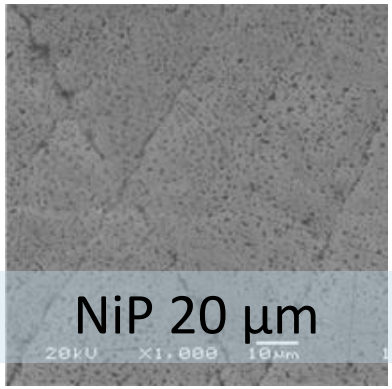
**(mixed features)**

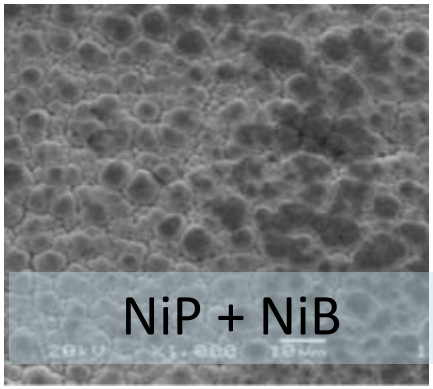

# Preliminary sample characterization

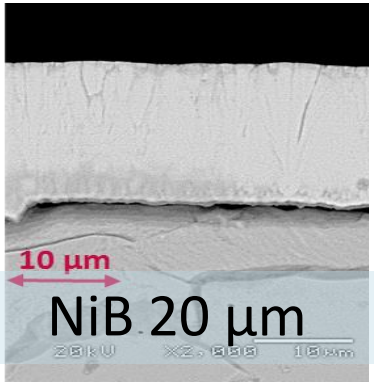
Heat treated samples

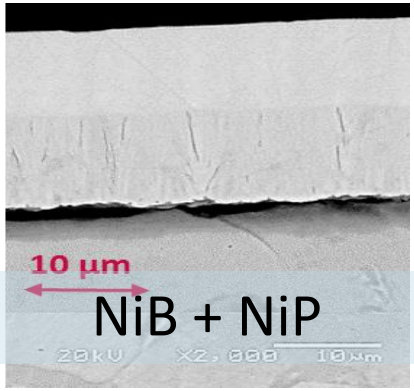


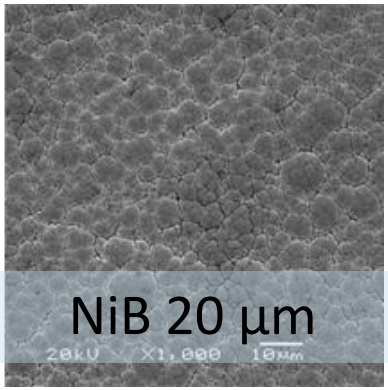



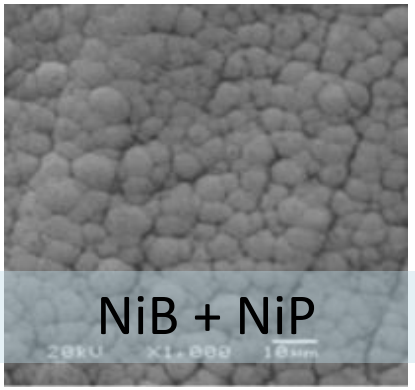



