Progress on the Study of Isotopic Composition in Metallic Thin Films undergone to Electrochemical Loading of Hydrogen

M. Apicella\(^{(1)}\), E. Castagna\(^{(2)}\), G. Hubler\(^{(4)}\), M. McKubre\(^{(3)}\), F. Sarto\(^{(1)}\), C. Sibilia\(^{(2)}\), A. Rosada\(^{(1)}\), E. Santoro\(^{(1)}\), F. Tanzella\(^{(3)}\), V. Violante\(^{(1)}\)

\(^{(1)}\) ENEA C.R. Frascati, V. le E. Fermi 45 00044 Frascati (Roma) Italy
\(^{(2)}\) La Sapienza University, Via Scarpa, 14 00100 (Roma) Italy
\(^{(2)}\) SRI International 333 Ravenswood Ave, Menlo Park CA 94025 USA
\(^{(3)}\) Naval Research Laboratory, 4555 Overlook Ave., S.W. Washington, DC USA
SUMMARY

• Experiments on thin films at ENEA
  
  Film deposition
  Hydrogen loading
  SIMS analysis

• Results
  
  Preliminary results
  Further investigations

• Questions

• Conclusions
Experiments on thin films at ENEA

• Reference and active Nickel films are deposited during the same deposition run

• The active film is loaded with H by electrolysis

• Reference and electrolysed films isotopic composition is analysed by Secondary Ions Mass Spectrometry (SIMS) to search deviations from the natural abundances (traces of nuclear processes)
**FILMS DEPOSITION**

**Substrate**
- Polyethylene substrate
- Class 1000 lab
- Chemical cleaning

**Ion Beam Etching**
- Strong adhesion to plastic substrate
- Surface roughness

**Ni Film sputtering**
- 6 samples per runs
- 99.98% purity Ni target
- thickness 450 Å

**Reduction of contaminants**

**Good film surface status after electrolysis**

**Identical reference and active films**
Films Deposition Details

**Rotating Sample Holder**
(6 identical locations)

Film Surface morphology
(by Atomic Force Microscopy)

Dual Ion beam Sputtering plant

**GUN1:**
- Sputtering
- Rate 1.3 Å/s
- $P \approx 10^{-2} \text{ mbar}$
- $T < 50^\circ C$

**GUN2:**
- Etching

O$_2$ gas
HYDROGEN LOADING

- Pure Polyethylene (Kartell)
- Pure Pt (99.98) wire
- Light water (18MΩ) LiSO₄ solution
- 3-40 hours
- Current = 5 - 190 mA
- Voltage = 3 – 7 V

Photo of the electrodes

Electrolytic Cell

- Anode
- Electric contact
- Plastic support
- Metallic film (400 A)
SIMS analysis

- SIMS technique
- Isotopic shift measurements
- Depth profile
- Active & reference in the same analysis conditions
Secondary Ion Mass Spectrometry (SIMS)

- Very suitable technique to reveal small traces of surface elements or compounds (not quantitative)
- Very accurate measurements of isotopic ratio
- Dynamic SIMS allows depth profile of elements/compounds concentration

**Leybold SSM200-Mass Spectrometer Module**
*Leybold IQE 12/38 ion source and Balzers Quadrupole Mass Analyzers with ion optics*

- **Primary beam**
  - heavy ions [Ar⁺], spot Ø ≈ 2mm, I≈0.5-2 µA, E=1-5 KeV, 45°
- **Emergent particles**: Positive and negative ions
- **Mass range**: m/e≥1 [0-511 a.m.u.]
- **Resolution**: 0.5 a.m.u.
- **Sensitivity**: 10^{12} at/cm² (0.1% of 1 atomic monolayer)
Reference and electrolyzed films are loaded together into the analysis chamber and positioned at 180 ° on a cylindrical support and analyzed in series under the same SIMS conditions.
Previous results (ICCF9)

Neutron Activation Analysis (NAA- ENEA Casaccia, Italy) of Nickel thin films indicates evidence of *isotopic shift* on Ag contaminant.

<table>
<thead>
<tr>
<th></th>
<th>Ni1b</th>
<th>Ni2b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag107</td>
<td>&lt;0.019</td>
<td>&lt;0.034</td>
</tr>
<tr>
<td>Ag109</td>
<td>0.025</td>
<td>0.06</td>
</tr>
<tr>
<td>Shift Ag%</td>
<td>29.37</td>
<td>47.39</td>
</tr>
</tbody>
</table>

Our SIMS signals on Ag masses are too low to obtain useful information on the isotopic shift.
Preliminary Results

SIMS analysis on Ni thin films indicates an apparent isotopic shift on the 63/65 Cu masses (*Cu has these only two isotopes!*)

