

Cu-Ni-Mn alloy wires, with improved sub-micrometric surfaces, used as LENR device by new transparent, dissipation-type, calorimeter.

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Abstract -- Starting in February 2011, we studied the feasibility of new Nickel based alloys that are able to absorb proper amounts of Hydrogen (H₂) and/or Deuterium (D₂) and that have, in principle, some possibility to generate anomalous thermal effects at temperatures >100°C.

The interest in Ni comes in part because there is the possibility to use H₂ instead of expensive D₂. Reports by F. Piantelli (since 1992), G. Miley (about 1995), 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 and could help the understanding of the phenomena involved (nuclear origin?) because use of such isotopes.

I. AN OLD ALLOY USED FOR NEW PURPOSES

Because theoretical considerations, and thank also to some sentences reported in a paper (on catalysis) not related to LENR studies (Ref.1: S. Romanowski et al.; Langmuir 1999, 15, 5773), we decided to explore the possibility to use the “large family” of CONSTANTANS alloys as starting material that could fit our purposes. One of the merit factor was, according to use, the ability to decompose H₂. One of the Constantans (Ni₃₇Cu₆₃), among the materials studied in the Ref.1, has the highest value (i.e. 3.2eV; in comparison, pure Ni and Pd have respectively values of 1.74 and 0.42eV) of such decomposition. Moreover, even with large changes (factor of about 2) in the relative atomic amounts of Ni in respect to Cu (i.e. from 0.37 to 0.62), the decomposition values remain almost constant (from 3.16 to 2.86eV).

We focused on a commercial (low cost) material, called ISOTAN44, nominal atomic composition Cu₅₅Ni₄₄Mn₁, developed many years ago by Isabellenhutte Heusler, GmbH, KG-Germany. The ISOTAN 44 was selected according to the following, overall, considerations (as pointed out by us at the “X International Workshop on Anomalies in Hydrogen-Metal Systems”, Pontignano-Italy, April 10-14, 2012; Ref. 2):

A. Measurable diffusion coefficient of Hydrogen, in even the pure (not alloyed) elements, i.e. Cu and Ni, at high temperatures: Cu=10⁻⁶cm²/s at 200°C, 10⁻⁴cm²/s at 700°C; Ni= 10⁻⁷cm²/s at 200°C, 10⁻⁶cm²/s at 350°C. In comparison, the (good) values for Pd are: 10⁻⁵cm²/s at 200°C, 10⁻⁴cm²/s at 420°C; at 600°C were reported values as large as 8*10⁻³cm²/s, but not reproducible.

B. Lower cost, overall, even considering the procedure to “build” nano-structure at the surface, in respect to Pd, very expensive precious metal.

C. Very good mechanical properties, especially in respect to aging effects due to cycles of both low->high->□ low temperatures and H₂ absorption-desorption: the sample of our long time lasting experiment was working for over 7 months and only after such long time of operations, we observed serious 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 77K and 300K under 1GPa pressure of H₂. We could think, only, that high temperatures have beneficial effects on reducing brittleness problems. Moreover, we never made experiments at 77K.

D. Extremely large values of measured catalytic power (ΔE, in eV) in respect to the dissociation of H₂ (Ref. 1), 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. The possibility, at least in principle, to produce *nano-micro structures* at the surface, or even deeper into the bulk, because *selective oxidation of Cu in such alloy* at high temperatures (650-1050°C). Both segregation of pure Ni among to CuO_x and cooling rate are key aspects of the preparation to be studied in deeper details.

Our studies, very exploratory, were devoted to finding simple, and reliable/reproducible procedures to get these kinds of structures. Experiments with the selected material were operated for time as long as possible: "strength" and aging tests.

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

Starting at January 2012, we developed completely new procedures of preparations, which were tested in June 2012 with a new, transparent, dissipation type, "calorimeter".