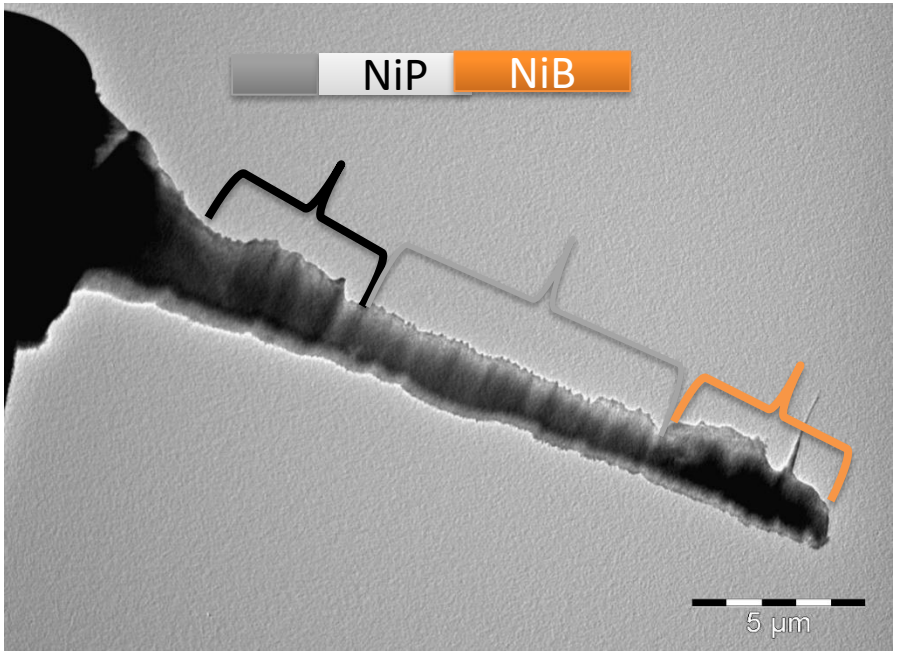



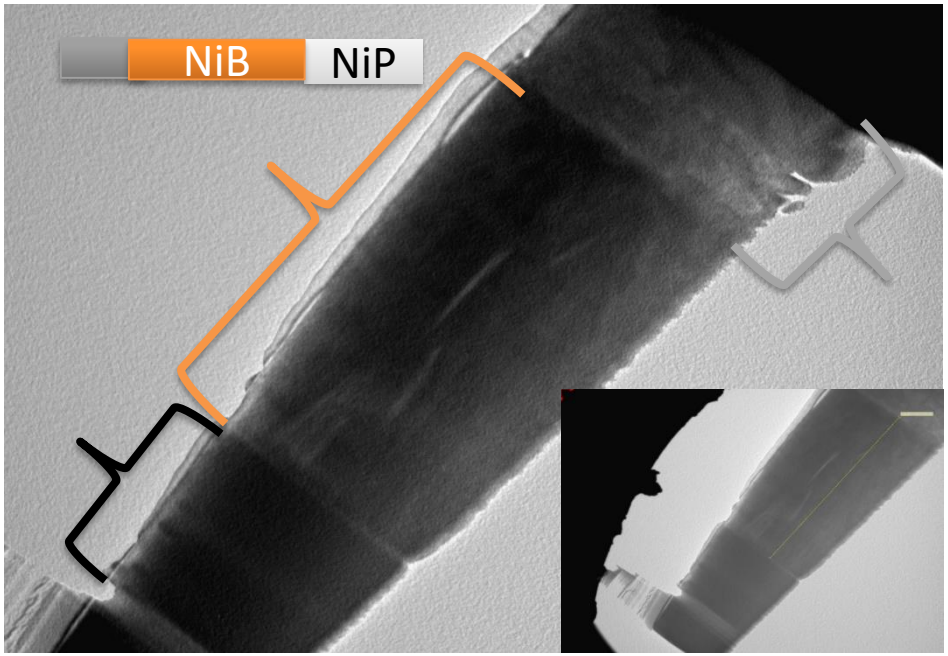




**No significant morphological modification**

# SEM observation of ‘lift out samples’

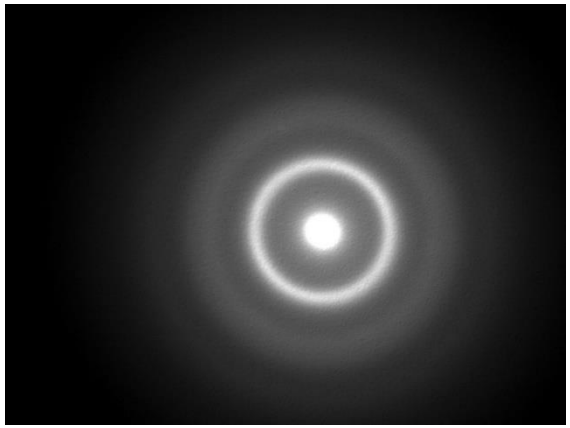


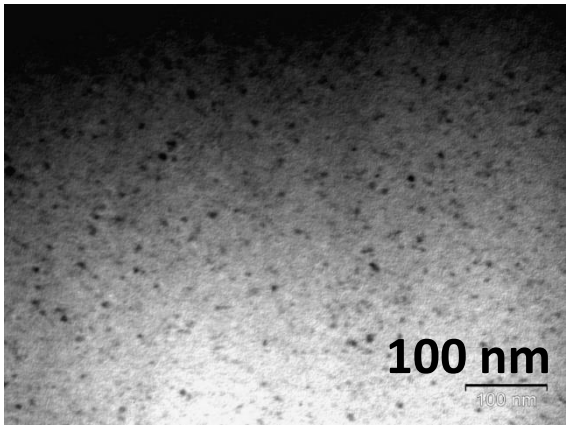




Clear view of all interfaces

