X International Workshop on Anomalies in Hydrogen Loaded Metals.

Experimental results on sub-micro structured Cu-Ni alloys under high temperatures Hydrogen/Deuterium interactions.

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OUTLINE

1) **Motivation.**
2) **Sample preparations.**
3) **Experimental set-up.**
4) **Active material and measurement procedure.**
5) **Selected results.**
6) **Further developments/comments/conclusions.**

Motivation

***In the framework of studies devoted to detect thermal and/or nuclear anomalies during the close interactions of H_2 and/or D_2 with Hydrogen-absorbing materials (e.g. Pd, Ni, Ti, Th, U, Fe, rare-earths, pure and their alloys), since March 2011, we made several experiments with a specific commercial alloy (ISOTAN 44 from Isabellenhutte, Germany) with nominal composition: Cu_{55}-Ni_{44}-Mn_1.**

***The Pd material, for comparison, has interesting performances (but, still now, at poor reproducibility level), about anomalous excess heat generation. The reproducibility increases, e.g., when the surface is nano-coated, multilayer geometry, with proper multiple materials (like Th, nano-Pd, Sr salts, colloidal silica, as we introduced since 2002).**

***In addition alloys, like Pd_{95}-Y_5, by Tanaka K.K.-Japan, provided ultra-short time D_2 absorption: only 8 sec to get a R/Ro ratio of 2.2 (i.e. D/Pd of about 0.7) at 25°C in gaseous environment. Related excess heat was also observed.**

***The main drawbacks of Pd are: high cost, very strong sensitivity to embrittlement problems (due to H_2 or D_2 absorption/desorption). Such last aspect is the weakest point on the use of thin (Φ=50-100μm) and long wires, as experienced by Preparata's group (since 1995) and later ourselves: the wires break quite frequently, and, as a main irony, almost in coincidence with the production of excess heat.**

***The embrittlement problems happen both in electrolytic and gaseous environments when the material is cycled at temperatures (< 350°C for pure Pd) where the α and β phases of Pd are separated.**

****As first key comment, we note that the embrittlement effect could be useful to create the nano-microstructured surface and bulk at the beginning of the experiments, but is deleterious over time because the wires are destroyed.***

***The embrittlement effect is initially slow at the cathode surface (bulk geometry, like rods or plates) in electrolytic environments and can explain the long times needed (weeks-months in F&P exps.) to observe "anomalous heat".**

***Different approach reduced this time:**

a) **thin wires (Preparata, Celani)**

b) **3μm thickness films (Preparata, 1999)**

c) **co-deposition procedures (M. Swartz, USA, 2000)**

d) **Repeated cycles of cathodic and anodic conditions have similar effects (observed growing of sub-micron structures at Pd wire surface by Celani with Pirelli Company group, 1998)**

e) **Nano-materials have even further short time of waiting (few seconds) as shown in the experiments of Arata, Takahashi and Kitamura, Celani, Ahern. Ahern provided some specific nano-materials to Takahashi and Kitamura group: $(ZrO_2)65\%$-$(Ni_7$-$Pd_1)35\%$.**

ISABELLENHÜTTE

ISOTAN®

Form of Delivery

ISOTAN® is supplied in the form of wires with dimensions from 0.03 to 10 mm Ø in bare condition. Enamelled wires are available in dimensions between 0.05 and 1.5 mm Ø.

ISOTAN® can also be supplied in form of stranded wire, ribbon, flat wire and rods. Please contact us for the range of dimensions.

Brand Name	ISOTAN®[1]
Material Code	2.0842
Abbreviation	JN / LN / TN / UN / EN / JNX / LNX / TNX / UNX / ENX / KNCB / CNC

Chemical Composition (mass components) in %.
Average values of alloy components

Cu	Ni	Mn
Balance	44	1

Thermoelectrical and Electrical Values in Soft-Annealed Condition [3]

EMF versus Cu/NIST 175 0 – 100 °C / mV	EMF versus Pt67/NIST 175 0 – 100 °C / mV	EMF versus Pt67/NIST 175 0 – 700 °C / mV	Electrical resistivity in µΩ x cm at 20 °C
– 4.1 to – 4.7	– 3.3 to – 3.9	– 29.6 to – 34.7	49

Physical Characteristics (Reference Values)

Density at 20 °C	Melting point	Specific heat at 20 °C	Thermal conductivity at 20 °C	Average linear thermal expansion coefficient between 20 °C and 100 °C	Magnetic at room temperature
g/cm³	°C	J/g K	W/m K	10^{-6}/K	
8.9	1280	0.41	23	13.5	no

Mechanical Properties at 20 °C in Annealed Condition [4]

	Tensile strength MPa	Elongation %	Hardness HV10
hard	> 740	2	> 230
soft	420	30	95

1) ISOTAN® is a registered trademark of Isabellenhütte Heusler GmbH & Co. KG.
2) Konstantan® is a registered trademark of KRUPP VDM GmbH.
3) The exact EMF values according to NIST 175 can be calculated with the "EMF-Software", which can be downloaded from our homepage.
4) The mechanical values considerably depend on dimension. The indicated values refer to a dimension of 1 mm diameter.

Notes on Treatment

ISOTAN® is easy to process. The alloy can be soldered and brazed without difficulty.
All known welding methods are applicable.

Features and Application Notes

ISOTAN®, also named Konstantan®[2], is used as negative leg of thermocouple types J and L as well as T, U and E.
In the version for extension leads, ISOTAN® is used for JNX, LNX as well as TNX, UNX and ENX. ISOTAN® is also used as compensating lead in type KNCB as well as negative leg for compensating lead type W5Re/W26Re.
The standardized temperature range of the different application possibilities of ISOTAN®, is available in the tables on pages 10 and 11, 14 and 15 as well as 18 and 19. See also "Special Remarks on the Alloy".
We supply various qualities of ISOTAN®, which are suited for different applications or standards.

***The ISOTAN 44 was selected according to the following considerations:**

a) **Measurable diffusion coefficient of Hydrogen, in even the pure (not alloyed) elements, i.e. Cu and Ni, at high temperatures:**

*** Cu=10^{-6}cm^2/s at 200°C, 10^{-4}cm^2/s at 700°C;**

*** Ni= 10^{-7}cm^2/s at 200°C, 10^{-6}cm^2/s at 350°C.**

*** In comparison, the (good) values for Pd are:**

10^{-5}cm^2/s at 200°C, 10^{-4}cm^2/s at 420°C; moreover, at 600°C were reported values as large as 8*10^{-3}cm^2/s, but not reproducible.

b) **Lower cost, overall, even considering the procedure to "build" nano-structure at his surface, in respect to the precious metal Pd;**

c) **Very good mechanical properties, specially in respect to aging effects due to cycles of both low-high temperatures and H_2 absorption-desorption: our samples were working from over 7 months and only recently we observed damages rising-up. Our results are, in some aspects, different from that obtained by A.W. Szafranski (J. of Alloys and Compounds 404-406, 2005, 195-199): he observed extreme brittleness in, as received, Cu-Ni alloy that was only cold rolled from 200μm to 20μm (the penetration depth of H in Ni is about 30μm) and then cycled between 77 and 300K under 1GPa pressure of H_2. We could, only, think that high temperatures has some beneficial effect on brittleness problem. Moreover, we never made experiments at 77K.**

d) Extremely large values of measured catalytic power (ΔE, in eV) in respect to the dissociation of H_2 (Langmuir 1999, 15, 5773, S. Romanowski et al.), as following:

$Ni_{0.3750}$-$Cu_{0.6250}$ ==> +3.16eV

$Ni_{0.6250}$-$Cu_{0.3750}$ ==> +2.86eV

$Ni_{0.8125}$-$Cu_{0.1875}$ ==> +2.10eV

Ni……..==> +1.74eV

$Ni_{0.1825}$-$Cu_{0.8175}$ ==> +1.57eV

$Ag_{0.8125}$-$Pd_{0.1875}$ ==> +0.57eV

$Ag_{0.625}$-$Pd_{0.375}$ ==> +0.51eV

$Ag_{0.1875}$-$Pd_{0.8125}$ ==> +0.51eV

Pd……==> +0.42eV

Cu…… ==> -1.11eV

Ag……==> -1.42eV

e) **Thanks to the presence of Ni, there is possibility to use H_2 instead of expensive D_2. Reports by F. Piantelli (since 1992), G. Miley, M. Patterson, F. Celani (since 2010) and, overall, *claims by A. Rossi and (later on) by Defkalion Company*, could be further investigated. Moreover, cross-comparison of results using Hydrogen instead of Deuterium can be made.**

f) **The possibility, at least in principle, to produce *nano-micro structures* at the surface, or even deeper into the bulk, thanks to *selective oxidation of Cu in such alloy* at high temperatures (650-1050°C). Both segregation of Ni among CuO_x and cooling rate are key aspects of the preparation to be studied in deep details.**

g) *Our studies, very explorative, were devoted to find simple, and reliable/reproducible procedures to get such kind of structures. Experiment was operated for time as long as possible: "strength" test.*

h) **We anticipated that we get only partial success and produced few material (only some%) of proper dimensionality at nanometric sizes. Finally, apart the absolute values of dimensions, to be further optimised, we obtained frequently tri-dimensional shapes of geometries, called *Skeleton type*. Such tri-dimensional geometry has several intrinsic potentialities in respect to gas absorbtion. We anticipated that a paper, dedicated to explain the several specific proprieties of Skeleton geometry about the absorbtion of almost any gas, is under preparation.**

Samples Preparation

a) In our explorative preparations/tests we used “standardized” wires: (“nuked”) Φ=200μm, l=105cm. Initial values of weight (e.g. 307.4mg), diameter (+-1μm) and resistance (e.g. 17.16 Ohm) were carefully measured.

b) The wires, at the beginning, were “cleaned-up” of the original plastic insulating layer (rayon type, as provided by Isabellenhutte) by Joule heating, in air, at current as large as 2000mA, time 5m. In such conditions the power dissipated was about 70W and the resistance ratio, in respect to the reference value (at 100mA of current injected) increased of only 1%, as expected for such kind of material (commercial name is *Constantan*, i.e. constant resistance).

c) **After first thermal treatment, the weight decreased of about 13mg, the resistance decreased from 17.16 to 17.02 Ohm.**

d) ***We found that increasing both the current (up to 2500-3000mA) and the time at high power (5-1000s), decreasing the cooling speed (from 100s down to <1s) had dramatic effects on the growing of nano-microstructures and their dimensionality. The role of O_2, because free air treatment, is quite important. The wire temperature, in some tests, was even larger than 1000°C (evaluation by colour; the melting point of pure Cu is 1083°C).***