**Electrolysed film:**
The Cu$^{63}$/Cu$^{65}$ isotopic ratio strongly differs from the natural value (2.25):

\[ \text{Cu}^{63}/\text{Cu}^{65} \approx 0.12 \pm 0.1 \]

**Reference film:**
The Cu$^{63}$/Cu$^{65}$ isotopic ratio respects the natural value

\[ \text{Cu}^{63}/\text{Cu}^{65} \approx 3.3 \pm 1 \]

the tuning of the instrumentation was checked by moving the argon beam on the stainless steal sample-holder where the Cu isotopic composition was always the natural one.
These new results add to the previous ones already shown (ICCF10): 3/5 experiments giving evidence of apparent isotopic shift

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Film STATUS after electrolysis</th>
<th>APPARENT ISOTOPIC SHIFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni 1bis</td>
<td>Ok</td>
<td>YES</td>
</tr>
<tr>
<td>Ni 3bis</td>
<td>Ok</td>
<td>YES</td>
</tr>
<tr>
<td>Ni P2</td>
<td>Ok</td>
<td>YES</td>
</tr>
<tr>
<td>Ni P3</td>
<td>Ok</td>
<td>NO</td>
</tr>
<tr>
<td>Ni 4</td>
<td>Ok</td>
<td>YES</td>
</tr>
</tbody>
</table>
SIMS scanning of the sample surface

- The SIMS analysis has been carried out on different points of the sample surface.
- The effect is more relevant in the middle of the sample.
- SIMS spot dimension $\approx 2\text{mm}$
Questions

**Mass interferences on 65 m/e signal?**

Our SIMS resolution is about 100 (m/δm), not enough to resolve different peaks with the same nominal mass.

1. Double ionised atoms
2. Organic contaminants (giving 65 mass fragments)
3. Ni^{58}Li^{7} due to Li_{2}SO_{4} electrolyte
4. Ni^{64}H compound
Mass interferences on 65 m/e signal?

Double ionised atoms?

No signal is observed from 130 atomic mass (Te$^{130}$, Ba$^{130}$), which could give a 65 m/e signal when double ionised.
Mass interferences on 65 m/e signal?

Organic contaminants?

- 65 mass C₅H₅⁺ ion is very reactive, but it could be produced during the SIMS analysis by fragmentation of higher mass organic molecules (hydrocarbons).

- Typical spectra of hydrocarbon contaminants show groups of odd mass peaks with 12 a.m.u. periodicity (due to 1 C atom increment in the chain fragment).

<table>
<thead>
<tr>
<th></th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>C₂H₃</td>
<td>C₂H₅</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₃</td>
<td>C₃H₅</td>
<td>C₃H₇</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃H₃</td>
<td>C₄H₅</td>
<td>C₄H₇</td>
<td>C₄H₉</td>
<td></td>
</tr>
<tr>
<td>C₄H₃</td>
<td>C₅H₅</td>
<td>C₅H₇</td>
<td>C₅H₉</td>
<td></td>
</tr>
</tbody>
</table>

References:

SIMS technical report by RIBER Instrumentation Ultra-vide, France


Organic Compound Database by Harold M. Bell at Virginia Tech., http://www.colby.edu/chemistry/cmp/cmp.html
Fragmentation pattern of organic contaminants is not observed

- 15, 43, 69 masses are not detected
- 51, 53, 55, 57 masses are masked by isotopes of clearly identified elements, present also in the reference sample (V$^{51}$, Cr$^{53}$, Mn$^{55}$, Fe$^{57}$)
Organic contaminants (continue)?

From the polymeric substrate?
• SIMS depth profile shows that the 65 signal is not correlated with the increase of the $^{12}\text{C}$ when the interface between the film and the substrate is reached.

<table>
<thead>
<tr>
<th>Mass peak ratio</th>
<th>On the surface</th>
<th>Close to the substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{58}$/C$</em>{12}$</td>
<td>35 ± 2</td>
<td>8.1 ± 0.5</td>
</tr>
<tr>
<td>Ni$<em>{58}$/mass$</em>{65}$</td>
<td>65 ± 6</td>
<td>49 ± 16</td>
</tr>
</tbody>
</table>

From the electrolyte?
• Gas chromatography analysis of the electrolyte shows that organic contaminants are less than 1ppb.

From the surface?
• The blank sample has been immersed for 2 days in iso-octane to remove organic contaminants eventually adsorbed on the surface. Gas chromatography analysis of the liquid did not reveal any organic contaminant down to 1ppb.
Mass interferences on 65 m/e signal?

Ni\textsuperscript{58}Li\textsuperscript{7} due to Li\textsubscript{2}SO\textsubscript{4} electrolyte?