II. SAMPLES PREPARATION (PROCEDURES USED FOR THE EXPERIMENT UP TO MAY 2012). SIMILAR MATERIAL DEVELOPED IN JAPAN.

In our exploratory preparations/tests we used "standardized" wires: ("nuked") $\Phi=200\mu\text{m}$, $l=105\text{cm}$. Initial values of weight (e.g. 307.4mg), diameter ($\pm 1\mu\text{m}$) and resistance (e.g. 17.16 Ohm) were carefully measured.

We point out that, although very promising (expected) results with pure Constantan, in our explorative test (2-3 days of operations each, time span from February to June 2011) under Hydrogen atmosphere, we NEVER got any type of anomalies (like changing of resistance) with wires with temperatures as large as 900°C under the following status: (1) as obtained from the Company (we call them ultra-virgin); (2) with the surface cleaned-up from the plastic protection (plastic removed by burning up to 600°C in air); (3) acid etching of wire after burning at 600°C.

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).

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

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 dimensions. The role of O₂, because free air treatment, is quite important. The wire temperature, in some tests, was even larger than 1000°C (rough evaluation by colour temperature; the melting point of pure Cu is 1083°C).

The quality of wire produced by this method was evaluated by SEM observations. According to us, as smaller were the particles at the surface and larger the total fraction in respect to the whole wire, as better was the procedure of preparation.

The "best material" that we were able to produce, at the end of July 2011, using thermal treatments were put in our (high resolution) flow calorimeter.

As previously noted, such material was extensively studied, both in Hydrogen and Deuterium atmosphere using a very accurate flow calorimeter (indetermination <2%). The time of experiments was really long (over 10 months) and only at the end the damages were so heavy to prevent further reliable interpretation of the experimental results. As quoted before, they were discussed, deeply, during the *X International Workshop on Anomalies...* on last April 2012.

We were very happy to know that also Akito Takahashi and Akira Kitamura (and Colleagues), respectively from Osaka and Kobe University (Japan), studied in secret (like us), an alloy of Ni-Cu (at nanometric size) dispersed in an inert matrix of ZrO₂. Such work was performed by them among a collaboration with the Research Group of Toyota Company (Technova). We got some information, by A. Takahashi and A. Kitamura, since January 2012, about promising results on a specific Ni-Cu-ZrO₂ alloy. Such material is a further development of the nano-material Pd_{35%}-ZrO₂_{65%} developed by Yoshiaki Arata (Osaka University) since 2005.

Such "short information" came because I was invited to give a Review Talk, on Anomalous effects in LENR studies, at the WSEC2012 Conference (World Sustainable Energy Conference 2012) organized by the ISEO (International Sustainable Energy Organization). The ISEO is an ONG linked to several not-politic Organizations (UNESCO, WHO, ILO, WWF, ...) connected to United Nations at Geneva. Obviously, I requested that everybody involved in LENR studies, worldwide, communicate the most recent and interesting results to include in my talk.

The overall behaviour of Ni-Cu alloys, in respect to Hydrogen and Deuterium absorption, and the amount of anomalous heat detected, were, in several aspects, similar.

Such kind of evidence reinforced our intention to develop a better material, keeping the Ni-Cu composition "constant". In other words, our efforts were devoted to improve the amount of active material at low dimensions (<<100nm) and, at the same time, avoid the adverse effect of "leakage" of the smallest particle from the surface.

III. NEW TRANSPARENT, DISSIPATION-TYPE, "CALORIMETER"

By the end of May 2012 we were able to produce sub-micrometric materials, with nominal overall performances several times better than the best material produced at the end of July 2011, with enough good reproducibility about preparation procedures.

The new method, although started from the old one in some key aspects, was really revolutionary about the practical parameters of: mechanical stability (no “leakage” of the best material from the surface), percentage of material at small dimensions. Such last parameter increased from 1-2% up to about 30% of the whole material.

Such big improvements were obtained because large economical (and man-power) help of an Italian Company that “believed” in our previous results. We were able to design, and achieve, specific electronics and mechanical set-up to produce such kind of sub-micrometric wires.