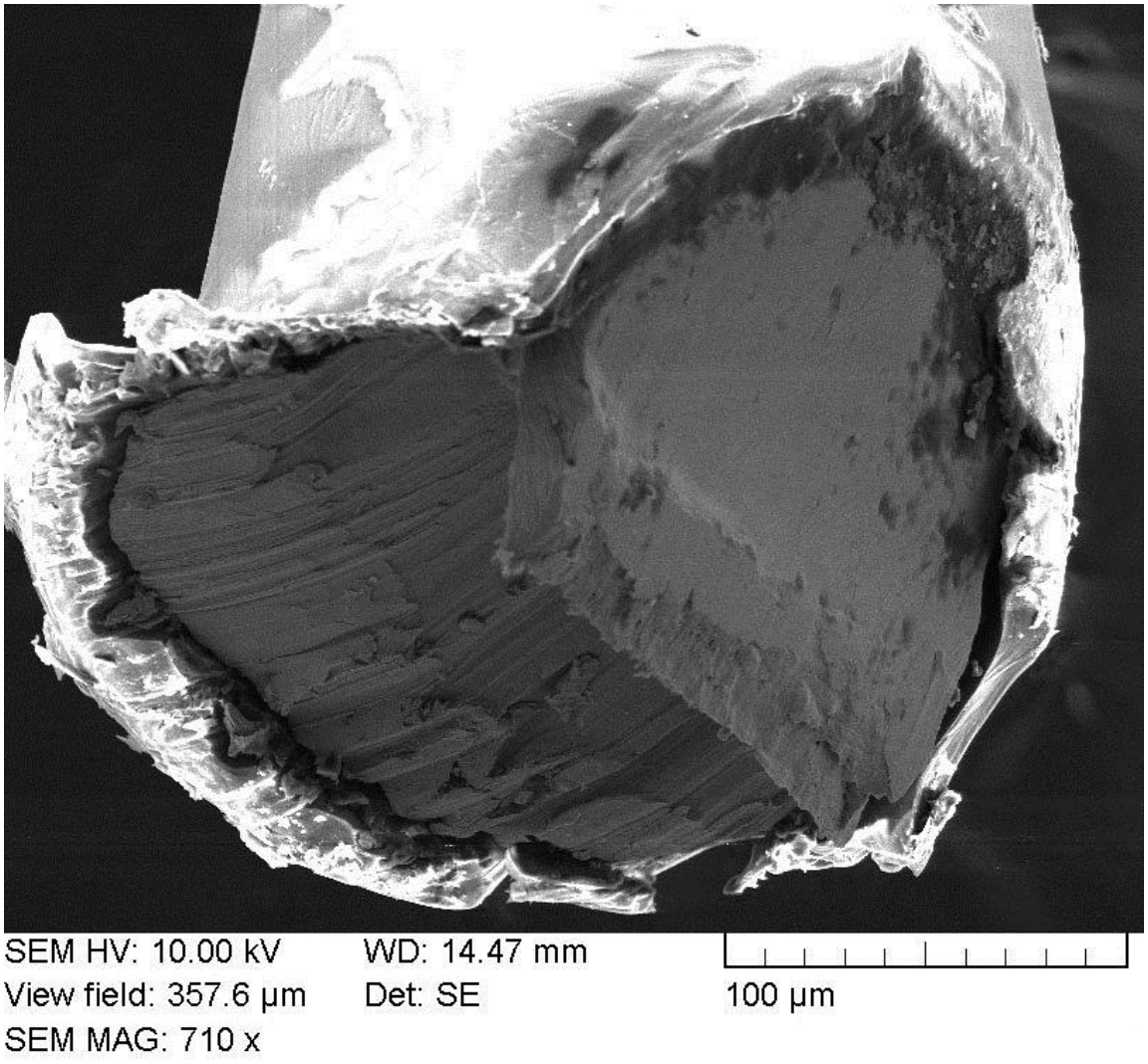
e) **More work, systematic and long/expensive, is necessary to optimize the multi-parameters operating conditions.**

f) **Some of the main results about surface geometries, obtained during few different kind of preparations, will be shown by SEM observations.**

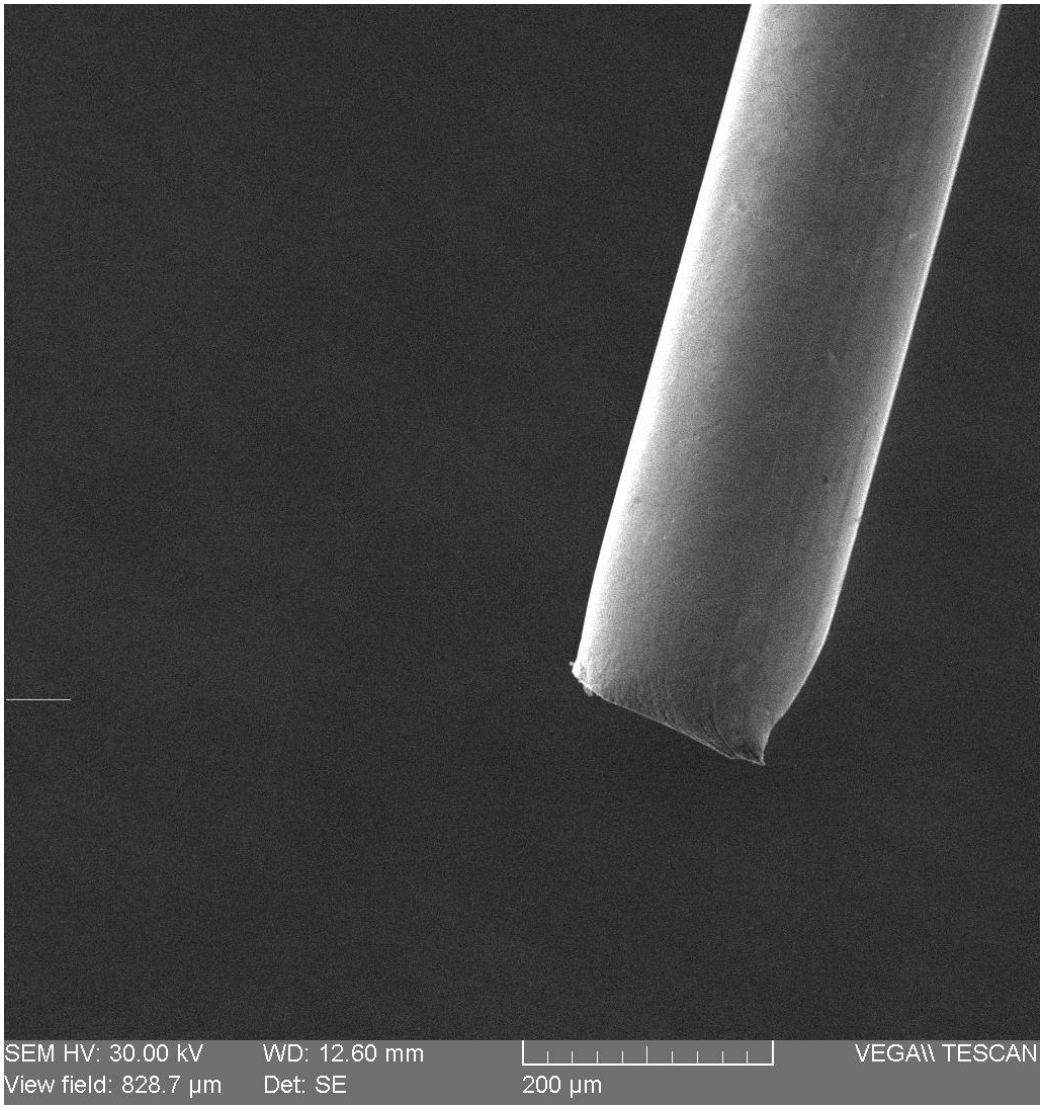
g) **Main comments, related to micro-analysis by EDAX, are shortly reported as following:**

The *local atomic compositions* of the wires, at the surface, changed from the original one (homogeneous), to not homogeneous one, specially the *ratio between Cu and Ni*. Possible reasons of the observed *Cu depletion* are: local hot spots with even Cu "evaporation" (anyway the boiling point of Cu is as large as 2595°C), formation of "weak" Cu oxides. In comparison, the bulk of the inner wire kept almost the starting original composition.

Mn, because its low content, it is difficult to be measured.

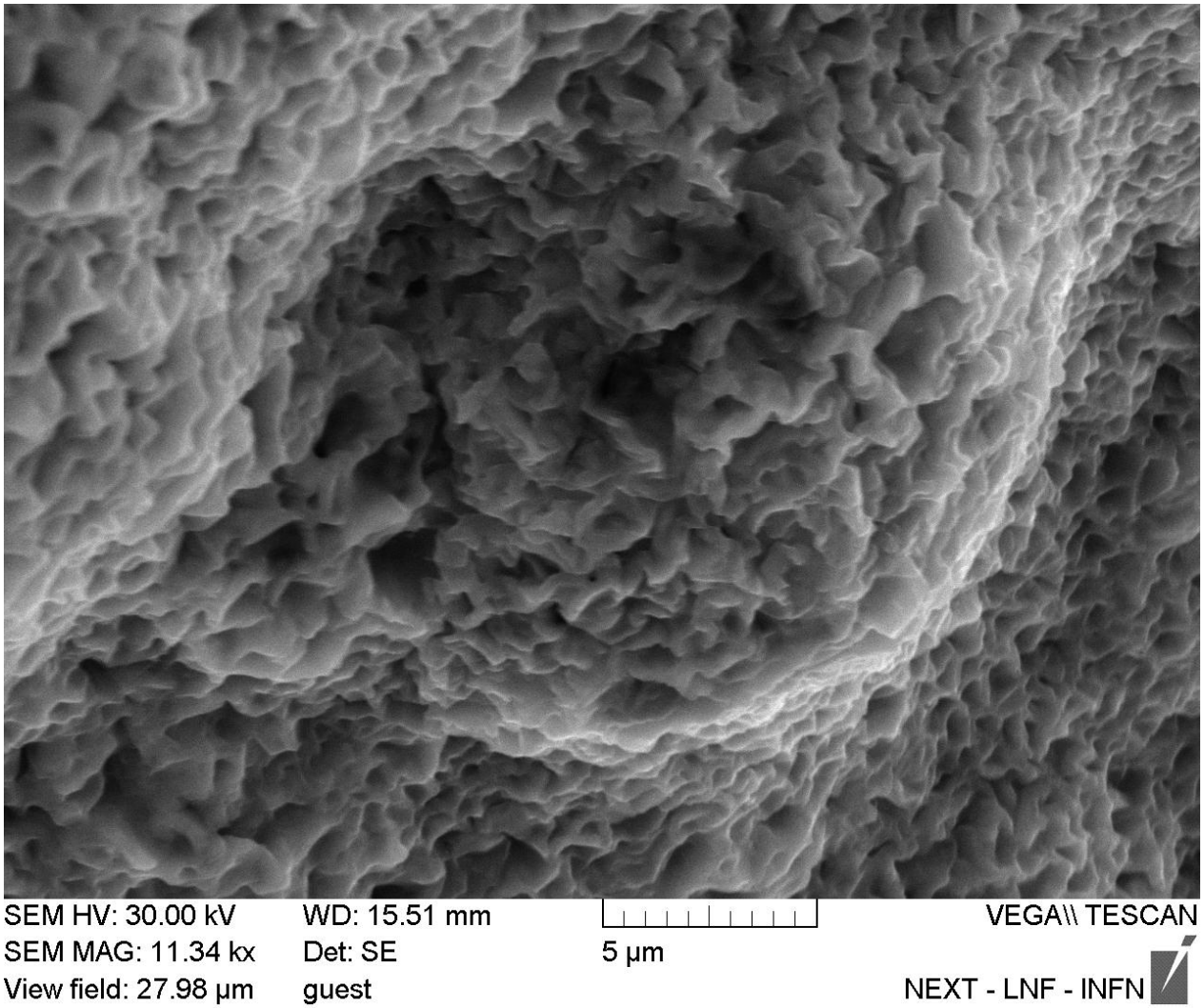


SEM. Cross section of virgin wire, as provided by Isabellenhutte, with "plastic" cover at the surface (lighter area at the microphotography).