# TEM observation

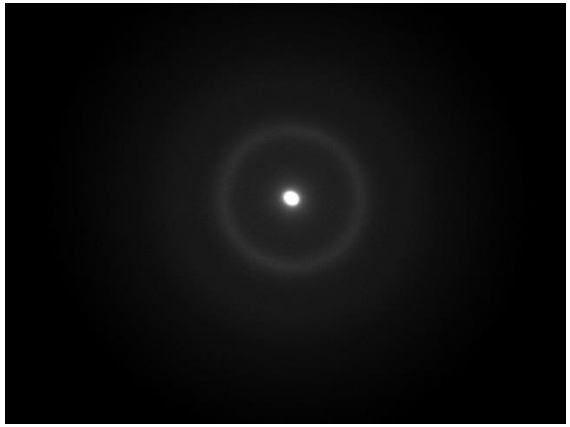
## ‘Bulk’ of NiP layers

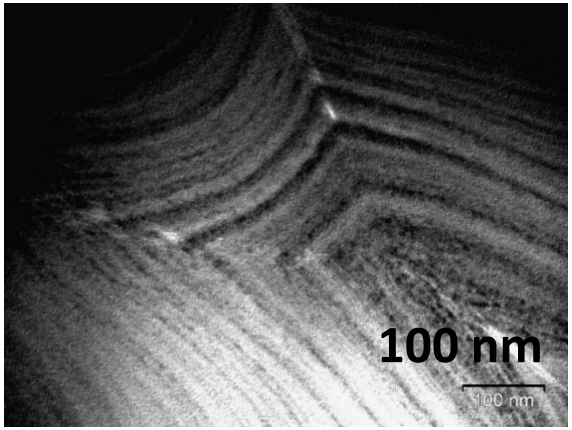





Nanocrystalline supersaturated nickel

## ‘Bulk’ of NiB layers

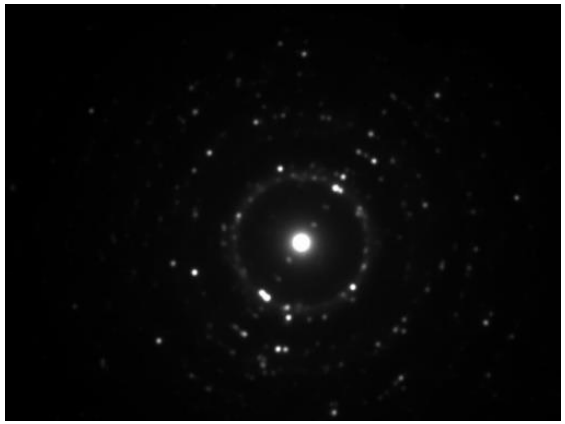


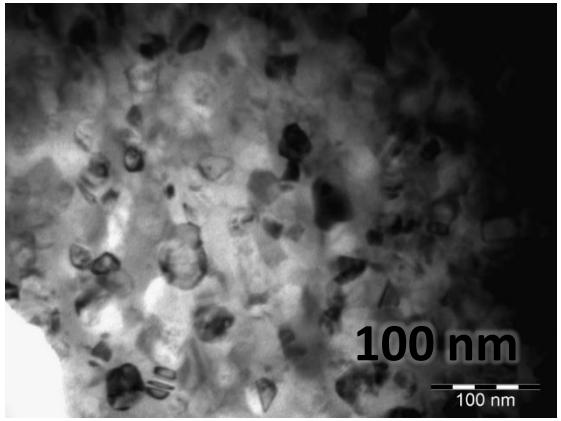



Quasi amorphous supersaturated nickel