Moreover, because one of our goals was to see, by naked eyes, if the wire was really stable about the leakage of “good” materials even after several cycles of low-->high-->low temperatures and Hydrogen loading (or even de-loading!), we build a *new transparent reactor* with borosilicate glass (Schott DURAN) of large wall thickness to withstand enough large pressure drops (up to 8bar, at wall temperatures up to 250°C).

For the calorimetric measurements, we adopted the simplified approach to measure the external glass wall temperature. Taking into consideration the temperature of interest, i.e. $T_{\text{wall}} > 100^\circ\text{C}$, the main channel of heat exchange to the environment is radiation of heat. In other words, it can be used the simple formula of Stefan-Boltzmann law:

$$P_{\text{out}} = 5.67 \cdot 10^{-8} \cdot (T_{\text{wall}}^4 - T_{\text{room}}^4) [W/m^2]. \quad (1)$$

In such formula the temperatures T are in K.

Calibrations were made using our usual procedure to add an inert wire, very close to the “active” one, and make several measurements. In the specific new set up, the wires were parallel, alternatively and helicoidally shaped, 22 turns. They were changed the input power, used different gases (He, Ar, Vacuum), fed the electric power alternatively to the inert and “active” wires.

Because in our real experimental set-up the geometrical dimension of the cell is constant (glass tube, external diameter 40mm, internal diameter 34mm, overall length of 280mm (central active length of 100mm), we can make a calibration curve just dividing the formula (1) by the input power.

IV. RESULTS WITH NEW WIRE

At the beginning of June, 2012 two wires were produced, both with the same nominal procedures.

One was used few days later to the experiment, the second one was just put inside a HDPE envelop and kept closed at Room Temperature (RT). We called the experiments: [a] wire#1 (started 06 Jun, 2012); [b] wire#2 (started 10 July, 2012).

The main improvements in respect to previous procedure of fabrication, according to SEM observations,

were the multilayered structures and total number of such layers extremely large: close to one thousand. The thicknesses, of such multi-layers, were in the range of 20-100nm.

The mechanical stability, against leakage of sub-micrometric materials, was largely improved.

The primary experimental procedures and results are listed as following:

1.) In order to use simple parameters easy to be managed by calculations, we adopted the usual term of R/R_o . R_o is the initial value of resistance at RT, i.e. 23.5°C (in that calibration), in free air atmosphere, inside the reactor. With our wires we measured a value of resistance of 16.9684 Ohm and 57.4394 Ohm, respectively for active and Ni-Cr wires. The measuring currents were just 4mA, to avoid self-heating of the wires.

2.) First of all, were made calibrations by inert gases, with power of 5, 15, 30 and 48W applied to the inert wire. The maximum internal temperature of the chamber was of the order of $180\text{--}220^\circ\text{C}$, depending on the gas composition. Some tests, as cross reference, were made also on active wire. Using the values of temperatures measured outside the glass cell (and ambient temperature) it was possible to evaluate the power exchange constant of the small reactor.

3.) After adding a H_2/Ar mixture (75/25 ratio) at 7 bar of total pressure, and using as monitor parameter the resistance of both the active and inert wires, it was given power (48W) to the inert wire. It was found that when the temperature inside the reactor was larger than 125°C , the resistance ratio of active wire, after a very limited increase (to 1.02), dropped to 0.92 in 2500s. Later on, in about 100000 sec, the R/R_o decreased to 0.88. *We observed a correlated increase of the “anomalous excess heat” (although quite unstable) with the R/R_o decreasing.* The temperature inside cell was about 180°C .

4.) After 103000 sec from the beginning, we stopped the power to the inert wire and allowed the reactor, and the wires, to cool to RT. The R/R_o value of active wire decreased to 0.80.