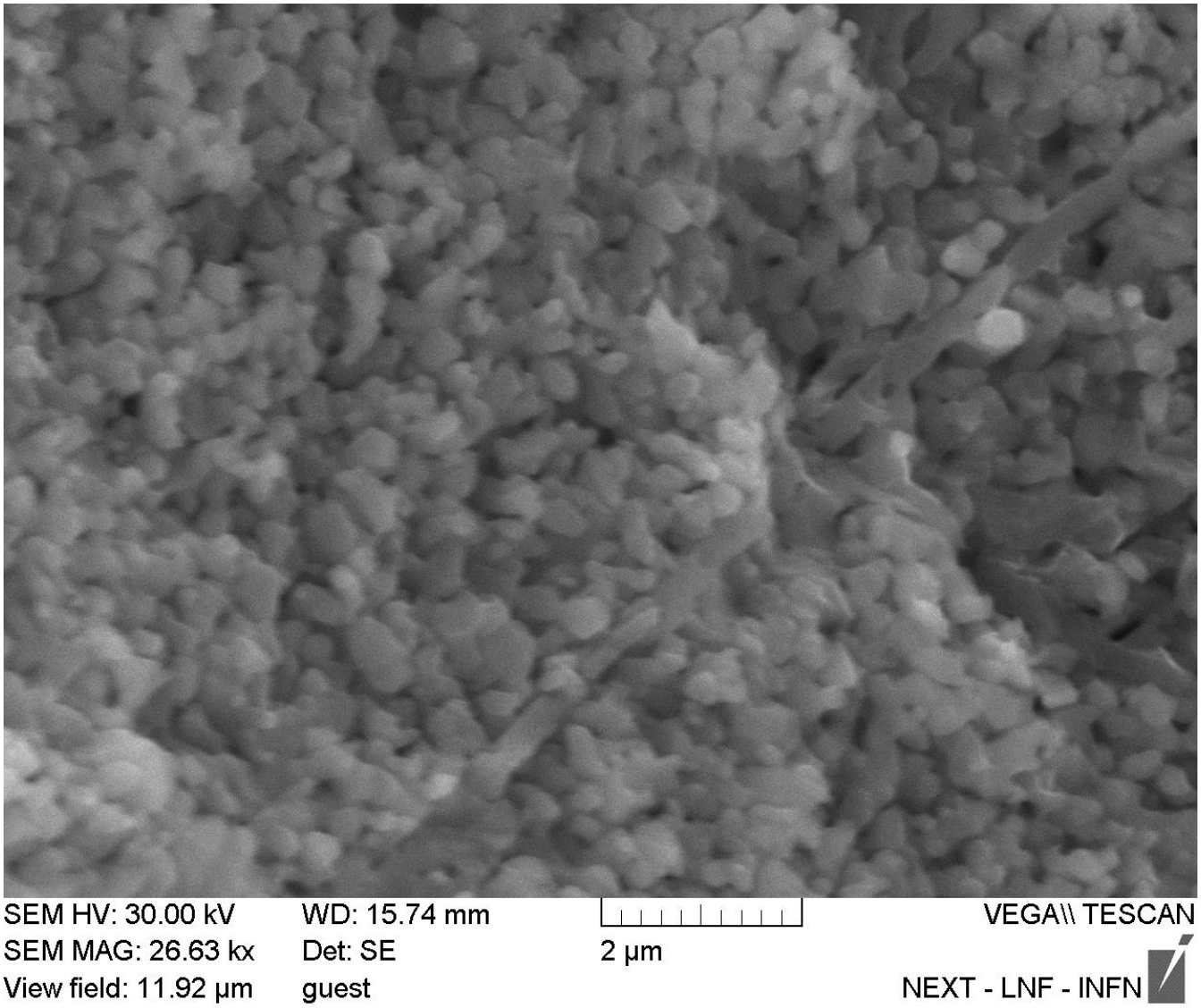


SEM. Wire after removing plastic cover by Joule heating at I=2000mA, 5m.

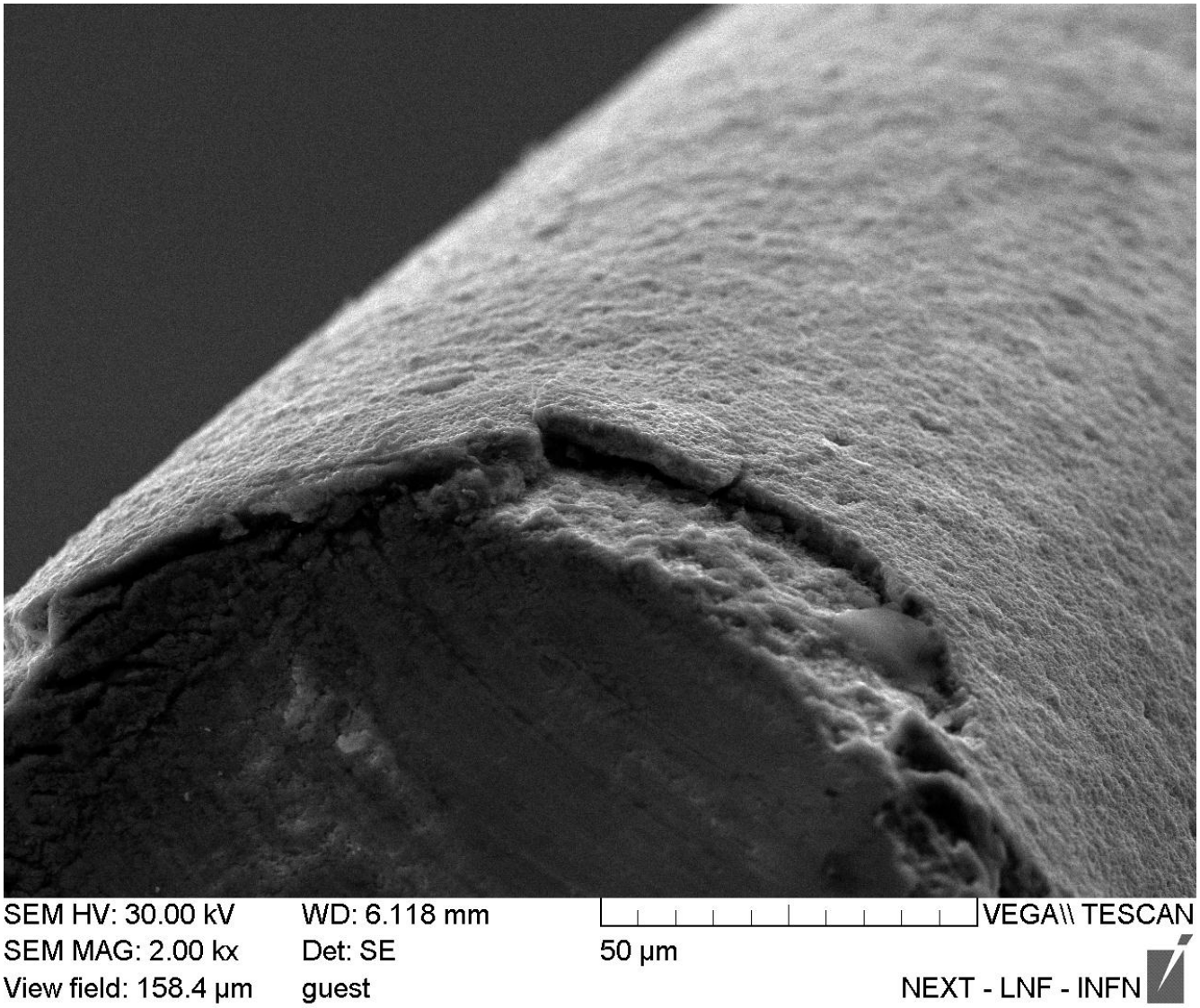
SEM. Details of wires after plastic removal: almost smooth surfaces.



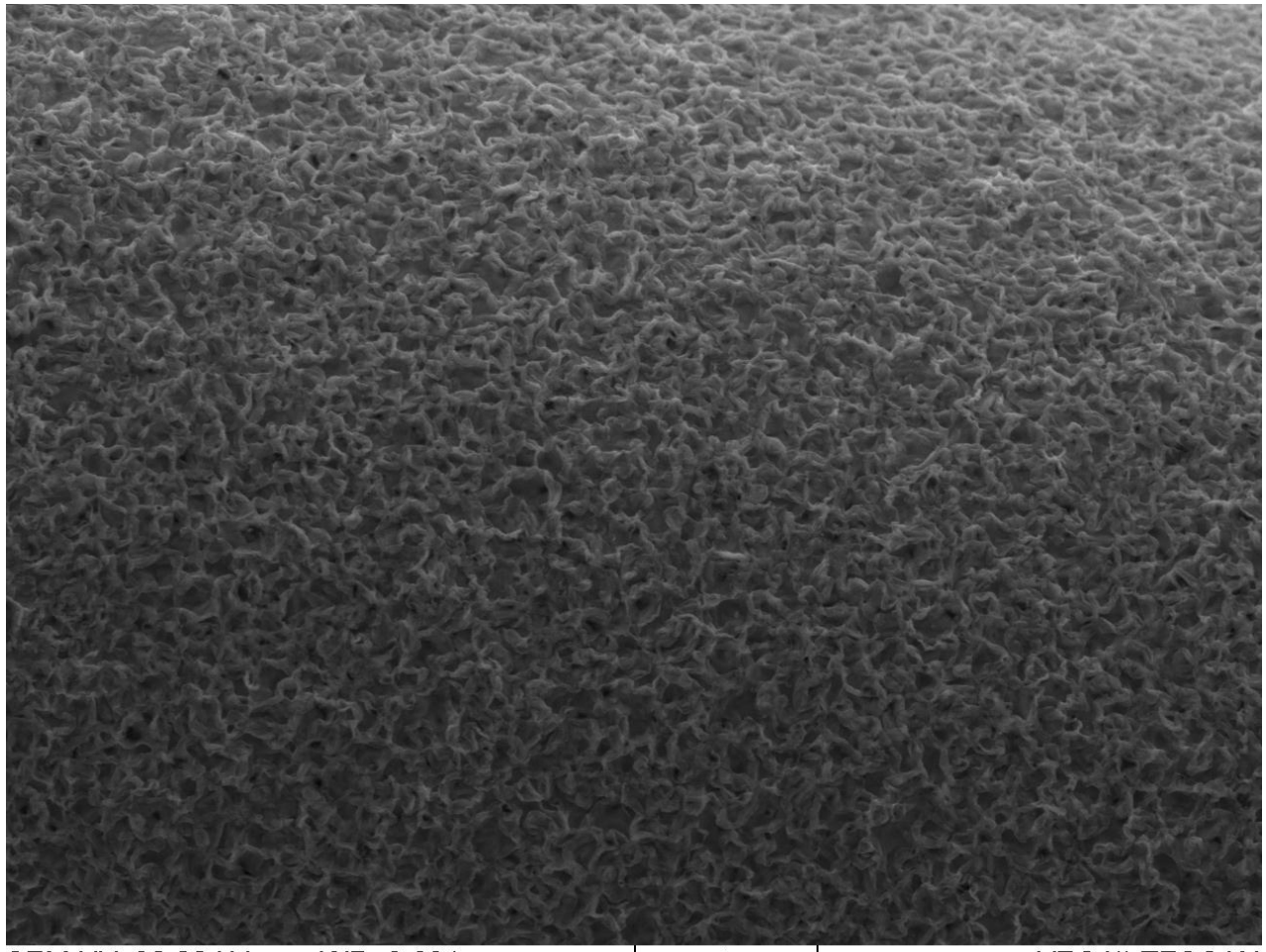
SEM. Wire's surface after heat treatments at I=2500mA, 5m.



