PROGRESS ON THE STUDY OF ISOTOPIC COMPOSITION IN METALLIC THIN FILMS UNDERGONE TO ELECTROCHEMICAL LOADING OF HYDROGEN

M. APICELLA AND V. VIOLANTE
ENEA Frascati Research Center, V. le E. Fermi 45, 00044 Frascati (Roma), Italy
E-mail: violante@frascati.enea.it

F. SARTO, A. ROSADA AND E. SANTORO
ENEA Casaccia Research Center, V. Anguillarese 301, 00060 S.Maria di Galeria (Roma), Italy

E. CASTAGNA AND C. SIBILIA
La Sapienza University, Via Scarpa, 14, 00100 (Roma), Italy

M. MCKUBRE AND F. TANZELLA
SRI International, 333 Ravenswood Ave, Menlo Park, CA 94025, USA

G. HUBLER
Naval Research Laboratory, 4555 Overlook Ave., S.W. Washington, DC 20375, USA

A research activity has started some years ago in the framework of collaboration between the ENEA (Italy) and the SRI (USA), aimed to the identification of traces of nuclear reactions in condensed matter. This work has also involved cross-linked analysis in order to identify effects due to contaminants that could affect the isotopic shift estimate. Nickel thin films have been sputtered on a polymeric substrate and loaded with hydrogen by electrolysis. Reference and active thin films have been prepared contemporaneously during the same sputtering process to have on both the same deposition and the same impurities composition. Secondary Ion Mass Spectroscopy (SIMS) has been used to analyze the isotopic composition of the electrolyzed and blank substrates. Preliminary results (Violante *et al.*, *Proc. 10th Int. Conf. Cold Fusion* (*ICCF-10*), Cambridge, 2003) indicated that a reasonable reproducible apparent shift of the isotopic composition of the Cu element occurred in some of the electrolyzed films, with an increasing of mass 65, while the natural value was always observed for all the blank samples. Cu was particularly suitable for being used as a marker elements because of its only two mass isotopes (63/65) that do not overlap with isotopes of other elements having the same masses. In this work, new experiments have been reproduced to increase the statitistics and further analysis has been performed in order to exclude that the revealed shift was traceable to an artifact.These included SIMS scanning of the sample surface, depth profile analysis by SIMS, mass spectrometric analysis of the electrolyte, SUPER-SIMS [2] analysis of one couple of reference and active films. In particular, the possible contribution from mass interferences on the 65-mass extra-signal has been considered, coming from contaminants or double ionized species. On the basis of the new results, a more complex scenario has been evidenced, suggesting that the former attribution of the Cu^{63}/Cu^{65} isotopic shift could be not correct. The indication of new experiments and tests that potentially should provide a complete understanding of the present results has been given. The work wants to stress that the identification of elemental transmutations in metal hydrides is an extremely complex topic, which necessitate of severe scientific accuracy, cross-matched analysis, multidisciplinary expertise, and the access to top performance experimental facilities. All these requirements can be fulfilled only in the framework of top-level international scientific collaboration.

1. Introduction

The detection of nuclear ashes inside metallic hydrides is one of the most direct evidences of the happening of nuclear reaction in the condensed matter. But this topic is also a very complex and delicate issue, first of all because of the low level of the signals to be detected, which can be easily overlapped by instrumental noise or background interferences.

The measurement of the isotopic composition of metallic hydrides is an efficient method to reveal nuclear products eventually formed during the hydrogen loading. Actually, the presence of “new” (i.e. “not detected before”) elements in the metal specimens cannot be assessed as products of a nuclear reactions, because the possibility of contamination from the environment or the diffusion of impurities inside the sample to the detection areas are very difficult to be excluded completely.

A research activity has started some years ago in the framework of collaboration between the ENEA (Italy) and the SRI (USA), aimed to the identification of traces of nuclear reactions in condensed matter.