Layered growth

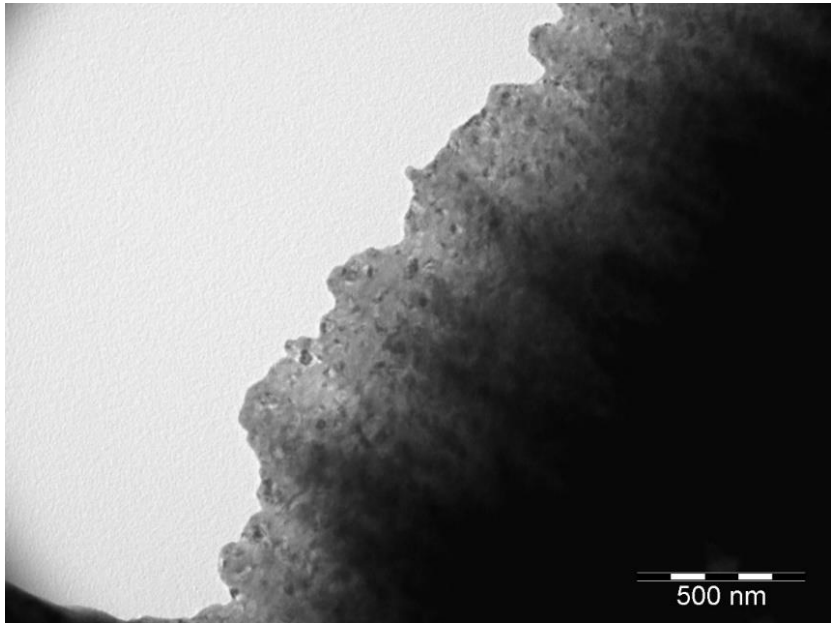
# TEM observation

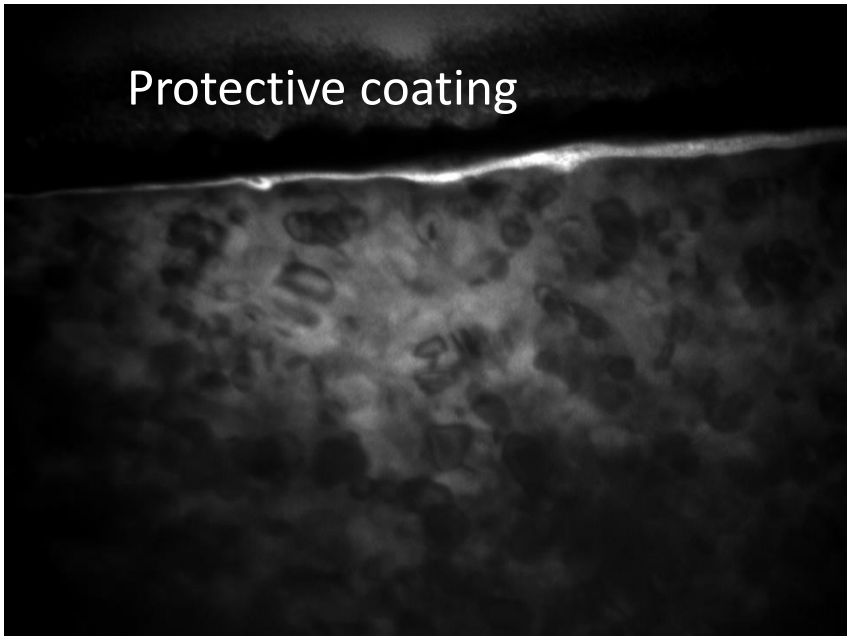
‘Bulk’ of NiP layers – heat treated





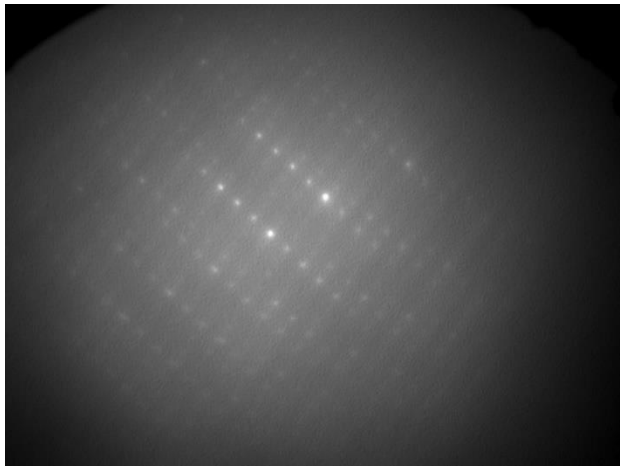

Bigger nanocrystalline grains
$Ni_3P$ phase



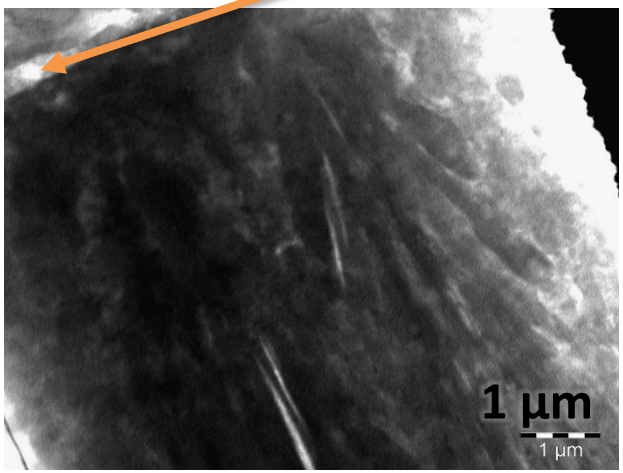