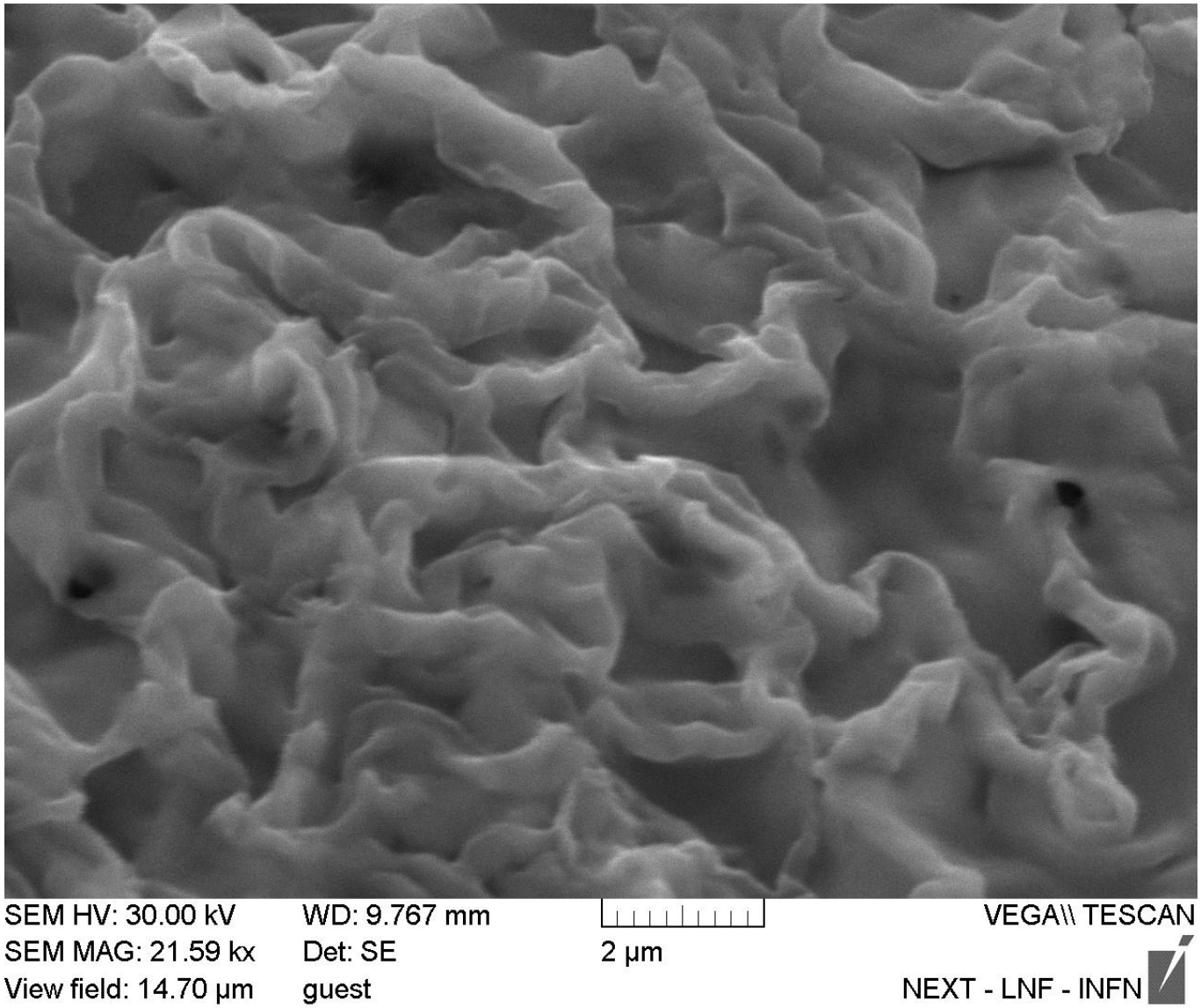
SEM. I=2500mA, 5m. Details of an inner surface at low dimensionality.



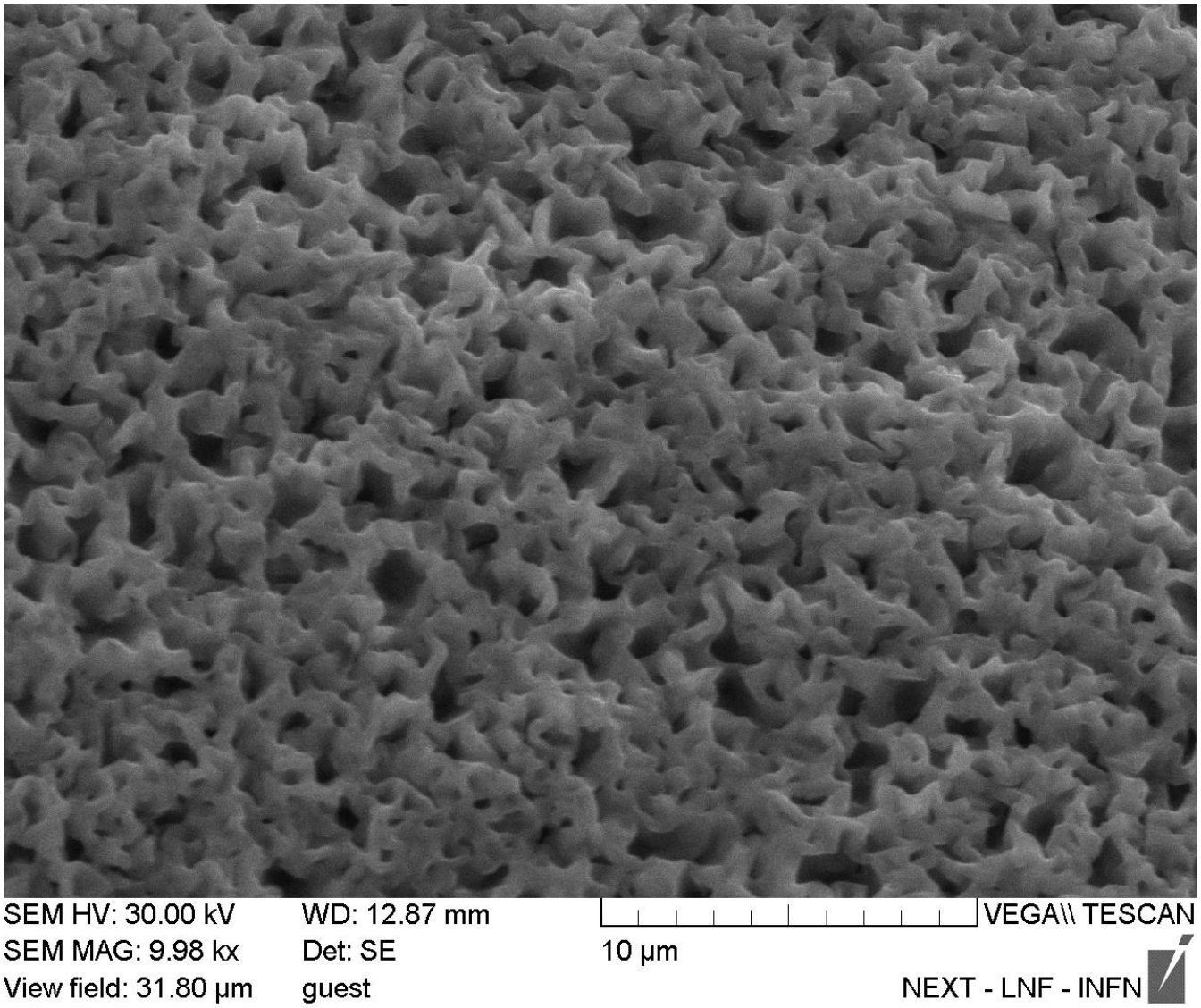
SEM. I=2800mA, 2m. Internal section is unchanged, external modified.



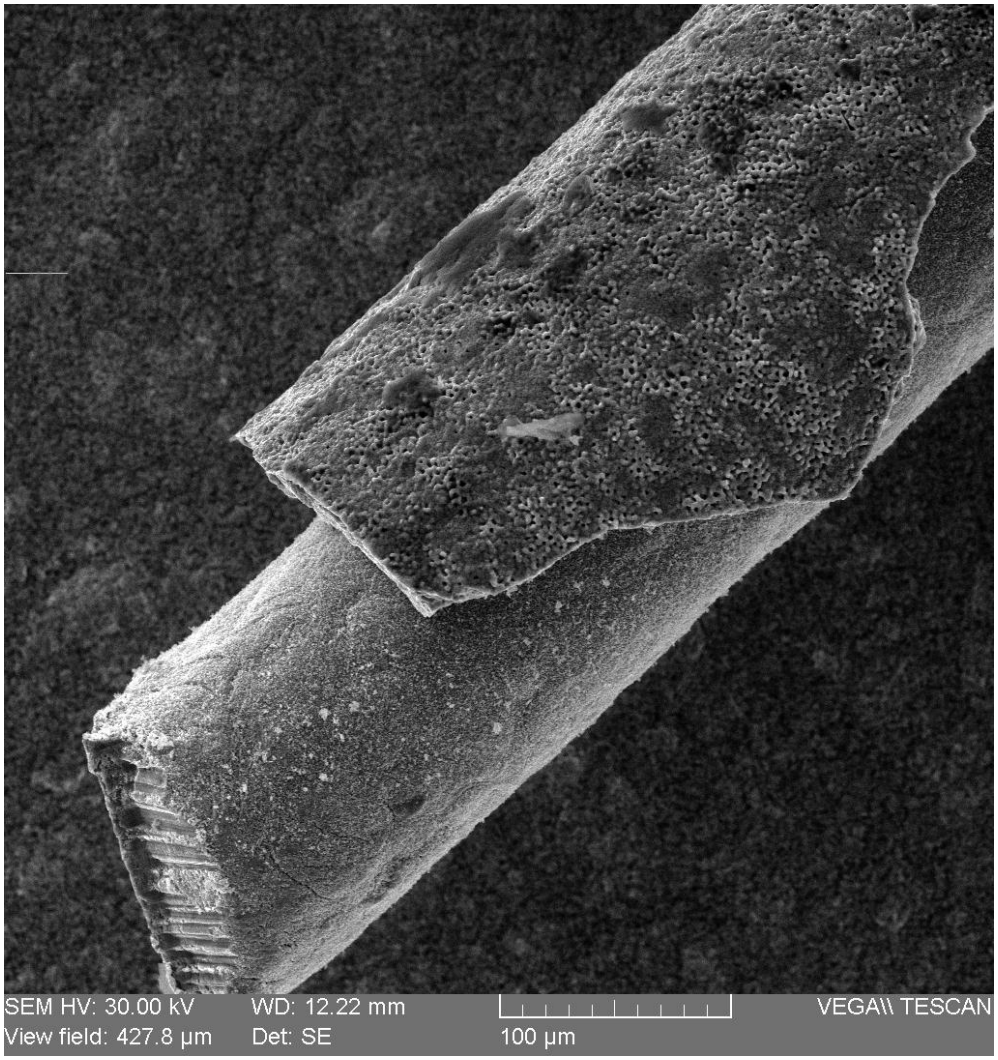
SEM . I=2900mA, 2m. Temperature too-large: re-sintering effect.



SEM. I=2900mA, 2m. Temperature too-large. Details of re-sintering.