Preliminary results[1] by Neutron Activation Analysis (NAA) have given indication of Ag isotopic shift occurring in Pd thin films after electrolysis. A first screening by Secondary Ion Mass Spectrometry (SIMS) of the isotopic composition of Nickel thin films undergone to similar experiments has also pointed out an isotopic ratio different from the natural one on the 63/65 masses imputable to copper.[2]

In this work, further reproduction of the previous experiments and a more accurate analysis of the experimental data have been performed. Cross-linked analysis has also been involved, in order to identify artifacts that could affect the isotopic shift estimate.

2. Experimental

The typical experiment, already described in Ref. 2, consisted in three steps:

- Deposition of two identical *Reference* and *Active* nickel films during the same deposition run;
- Hydrogen loading of the *Active* film by electrolysis;
- SIMS analysis of both *Reference* and an *Active* sample isotopic composition, to search deviations from the natural abundances.

Steps (1) and (2) have been carried out in a class 1000 clean room laboratory, by using clean room grade gloves and papers in order to reduce source of contaminants. To the same aim, a reduced number of high-purity materials have been used both for sample production and electrolysis cell assembling.

2.1. *Metallic Film Deposition*

The films (with 45 nm thickness) have been deposited by ion beam sputtering of a Ni target (MRC, 99.98% purity) on polyethylene (kartell) 12 mm diameter – 1 mm thick disks. Before deposition, the substrates have been chemically cleaned as reported in Ref. 2, and ion beam etched to improve film/substrate adhesion and to assure good film surface status after electrolysis.Up to six identical *Reference* and an *Active* nickel films have been deposited during the same run, loaded on a rotating sample holder.

2.2. *Hydrogen Loading*

The hydrogen loading of the *Active* film has been carried out by electrolysis, in Light water (18 MW) $LiSO_4$ solution (1 M). The cell was realized in polyethylene (Kartell), with high purity (99.98%) Pt electrodes (see photo in Ref. 2). Typical values of the current and voltage used during the experiments ranged between 5–190 mA and 2–7 V, respectively. Loading times went from a minimum of 3 h to a maximum of 40 h.

2.3. *SIMS Analysis*

Secondary Ion Mass Spectrometry measurements have been carried out with a Leybold SSM-Mass Spectrometer Module, operating at the ENEA research centre in Frascati (Rome, Italy). The Mass Spectrometer is equipped with a source Leybold IQE 12/38 ion source and a Balzers Quadrupole Mass Analyser working in the mass range 0–511 a.m.u. The primary beam was fed by Ar^+ ions at 5 keV. The beam spot had a diameter of about 2 mm, small enough to allow scanning of the sample surface. Typical sensitivity and resolution were 0.5 a.m.u. ($m/\delta m \approx 100$) and 10^{12} at/cm^2, respectively.

Reference and electrolyzed films have been loaded together into the analysis chamber, positioned at 180^o on a cylindrical support and analyzed in series under the same SIMS conditions.

3. Results

Preliminary results reported in Ref. 2 showed an apparent isotopic shift on the ^{63}Cu/^{65}Cu masses in nickel thin films undergone to electrolysis (*active* films), whereas an isotopic composition matching the natural abundance was always detected in the not-electrolysed (*reference*) films.

Table 1. Synoptic of the new experiments described in this work

Sample	Film status after electrolysis	Apparent isotopic shift	
		Electrolysed	Reference
Ni 1bis	Ok	Yes	No
Ni 3bis	Ok	Yes	No
Ni P2	Ok	Yes	No
Ni P3	Ok	No	No
Ni 4	Ok	Yes	No

The tuning of the SIMS instrumentation was checked during each of the analysis runs, by moving the sputtering argon beam on the stainless steal sample-holder where the Cu isotopic composition was always found to be the natural one. We have repeated the same experiment in order to increase the statistics and evaluate its reproducibility.

A synoptic of the new experiments has been reported in Table 1, giving evidence of the apparent isotopic shift in 4/5 cases.

The SIMS analysis has been carried out on different points of the sample surface, showing a more relevant effect in the middle of the sample (see Fig. 1).

Furthermore, a dynamic SIMS analysis has been done in order to check if the shifted isotopic ratio was maintained below the surface. The depth profile of the 63, 65, 58, and 12 masses has been recorded, showing that the 63/65 shift survives beyond the surface down to the film/substrate interface, and it is not coupled with the C^{12} signal of carbon but with the Ni^{58} signal, originated by from the main constituent of the film (see discussion below).