# TEM observation

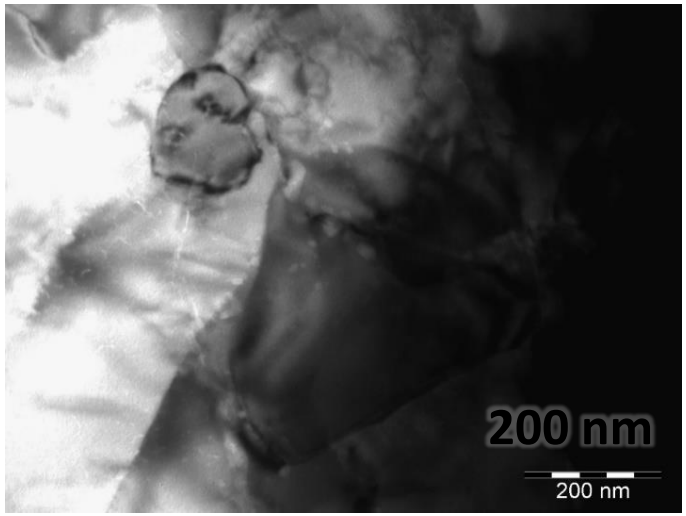
‘Bulk’ of NiB layers – heat treated

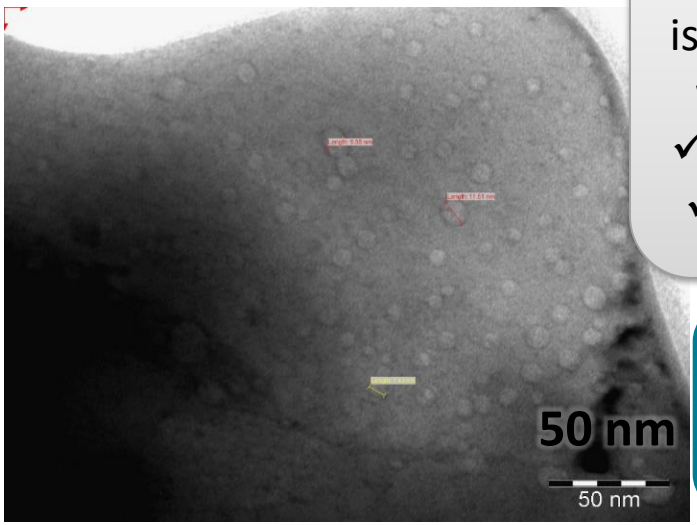


Steel substrate




Directly on steel : dendritic growth



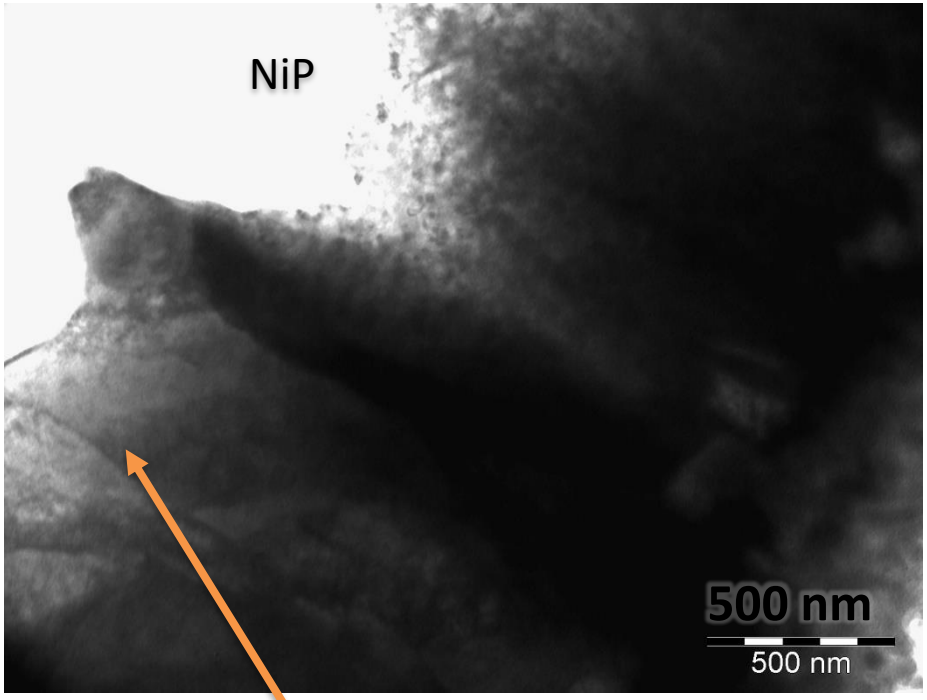

On NiP:
isotropic grain growth with 2 populations:
- ✓ $Ni_3B$ : 100- 200 nm
- ✓ Ni or $Ni_2B$: 10 nm