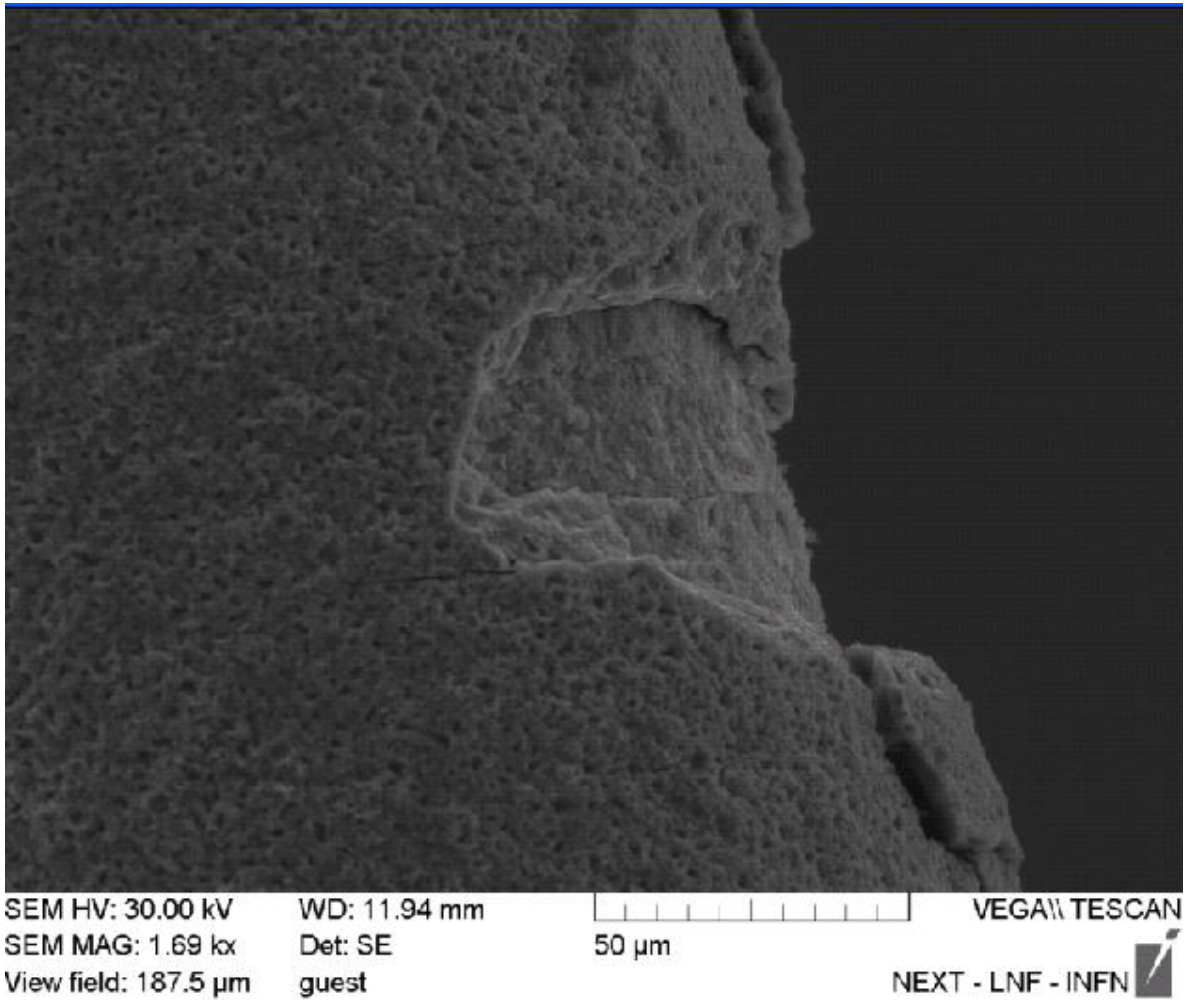


SEM. I=2800mA, 3m. Extra treatments with HNO_3 at 65%, 500s. Strong reduction of Cu.



SEM. I=2800mA, 3m. Extra treatment with HNO_3, 1000s.

Outer surface almost detached from inner.



SEM. I=2900mA, 15s. Details of inner and outer surfaces not detached.

Experimental set up: schematic and real

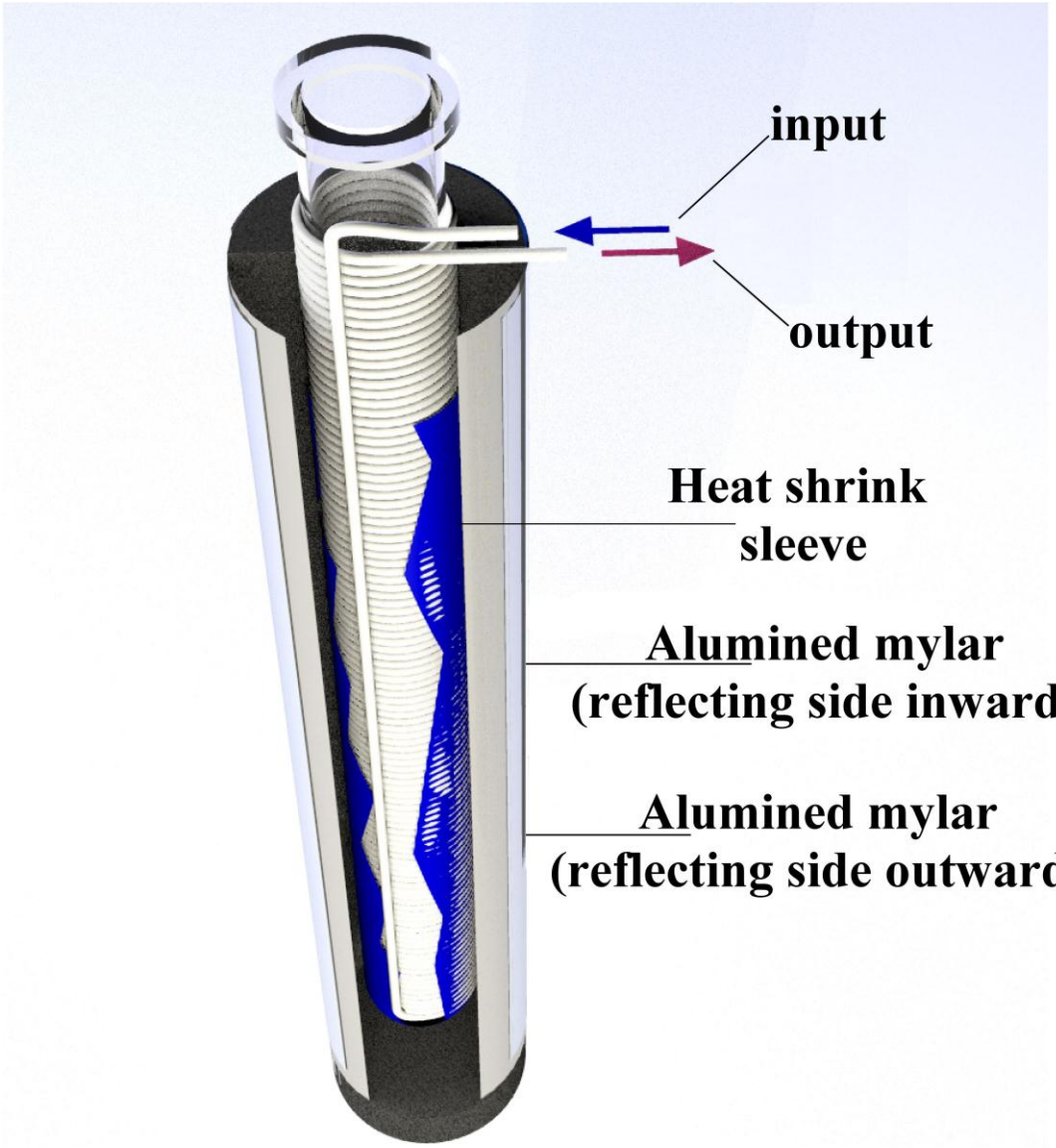
h) The first wall of the pressurised reactor, at high temperatures, is made by shape modified (Vetreria Scientifica Spaziani-Italy) borosilicate glass tube (Schott DURAN-Germany), to avoid problems due to sulphur leakages of usual SS (even type 304 or 316N). The sulphur has deleterious effects on catalytic proprieties of almost any kind of materials. The thickness of the glass wall reactor is large (3mm) and its inner diameter is small (32mm), to allow large pressures operations (10Atm) even at high temperatures of the wall (200°C).

i) **The problems of gas leakages, from the several connections and feed-troughs, up to now, weren't fully resolved.**

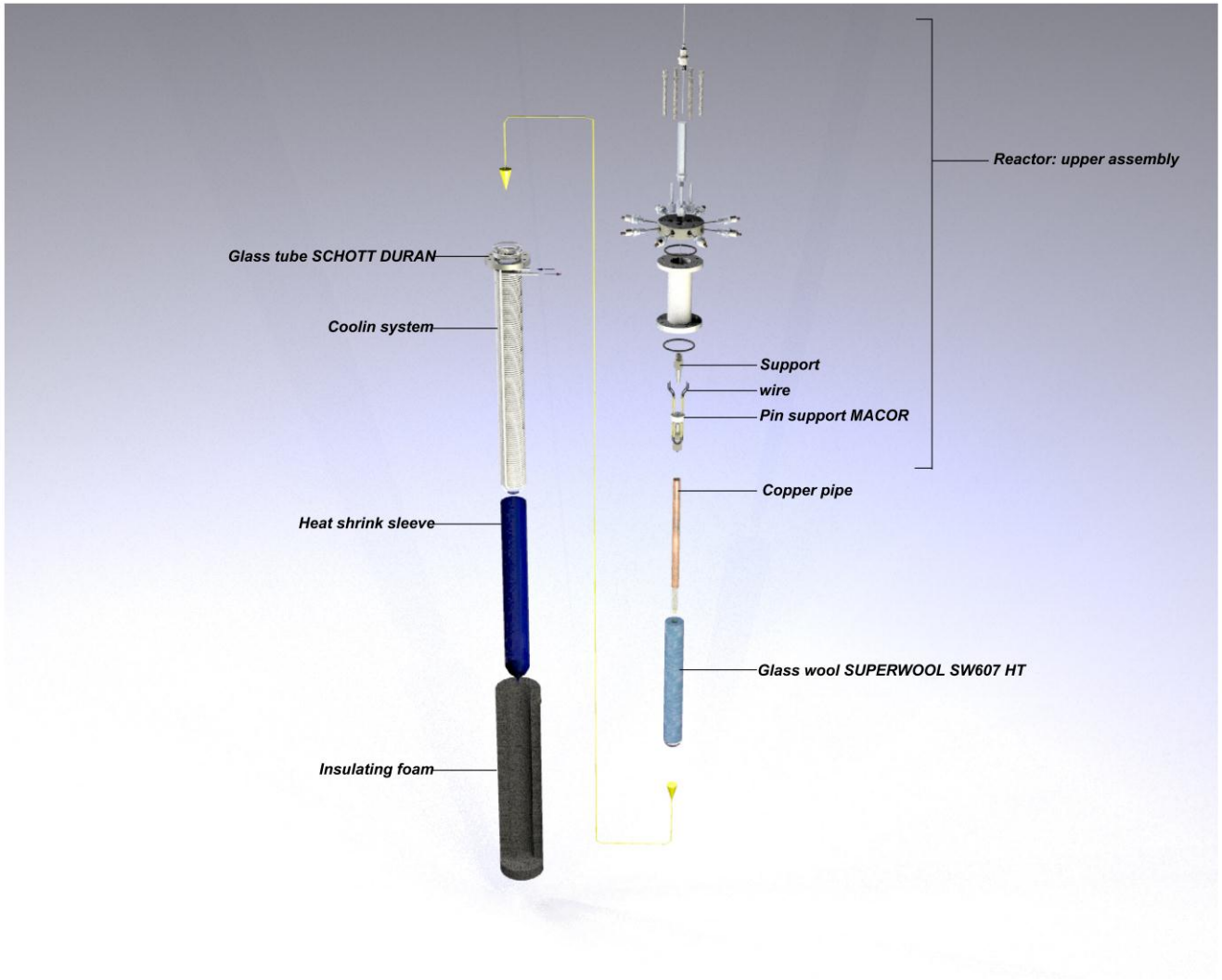
j) **The cooling system is based on thermally stabilised, flux stabilized, tap-water: it is carefully filtered and chemically conditioned to avoid calcium salts precipitation.**

k) **The flux of water is carefully and continuously measured by flow meter. Cross-checks were routinely performed, 3 times/day, by weight/time measurement procedures (indetermination< 0.1%).**