In addition, a cross-linked analysis has been done by using the SUPER-SIMS facility located at the ETH, in Zurich (Switzerland).[3] The instrument used Cs^+ primary ions and the analysis revealed negative secondary ions. A couple of *Reference* and *Active* samples have been analyzed to verify the above results. Due to unwanted charging of some parts of the extraction section, causing signal instability, the Cu^{63}/Cu^{65}isotopic ratio measurement needed calibration by a pure standard. Then, a sequential procedure has been followed to carry out the measurements, consisting in the analysis of a pure Cu standard, the *Reference* sample, the pure Cu standard again and the *Active* sample. The values measured for each sample, after calibration, showed some discrepancies with the measurements performed in Rome, giving $Cu^{63}/Cu^{65} = 2.40 \pm 0.31$ for the *Active* sample and $Cu^{63}/Cu^{65} = 1.79 \pm 0.02$ for the *Reference* sample. In the following discussion, both results are carefully analyzed, in order to get informing conclusions.

4. Discussion

An alteration of the isotopic ratio of the copper is relatively simple to detect because copper has only two stable isotopes, which do not overlap with isotopes of other elements having the same masses. However, mass interferences on the considered

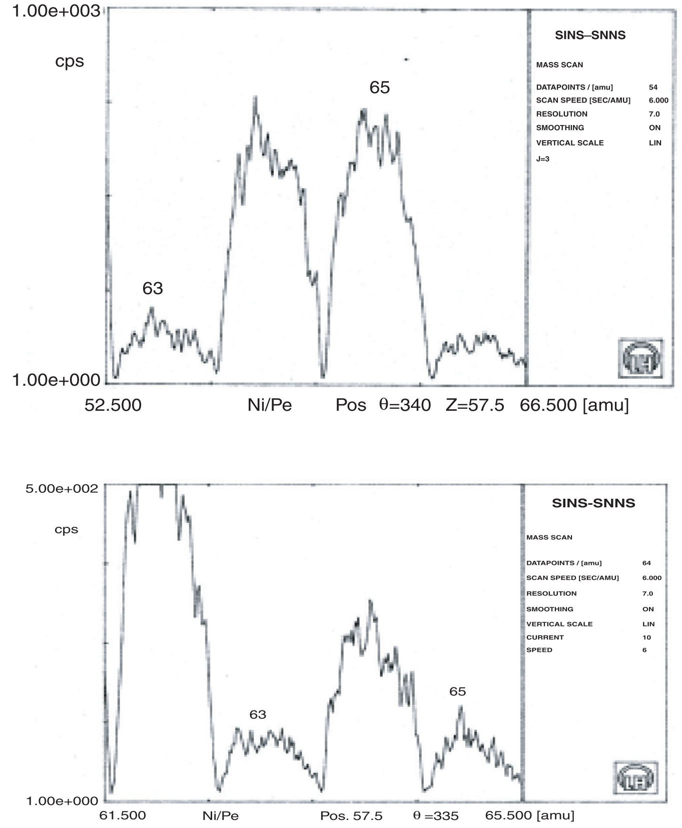

Figure 1. SIMS spectrum of the *Active* sample in the midway of the specimen (left) and close to the edge of the specimen (right).

65 and 63 m/e signals from compounds or double ionized species could affect the results, when using a conventional SIMS facility with limited resolution. Therefore, a careful analysis of all possible contribution to the 65-m/e signal in the SIMS spectrum has to be done, concerning the above described results.

$Ni^{64}H$ (65 mass) detection has been considered unlikely, because the isotopic ratio $Ni^{62}H$ (63 mass)/$Ni^{64}H$ (65 mass) of Ni more abundant isotopes did not match the natural value (3.9), being the observed isotopic shift just into the opposite direction.

The contribution to the 65 m/e signal from double ionized ions had also to be excluded because of the absence of signals at 130 m/e, relative to the corresponding single ionized elements (Te^{130} or Ba^{130}?).