- Despite of NiLi is not a stable compound however Li is detected on the film surface after electrolysis by SIMS.
- Ni\textsuperscript{60}Li\textsuperscript{7} and Ni\textsuperscript{58}Li\textsuperscript{7}OH , Ni\textsuperscript{60}Li\textsuperscript{7}OH mass peaks should be observed together the Ni\textsuperscript{58}Li\textsuperscript{7} signal.

In our SIMS spectrum 65, 67 and 82, 84 mass peaks are present, which can be associated to the Ni\textsuperscript{58}Li\textsuperscript{7} , Ni\textsuperscript{60}Li\textsuperscript{7} and Ni\textsuperscript{58}Li\textsuperscript{7}OH , Ni\textsuperscript{60}Li\textsuperscript{7}OH compounds.

The ratio between these peaks intensity turns out to be equal to the natural isotopic ratio of Ni\textsuperscript{58} and Ni\textsuperscript{60}.

|                  | Value  
<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Ni\textsuperscript{58}Li\textsuperscript{7}/Ni\textsuperscript{60}Li\textsuperscript{7}</td>
<td>2.0±0.5</td>
</tr>
<tr>
<td>Ni\textsuperscript{58}Li\textsuperscript{7}OH/Ni\textsuperscript{60}Li\textsuperscript{7}OH</td>
<td>2.5±0.5</td>
</tr>
<tr>
<td>Ni\textsuperscript{58}/Ni\textsuperscript{60}</td>
<td>2.71±0.01</td>
</tr>
<tr>
<td>Ni\textsuperscript{58}/Ni\textsuperscript{60} nat.</td>
<td>2.60</td>
</tr>
</tbody>
</table>
Ni$^{58}$Li$^7$ due to Li$_2$SO$_4$ electrolyte? (continue)

*but*

The isotopic ratio of the compound related to the Li$^7$, Li$^6$ isotopes (Ni$^{58}$Li$^7$/Ni$^{58}$Li$^6$) does not match the natural value, but it cannot be determined with enough accuracy due to the Ni$^{64}$ contribution to the 64 mass peak.

Some samples have been electrolysed but have not shown the 65-mass extra signal

*Contribution to the 65 mass peak from Ni$^{58}$Li$^7$ ion cannot be excluded.*
Mass interferences on 65 m/e signal?

Ni$^{64}$H compound?

Ni$^{64}$H (65mass) detection is unlikely because the isotopic ratio Ni$^{62}$H (63 mass) / Ni$^{64}$H (65 mass) of Ni isotopes does not match the natural value (3.9): the observed results goes into the opposite direction!
CONCLUSIONS

• Previous NAA results revealed isotopic shift for Ag contaminant in Ni electrolysed films.

• Preliminary results gave evidence of an apparent isotopic shift on the Cu masses (65 too high) in Ni hydrogenated films.

but

• All possible interpretations of the experimental data must be considered in order to get certain results.

• The system complexity and the very small size of the foreseen effects requires suitable and very high performance experimental apparatus.

• Cross matched analysis are necessary to get completely convincing conclusions.
Towards a deeper understanding

In the present experiment, something more for the next:

- Ultra-high resolution SIMS apparatus ($\delta m \leq 0.02$, $m/\delta m > 3000$)
- Test experiments by changing the electrolyte (for ex. NaOH)
- Cross matched analysis by other methods (for ex. Nuclear Activation Analysis)
The authors thank Dr. K. Grabowski and Dr. M. Melich for the important help received on this matter.
Calculated cross section for different nuclear reaction

By NOT-SMOKER web database by Prof. Thomas Raucher.
TOF-SIMS analysis at ETH

- A couple of reference and active samples have been also analysed by TOF-SIMS at ETH, to check our results.
- Cs\(^+\) primary, negative secondary ions
- Cu\(^{63}/Cu^{65}\) isotopic ratio after calibration of data with a standard:
  - *Electrolysed* sample: Cu\(^{63}/Cu^{65}\) = 2.40±0.31
  - *Reference* sample: Cu\(^{63}/Cu^{65}\) = 1.79±0.02
Lateral Position Spectra

Peak in gate PRE7: $^{65}\text{Cu}$
Peak in gate PRE7B: $^{63}\text{Cu}$
Peak around channel 550: mass 64, $^{64}\text{Ni}$
Mass interferences on 65 m/e signal?

Ni$^{58}$Li$^{7}$ due to Li$_2$SO$_4$ electrolyte?

- Despite of NiLi is not a stable compound however Li is detected on the film surface after electrolysis by SIMS.
- Evidence of PdNa$^+$ compound comes from reference SIMS spectra of standard samples (by RIBER). The PdNa$^+$ mass peaks are coupled with the presence of PdNaOH$^+$ and PdNaO$^+$ mass signals.
- NiLi$^+$ formation is possible because Ni and Li belong to the same groups of Pd and Na respectively on the periodic table of the elements.