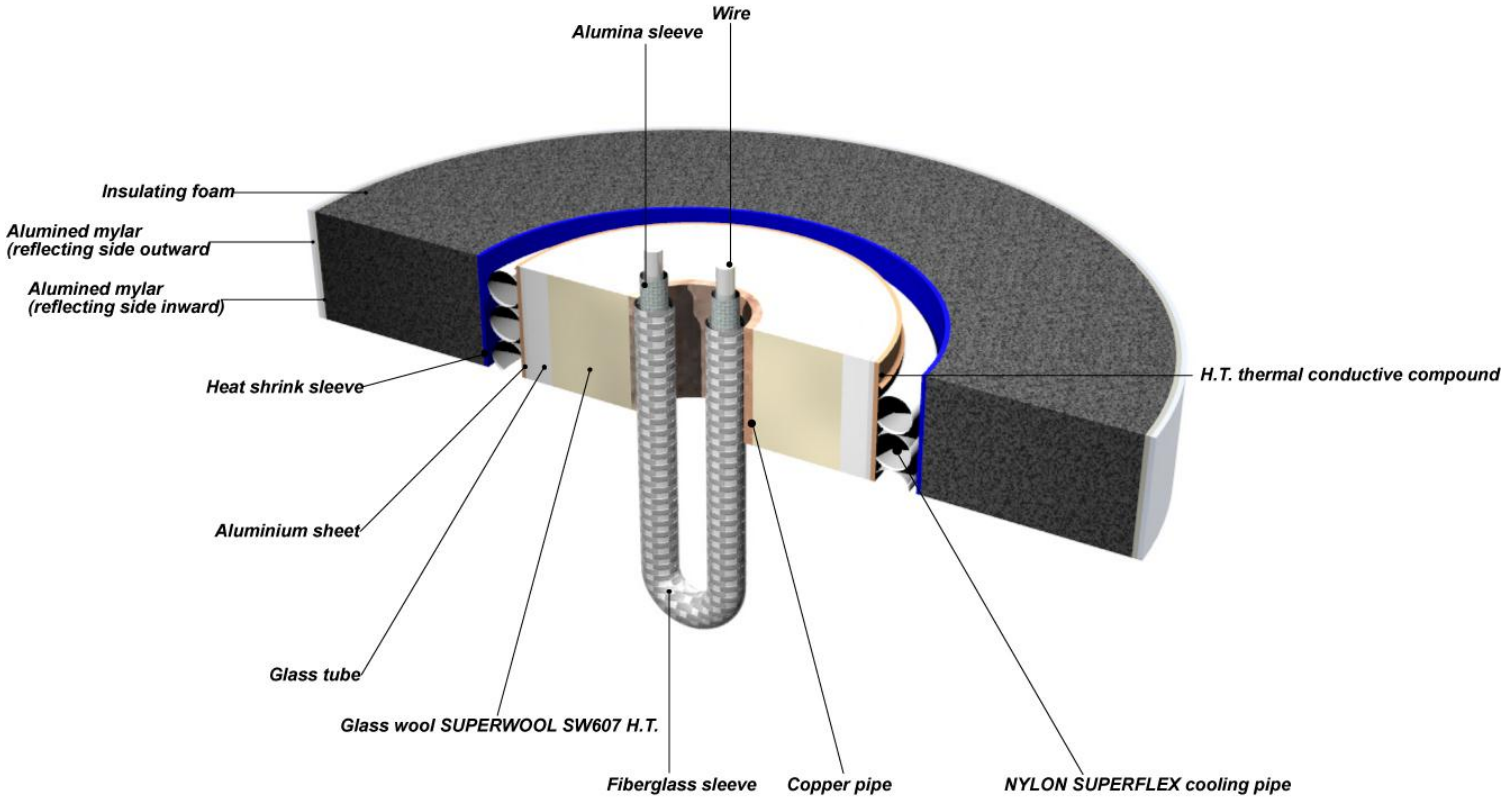
Schematic of assembling procedures of glass reactor, heat exchange system and outer thermal insulation.



Schematic of the multilayer reactor with, 9 m long, cooling system fed by water.

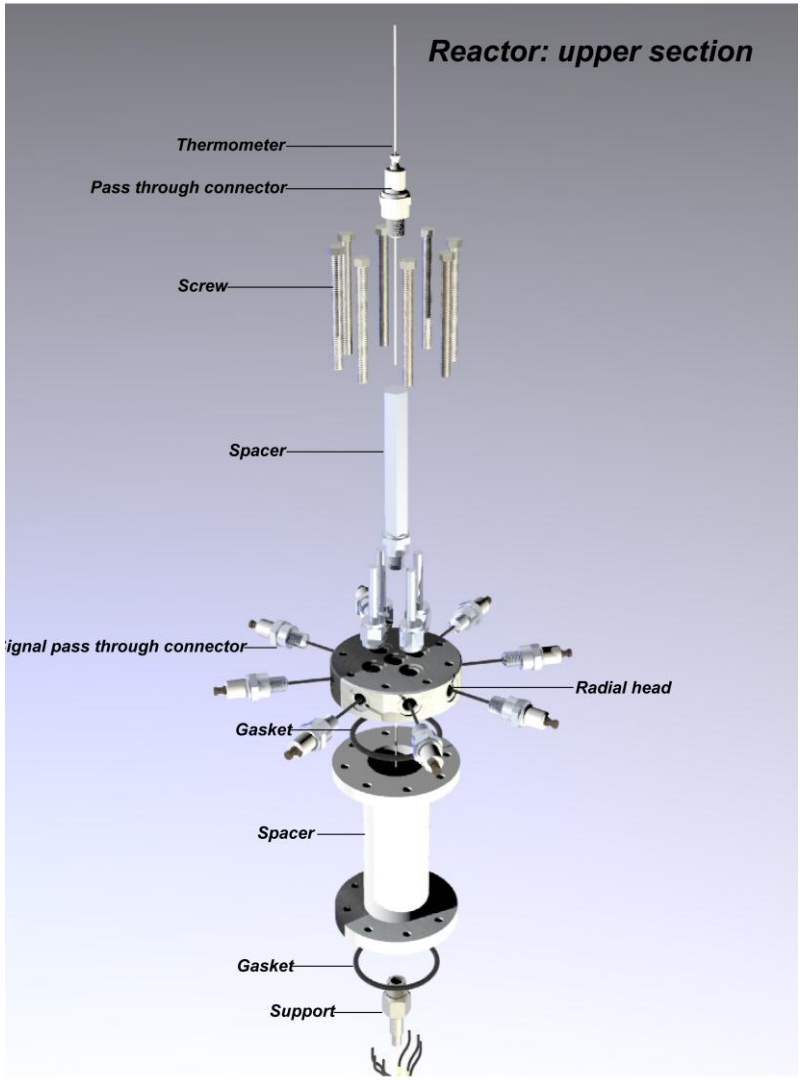


Schematic of each component subsystem. The core of the reactor, i.e. the 3 wires, are IR reflected by Cu tube and thermally insulated by *Superwool SW607 HT* (UK).



Intermediary section of the reactor

Schematic, fully detailed, of head of the reactor.
It is shown only 1 over the 3 wires used.

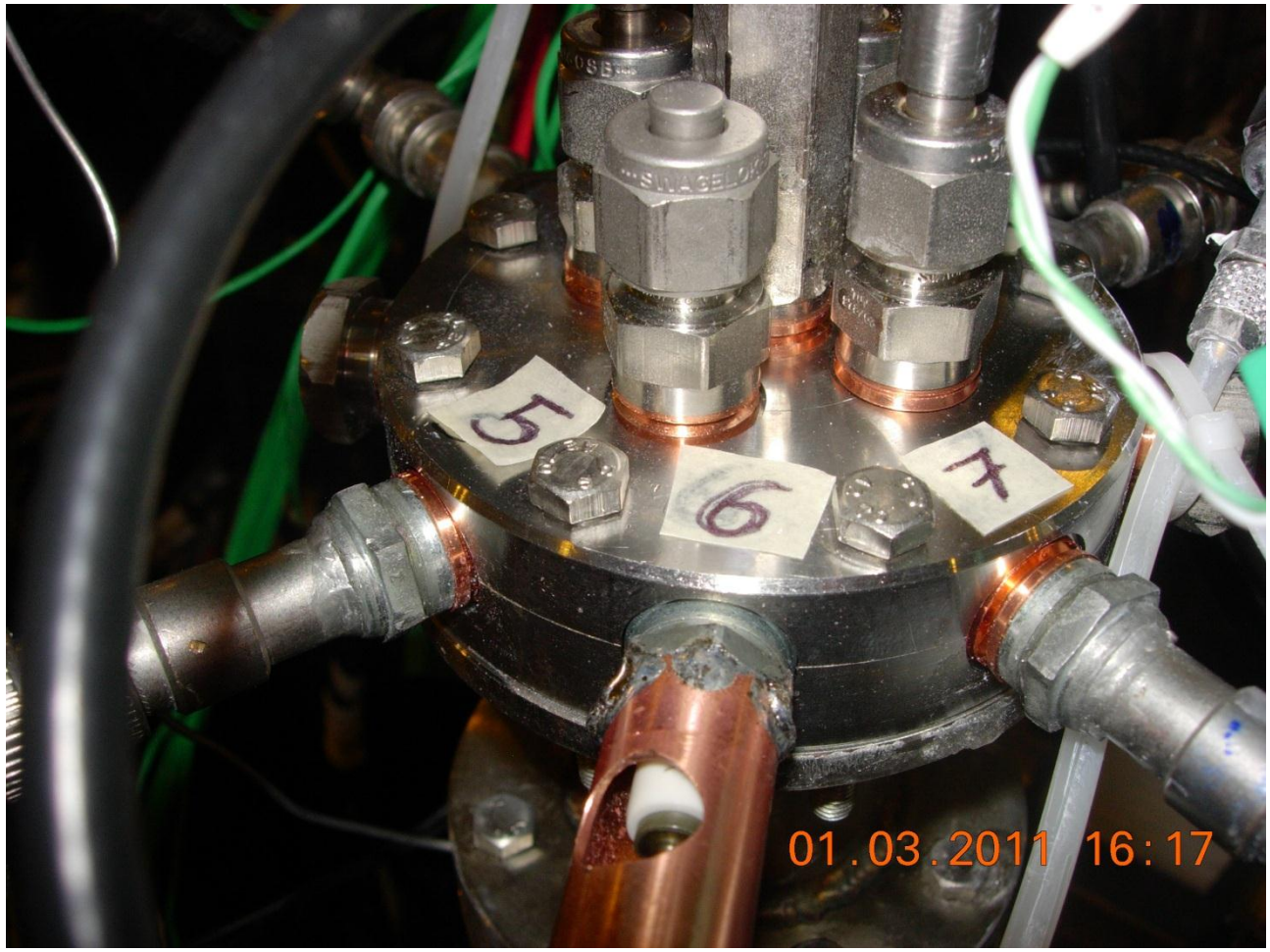


Schematic of head assembly with electric connections

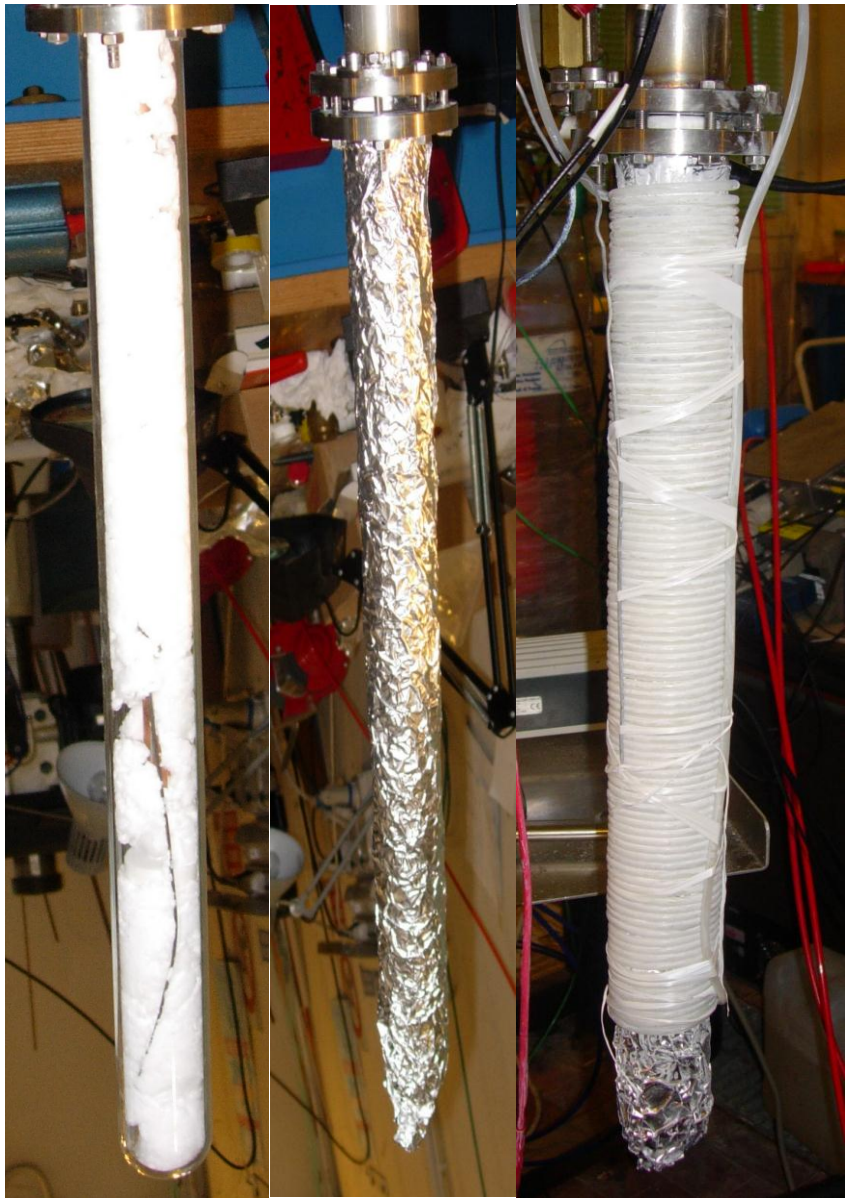
Real assembly: details of "head" with electrical feed-through, under assembling.