A more complicate issue consisted in excluding possible interferences from organic contaminants, which could produce positive ion fragments having 65 molecular masses. Actually, 65 mass $C_5H_5^+$ ion is very reactive, but it could be produced

Table 2. Peak intensity ratio of the SIMS signals during the dynamic analysis of the *Active* sample: column 2 shows values at the film surface, column 3 at the interface between the film and the substrate

Mass peak ratio	On the surface	Close to the substrate
Ni^{58}/C^{12}	35 ± 2	8.1 ± 0.5
$Ni^{58}/mass^{65}$	65 ± 6	49 ± 16

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).[4] Fragmentation patterns of hydrocarbons involving 65-mass positive ion are reported in literature,[4–6] but they were not clearly readable in our SIMS spectrum [see Fig. 2: masses 15, 43, 69 are not detected masses 51, 53, 55, 57 are masked by signals due to isotopes of clearly identified elements, present also in the reference sample (V^{51}, Cr^{53} 53, Mn^{55}, Fe^{57})].

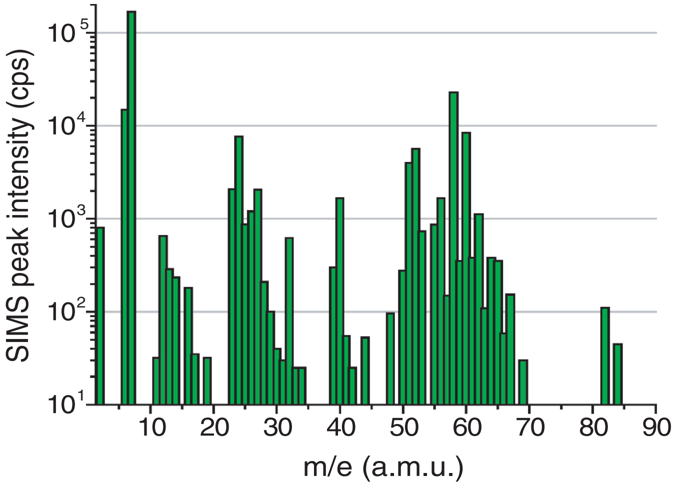

Figure 2. SIMS spectrum of the *Active* film in the wide mass range.

Furthermore, the dynamic SIMS analysis showed that an increasing of the C^{12} signal due to the substrate was coupled with a decreasing signal of other species but without any change in the Cu isotopic ratio, so that one may exclude an effect of the polymeric substrate on the increasing signal of mass 65. In Table 2 the peak intensity values of the SIMS signals at the masses 12 (carbon), 58 (nickel), and 65 have been reported as they have been measured at the film surface and close to the film/substrate interface.

The possibility of organic contamination of the film surface from the electrolytic solution has been also considered. Gas chromatography analysis of the electrolyte has been performed, showing that organic contaminants are less than 1 ppb.

On the basis of the above-mentioned observations, one should exclude a contamination due to organic substances at mass 65.

Finally, the possible interference from inorganic compound contaminant matching 65 mass has been considered. By seeing at the more abundant elements revealed in the whole range SIMS spectrum, detection of $Ni^{58}Li^{7}$ (total mass = 65) compound could be expected. In fact, despite of NiLi is not a stable compound; Li is clearly detected on the active film surface, coming from the electrolytic solution. Supporting this assignation is the detection in our SIMS spectrum of the 65, 67, 82, and 84 mass peaks, which can be associated to the isotopes of the NiLi and NiLiOH compounds (mass 65 $\Rightarrow$ $Ni^{58}Li^{7}$, mass 67 $\Rightarrow$ $Ni^{60}Li^{7}$, mass 82 $\Rightarrow$ $Ni^{58}Li^{7}OH$, mass 84 $\Rightarrow$ $Ni^{60}Li^{7}OH$). In Table 3 are reported the intensity ratios between the SIMS peaks associated with the above compounds. The obtained values match the natural isotopic ratios in the case of the Ni^{58} and Ni^{60} isotopes, but nothing can be said in the case of Li^{7}, Li^{6} isotopes, due to the poor accuracy of the data, affected by the Ni^{64} contribution to the 64 peak.