Linked with surface chemistry modification

# TEM observation

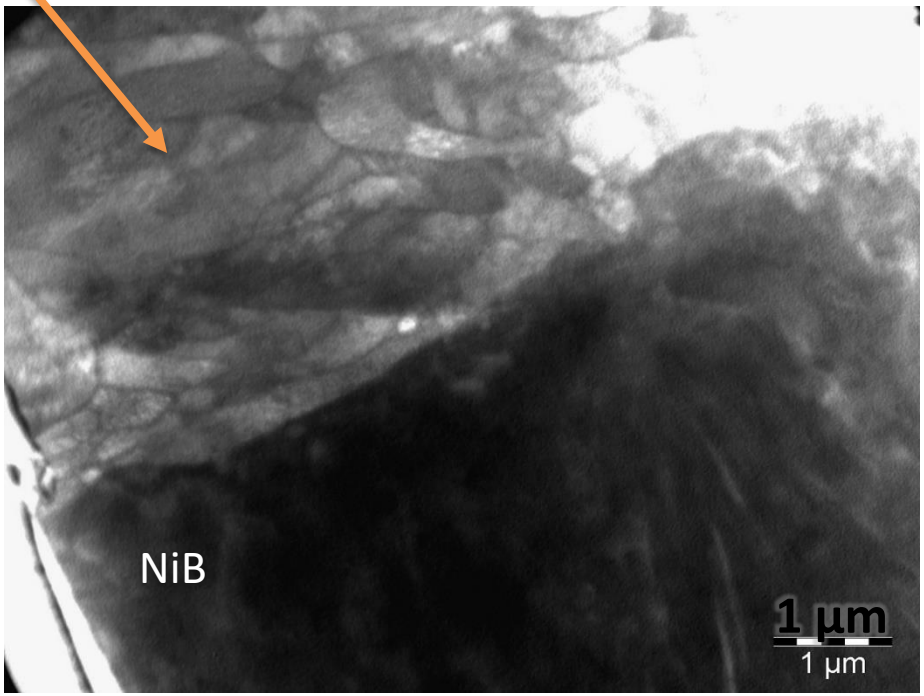
Interfaces

As plated




Steel substrate

Steel substrate



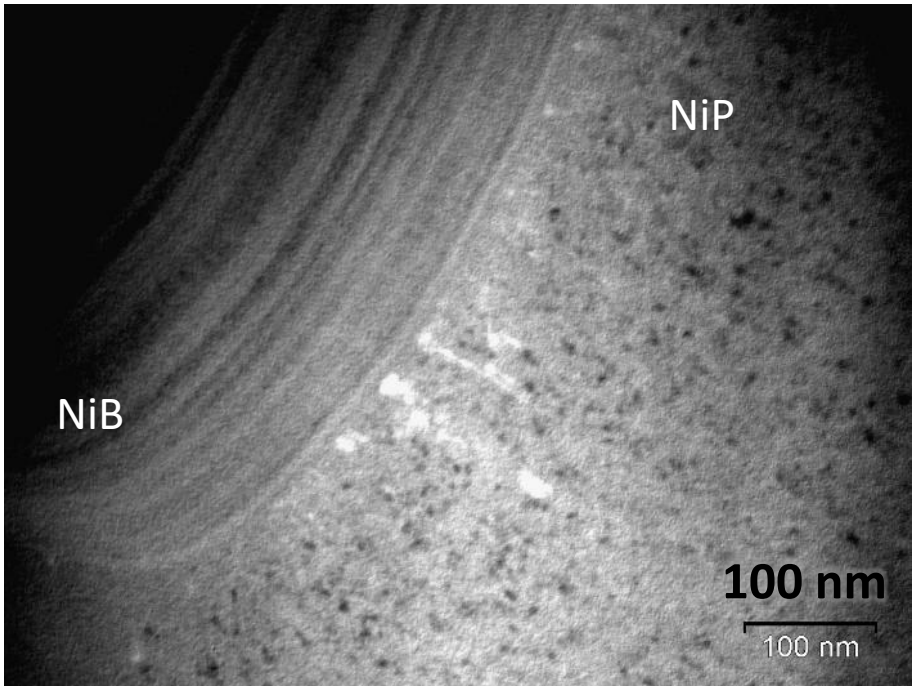

Isotropic growth

Feather-like morphology

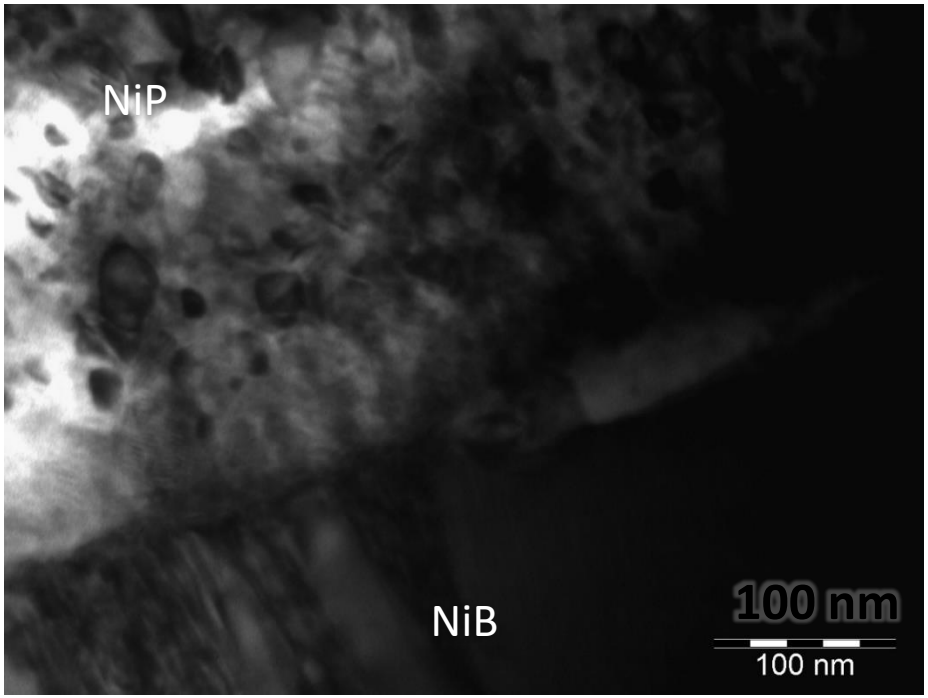