***The material of high temperature ceramic insulator, pink colour, is Macor (USA).**
***All the component in SS are kept at low temperatures (<150°C), by thermal contact to room temperatures, to reduce Sulphur "leakages": drawbacks are poor performances (70-75%) of energy recover of the calorimeter.**

***Further work, in deep, is necessary to improve the over-all set-up.**

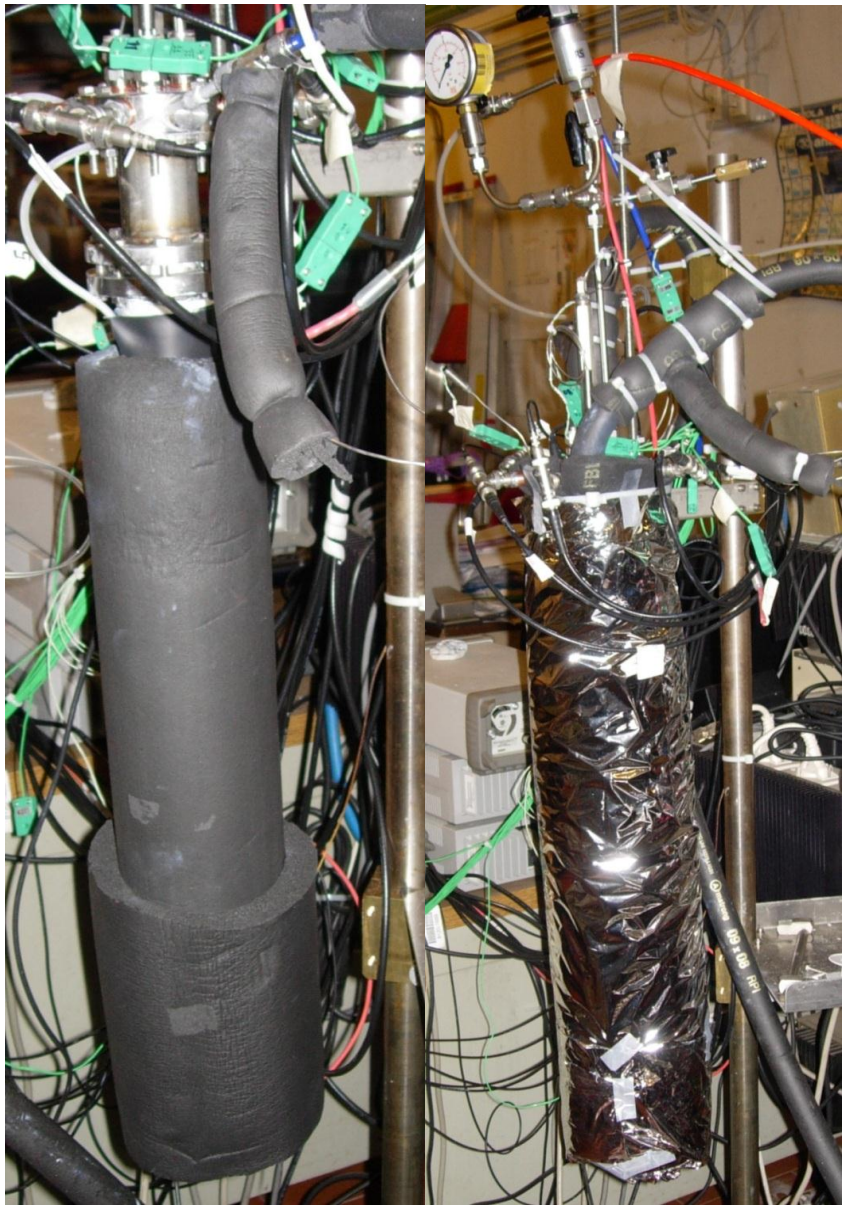


Real assembly: details of head closed assembly with gas tight electrical connections made by modified mini spark plugs (NGK: 5812 CM-6, Japan)

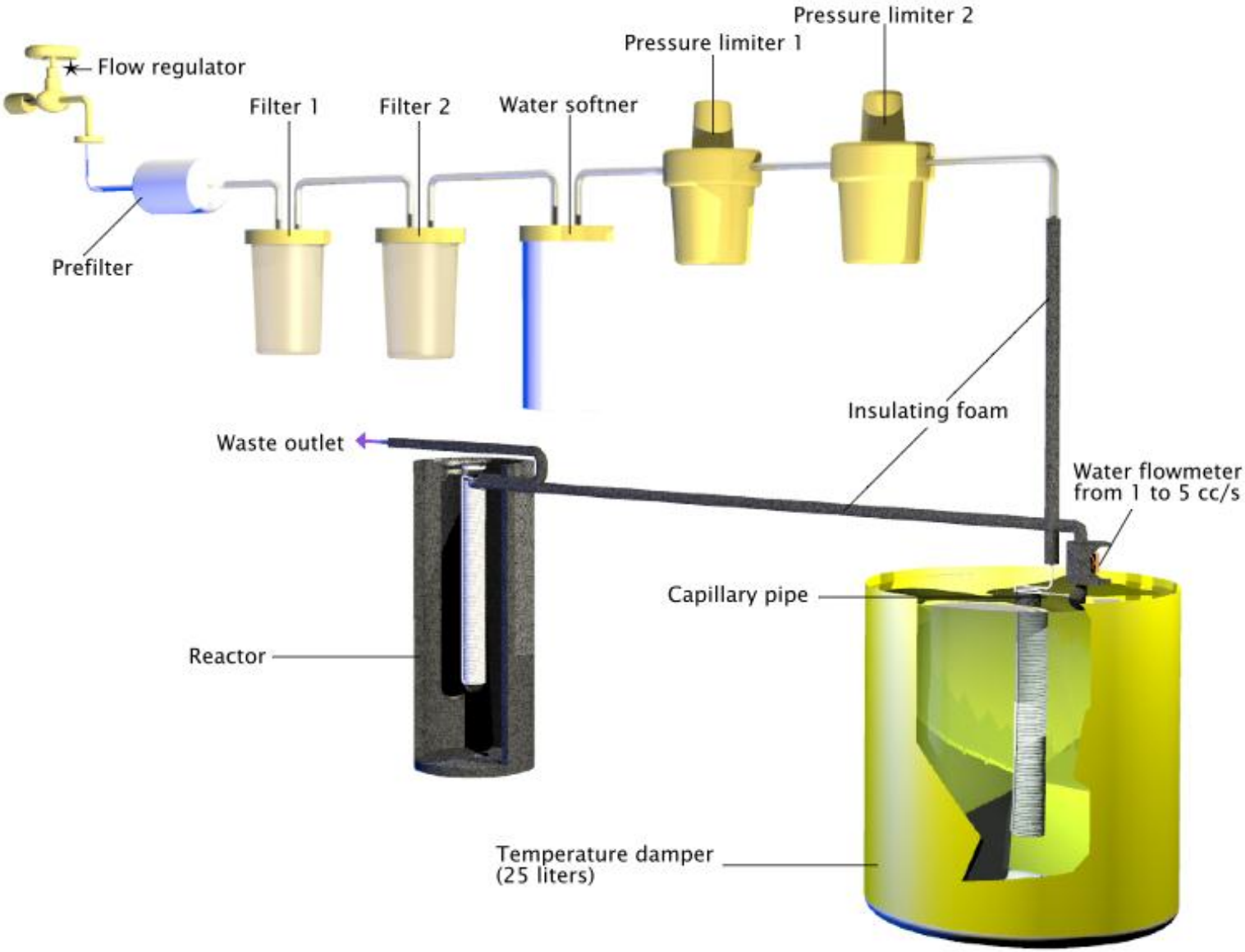


Real reactor: steps 1-3 of assembly.

Real reactor: steps 4-5 of assembly.



Real reactor: steps 6-7 of assembly, final thermal insulation.



Schematic of the cooling system

Active material preparation line-guide

*** The preparation procedure of nano-micro material, in short, was "inspired" by the original procedures developed by Yoshiaki Arata (Osaka University, Japan) group and Collaborators specialised in nanomaterials developing (Tohoku University) since 2002: melt spinning (at 1600°C) and quenching of $Zr_{65\%}$-$Pd_{35\%}$ alloy, selective oxidation of Zr at 300°C to get ZrO_2. In our situation we reached, in some preparations, temperatures close to liquid state of the alloy and subsequently they were cooled in air (more or less quickly). In other words, a low-cost approach. The complex effects of oxygen have to be fully studied.**

Measurement Procedure

a) The measurement procedure is based on our previous, well experienced, method (since 2006), continuously improved about accuracy and redundancy of peak-up. Data acquisition/monitor is based on NI Lab-View system and Agilent ADC-MUX. Key information are on-line elaborated and shown.

b) Inside the reactor, innermost area (inside a Cu tube used for IR reflection), are inserted 3 long (about 80cm each) and thin (Φ= 200μm) wires, U shaped. Each wire is electrical insulated by, double, alumina and glassy sheath.

c) **The composition of the 3 wires are: a) Pt (main reference); b) Constantan thermally treated to produce nano-micro structures (cross reference of the really active one); c) same as b) but with a final coating of Pd (i.e. liquid $PdNO_3$ that underwent thermal decomposition) at sub-micrometric thickness.**

d) **The reactor was filled with inert (He, Ar, Xe, dynamic vacuum) gases and was given power, to the wires, by Joule heating. The output power [4.18*(T_2-T_1)*g/s], recovered by the flow calorimeter, is recorded for several combinations of gas/wire/input power. T_2-T_1 is the usual temperature drop (in °C) at the input and output of cooling system; g/s is water flux.**

e) **At the end, it is introduced H_2 (pressure: 6-8Atm). Some test were performed also with D_2. Occasionally, was introduced air under continuous flow, to "burn" (at high temperatures) possible impurities formed.**

f) **In order to evaluate the different heat conductions (due to different gases adopted) from the reactor centre toward external cooling pipe, are measured the temperatures (by SS screened type K thermocouples) at: centre of the cell, Cu tube surface, main glass tube internal surface.**