In conclusion, the contribution to the 65 mass peak from $Ni^{58}Li^{7}$ compound seems to be the only reasonable explanations of the reported results, out of the copper isotopic shift hypothesis.

This supposition could also be consistent with the SUPER-SIMS results, which indicated a value for the isotopic composition of copper similar to the natural one for both the active and reference films analyzed.

Some uncertainty still affect our results, concerning the fact that Li contamination from the electrolyte is expected in all electrolyzed samples while in some of them the 65 extra signal has not been revealed. As concerning the SUPER-SIMS measurements, the information is limited to a restricted area of the film surface, because only one point of the surface of each sample has been analyzed, which could be not representative of the whole sample surface, since a gradient effect in the isotopic composition has been demonstrated by the conventional SIMS surface scanning analysis.

Further experiments and tests could be useful in the future, to completely understand the present data. In particular, surface scanning by ultra-high resolution SIMS apparatus ($m/\delta m > 3000$, enough to resolve mass interferences), cross-matched analysis by other methods (e.g. Nuclear Activation Analysis), similar experiments with changed electrolyte (e.g. NaOH instead of $LiSO_4$).

Table 3. Intensity ratios between the SIMS peaks associated with the NiLi and NiLiOH compounds

Isotopes ratio	SIMS peaks ratio	Natural isotopic ratio
$Ni^{58}Li^{7}/Ni^{60}Li^{7}$	2.0 ± 0.5	2.60
$Ni^{58}Li^{7}OH/Ni^{60}Li^{7}OH$	2.5 ± 0.5	2.60
Ni^{58}/Ni^{60}	2.71 ± 0.01	2.60

5. Conclusions

Based on preliminary results, showing evidences of isotopic shift on the Cu masses (65 too high) in Ni hydrogenated films, a new set of experiments has been reproduced and further analysis have been performed in order to exclude that the revealed shift was traceable to an artifact. These included SIMS scanning of the sample surface, depth profile analysis by SIMS, mass spectrometric analysis of the electrolyte, SUPER-SIMS analysis of one couple of reference and active films.

On the basis of the new results, a more complex scenario has been evidenced, suggesting that the former attribution of the Cu^{63}/Cu^{65} isotopic shift could be not correct.

The work wants to stress that the identification of elemental transmutations in metal hydrides is an extremely complex topic, which necessitate of severe scientific accuracy, cross-matched analysis, multidisciplinary expertise and the access to top performance experimental facilities. All these requirements can be fulfilled only in the framework of top-level scientific collaboration worldwide.

Acknowledgments

The authors thank Dr. K. Grabowski and Dr. M. Melich of Naval Research Laboratory (Washington, DC, USA) for the important help received on this matter. The contribution of Dott. Luigi Nardi of ENEA research center Casaccia (Rome, Italy) in performing the gas cromatography analysis is sincerely acknowledged.

References

1. V. Violante, M. L. Apicella, L. Capobianco, F. Sarto, A. Rosada, E. Santoro, M. McKubre, F. Tanzella, and C. Sibilia – Search for nuclear ashes in electrochemical experiments. *Proc. of 10th International Conference on Cold Fusion (ICCF-10)*, Cambridge, MA, August 24–29 (2003), World Scientific Inc., Singapore.
2. SUPER-SIMS analysis has been performed by the facility located at ETH, by Dr. M. Doebely.
3. V.Violante, P.Tripodi, D. Di Gioacchino, R. Borelli, L.Bettinali, E.Santoro, A. Rosada, F.Sarto, A.Pizzuto, M.McKubre, F.Tanzella, X-ray emission during electrolysis of light water on palladium and nickel thin films. *Proc. of 9th International Conference on Cold Fusion, (ICCF9)*, Beijing, May 19–24 (2002).
4. SIMS technical report by RIBER Instrumentation Ultra-vide, France.
5. Integrated Spectral Data Base System for Organic Compounds by National Institute of Advanced Industrial Science & Technology, SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/.
6. Organic Compound Database by Harold M. Bell at Virginia Tech., http://www.colby.edu/ chemistry/cmp/cmp.html.