# TEM observation

## Interfaces

As plated




Heat treated

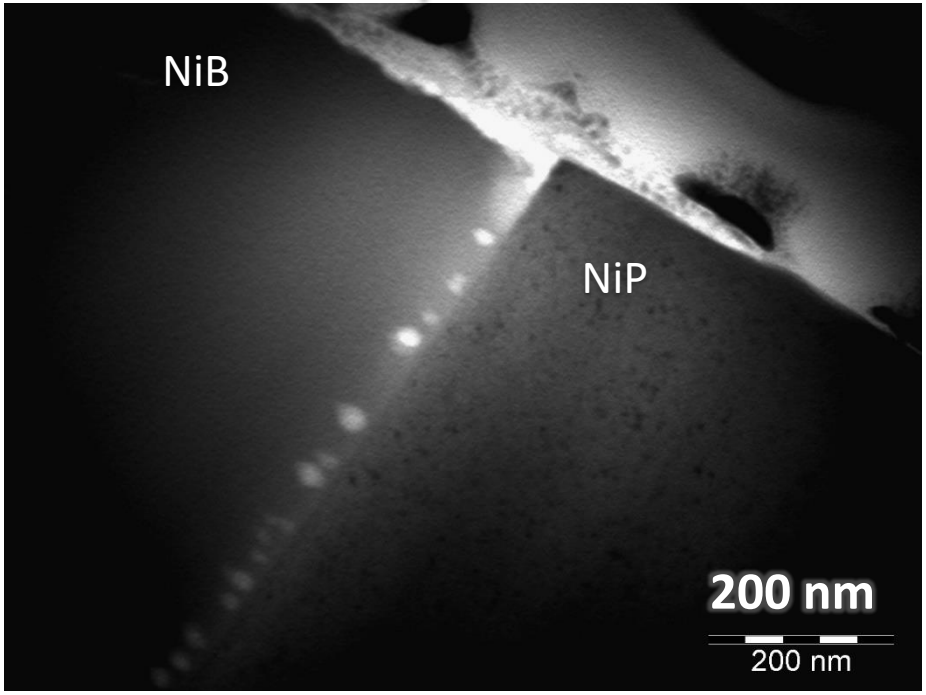



NiP on NiB:
'wavy' interface
Isotropic growth of NiP

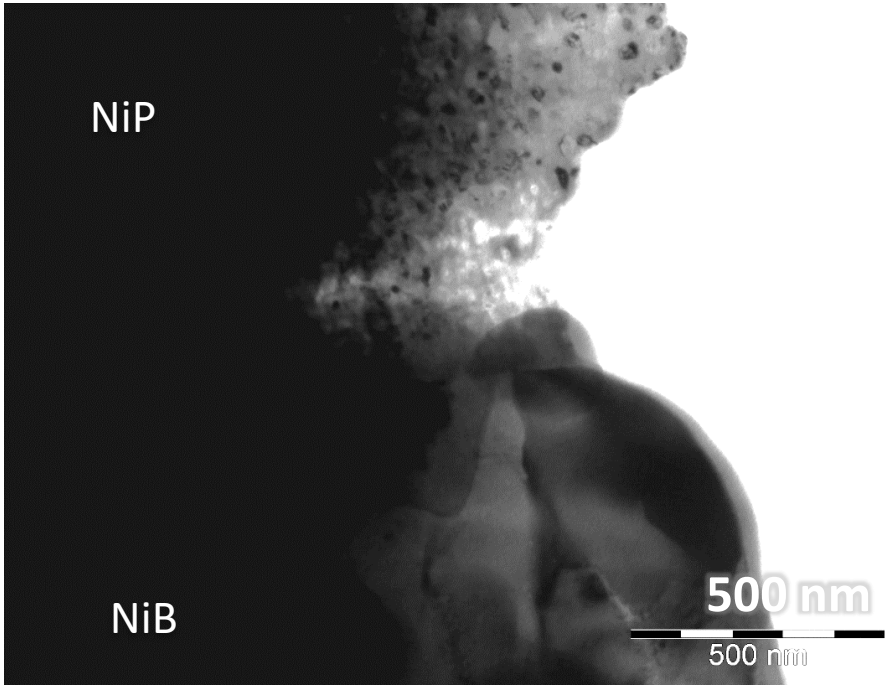
# TEM observation

## Interfaces

As plated




Heat treated




NiB on NiP:
'flat' interface
No observable features in as-deposited state – columnar growth after heat treatment

# Conclusions

- Modified FIB-SEM lift out method allows observation of interfaces
- Growth features from NiB present at small scale : waviness of profile and columnar features
- Influence on ‘underlayer’ on crystallization


**Acknowledgements: F. Tosar and S. Gobeaut**