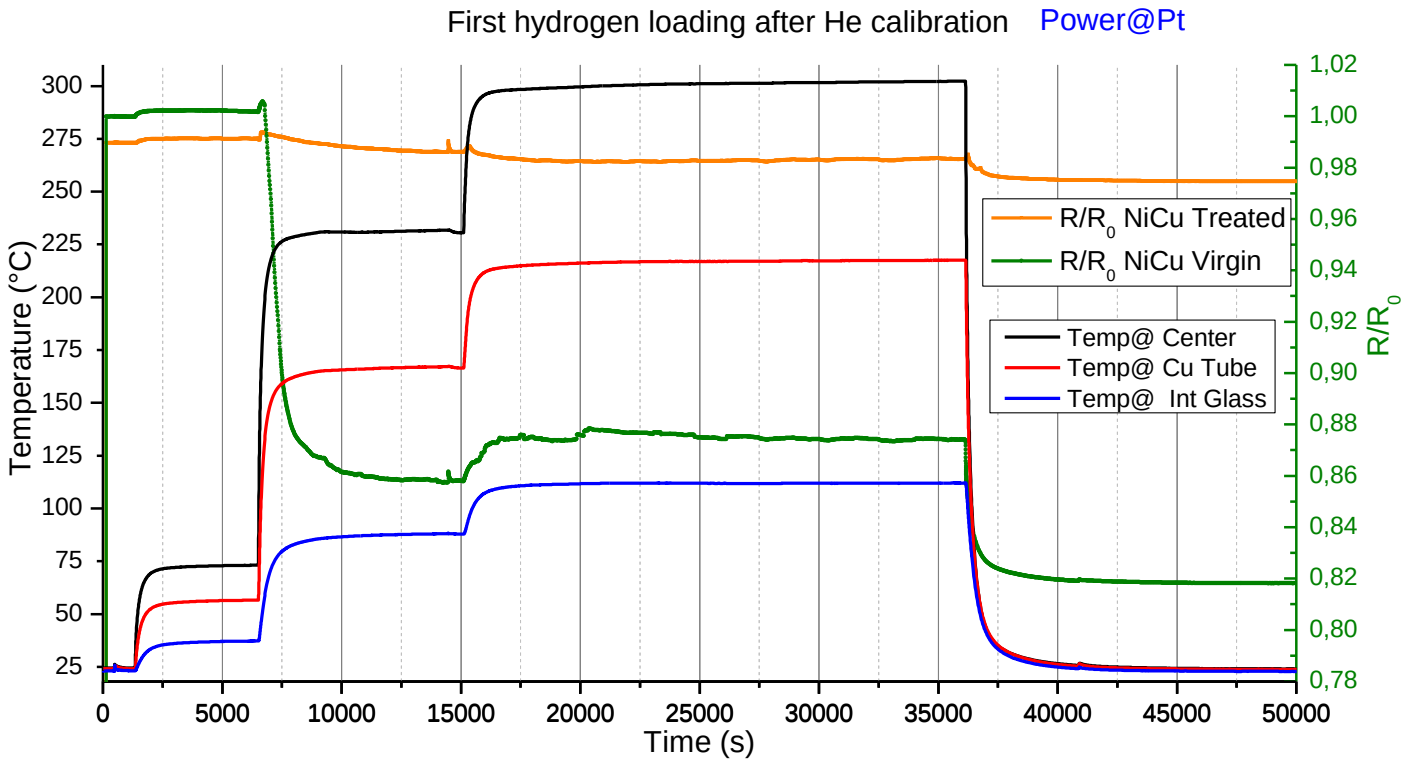
RESULTS

1) **Just after the first H_2 intake, at 8 Atm, starting from 75°C cell temperature, it was observed a decreasing of resistance ratio (R/Ro, with Ro the initial value at room temperature before H_2 intake) of the alloy ISOTAN44 nano-micro structured. Such effect was magnified by temperature increases: at 225°C was reached a value as low as 0.86 due to larger power applied at Pt wire. Further increase of the temperature to 300°C made a slight increase of R/Ro to 0.88 that showed, anyway, a slow trend to decrease at very long times. After cooling down to 25°C, the R/Ro further decreased to a stable value of 0.82, i.e. a decreasing, in total, of 18% of resistivity.**

2) **The constantan that had the surface covered by several layers of Pd showed such effects at very low intensities. It decreased only later on, flowing the time, after repeated loading-deloading cycles and low-high temperatures cycles.**

3) **The effect of resistance decreasing is exactly the reverse of what observed in Pd-H system.**

4) **The effect of resistance decrease due to H_2 absorption was reported also by Szafranski in his paper (ref. 3, H. J. Bauer and F.E. Wagner, 2004) and happened only after large H_2 absorption while, for low H_2 absorption, was measured a slightly increase of resistance. Exactly the same effect was observed in our sample.**



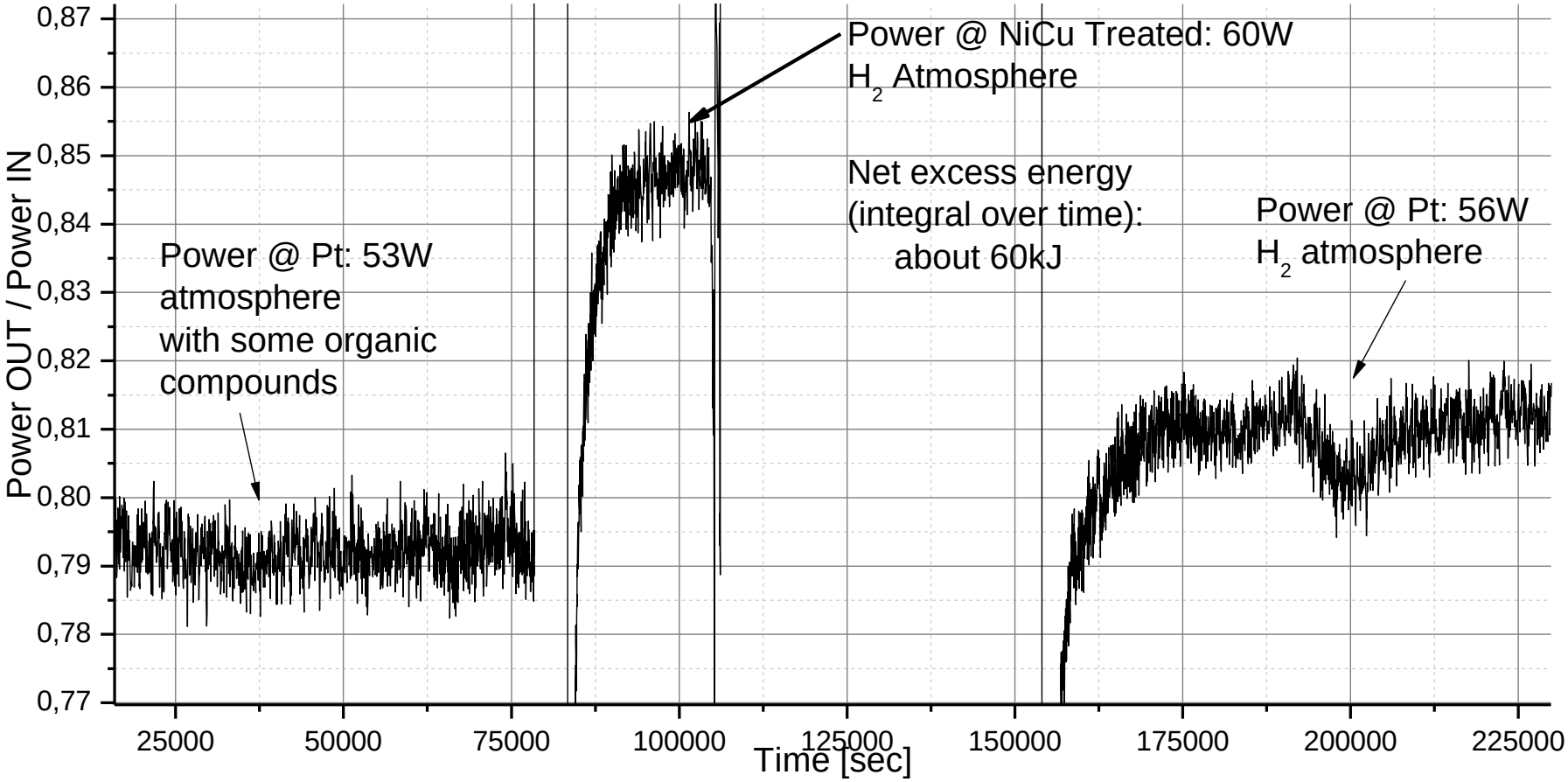
First loading with H_2 at 8Atm. Are reported the R/Ro values for Costantan without extra coating of Pd (virgin; green curve) and coated (orange curve). Moreover are reported the temperatures at the inner side of the cell (black), Cu external surface (red) and glass interior (bleu). The constantan mean temperature is equal to the black curve.

About anomalous heat production, we observed several events were such phenomena happened, for long times (several days) but at low intensities. The phenomenon increased, systematically, when the power was applied to the wires with nanostructures. In other words, the experiment with power on Pt can be considered as blank, although with can't excluded that some anomalous effect, because indirect heating of Isotan, could happen.

At the moment the sensitivity of the calorimeter isn't enough high to can discriminate such conditions.

As further information, previous (short time)experiment, with Isotan 44 without thermal treatments (i.e. only plastic removed), never give anomalous results.

A clear event of anomalous heat, with excess energy over 60kJ, is reported. Taking into consideration just this specific event, and neglecting all the others, considering the amount of material used (about 80cm of wire, i.e. 224mg with Ni=98mg), the integral of the energy is larger than 380eV/Ni atom, i.e. over 95 times the chemical limit of 4eV/atom Ni.


Power @ NiCu Treated: 60W
H2 Atmosphere
Net excess energy
(integral over time):
about 60kJ
Power @ Pt: 53W
atmosphere
with some organic
compounds
Power @ Pt: 56W
H2 atmosphere
Power OUT / Power IN
Time [sec]
0,87
0,86
0,85
0,84
0,83
0,82
0,81
0,80
0,79
0,78
0,77
25000
50000
75000
100000
125000
150000
175000
200000
225000

Further Developments/Comments/Conclusions

a) It was experimental found that even low cost material, like commercial Cu-Ni-Mn alloy (named Konstantan or ISOTAN 44), when its surface is properly modified from the point of view of dimensionality, can be used as material able to produce anomalous heat effects because close interaction with Hydrogen (or Deuterium, but at lower intensity) at high temperatures (>300°C).

b) Moreover, such alloy has intrinsically the propriety of extremely large capability of catalysis in respect to H_2 dissociation.

c) We have found that the amount of anomalous heat increases when the sub-micro structured material is covered by a thin layer of Pd. At the moment the result are of modest entity, perhaps because the geometry isn't optimal.

d) **Moreover, in respect to indirect heat warming, we found that the effect increases when there is a direct flow of current along such material (i.e. electro-migration and/or forced not-equilibrium conditions), in the shape of thin and long wire. Such behaviour was previously found also in experiments using Pd/Deuterium: it can be speculated that it could be, again, a situation where the so-called "Preparata effect" could be realized.**

e) **It is quite interesting, and intriguing, that also a group well expert on nano-materials and production of anomalous heat effects (i.e. Akito Takahashi and Akira Kitamura with co-workers, from Osaka&Kobe Universities and Consultant of Technova Company-Japan), *independently from us and without knowing each-other of the specific tests in progress*, decided to explore an alloy based on Ni-Cu-ZrO_2, dimensionality of the order of 2-10nm (similarity to Pd-Ni-ZrO_2). Their results look really promising (2 reports at this Workshop).**

f) **The effects of other impurities present inside the reactor, at least in our experiments, have to be more deeply investigated.**

g) **Another phenomena that we observed, *after 5 months of experiments*, is the apparent NTC (Negative Temperature Coefficient of the resistivity) behaviour of nano-structured alloy, after interaction with hydrogenated compounds. Anyway, a new experimental set-up, *as simple as possible,* is needed to study such unexpected/interesting effect and rule-out any uncontrolled interference.**

h) **More systematic work is necessary, especially for material preparation and characterization, specially SEM and (hopefully) TEM analysis.**

i) **In conclusion, the Cu-Ni alloy, at nano-μ sizes, interacting with hydrogenated materials at high temperatures (>300°C), could be a simple and low-cost candidate for "new" energy production, over the values of usual chemistry (4eV/atom). Further efforts on experimental activity could, soon, pay-back.**