5.) Just after that, we give the same previous power to inert wire and after others 150000s from the interruption we measured an R/R_o value of 0.867. The anomalous excess power increased further, in a way that, at a first observation, *depends mainly on the time lasted and not to the R/R_o value.* The instability of excess power, *if there weren't other uncontrolled parameters to fake it*, had values quite large and was correlated to the small oscillations ($<1\%$) of R/R_o values.

6.) We observed that the instabilities of room temperatures (usually $23\text{--}27^\circ\text{C}$) “helped”, in some aspects, the anomalous heat production, because, speculatively, introduced some non-equilibrium conditions. *In other words, in order to avoid misinterpretations of the results, after proper long times, the values of room temperature were the same at the starting while the anomalous heat increased over time.*

7.) Among others, the positive effect, of long time lasting under Hydrogen gas, was observed also by the A. Takahashi and A. Kitamura group and reported at the

Pontignano Workshop last April 2012. According to them, under their experimental conditions, constrains and materials, in 2 weeks of experiments the anomalous excess power slowly increased from 0 up to 3W.

8.) We observed that the minimum cell temperature to stop the anomalous heat is around 120°C, i.e. similar to the first “loading” temperature (i.e. 125°C).

9.) After 330000 sec from the first H₂/Ar intake, the power was given to active wire.

10.) We observed a further increasing of anomalous power that, if there are no mistakes around, was about twice (i.e. absolute value of over 10W) of that detected when the power was applied to inert wire. The R/Ro value, after initial increasing, stabilized to 0.808.

11.) A possible explanation was that the local temperature of active wire, because Joule heating, was larger than that when the power was indirect. A very rough valuation of temperature is the range of 350-400°C, in respect to about 200°C with indirect heating.

12.) If the consideration at point 11) is correct, we can think that the reaction, apart some temperature threshold, has a *positive feedback with increasing temperature*. A similar effect was found by: our self (with the old wire, and experiment, up to may 2012); A. Takahashi and A. Kitamura group with Ni-Cu-ZrO₂ powders. Among our experimental activity, on 2010, with a pure (50micron diameter) Ni wire, surface nano-coated with several different elements, we measured the best excess power at wire temperatures as large as 900°C.

13.) After 360000s from the H₂/Ar gas intake, the power was switched off: the R/Ro, at RT, drop to 0.71. In other words, the direct heating (electro-migration phenomena) improved largely the loading, and then the anomalous power.

14.) After 410000s from first H₂/Ar intake, we made vacuum and added H₂ at 100% concentration.

15.) The results were similar to H₂/Ar gas and even better about anomalous heat production.

16.) We can't discriminate if the further improvements of performances were due to effects of pure H₂ or just time lasted under active gas.

17.) After another week of miscellaneous test, we decided to de-load the wire from H₂ absorbed, to be sure that the resistance reduction observed was due to a real absorption and not to a variation of resistance due to the reduction of oxides (by H₂) at the nano-particles surfaces.

18.) To get de-loading we put the cell under dynamic vacuum and increased the temperatures.

19.) After several hours, we get the original starting value of R/Ro at 1: *the test was fully successful*.

20.) We reloaded again the wire and get behaviour of R/Ro decreasing and anomalous heat not too different from the first cycle.

21.) Again we de-loaded the wire from H₂ to make experiments with Deuterium gas. This time the final value of R/Ro was 0.93 and not 1, as expected. We supposed that some H₂ was stored some-where in the lattice.

22.) After D₂ intake, we increased, as usual, the temperature by power to the inert wire. The absorption was really of small amount.

23.) We observed, for the first time in our

experimentation with such kind of materials, some X (and/or gamma emission), coming-out from the reactor during the increasing of the temperature from about 100°C to 160°C. We used a NaI(Tl) detector, energy range 25-2000keV used as counter (safety purposes), not spectrometer. Total time of such emission was about 600s and clearly detectable, burst like.

24.) About thermal anomalies, we observed, very surprising, that the response was endothermic, not esothermic. The second day the system crossed the zero line and later become clearly esothermic. Similar effects were reported also by A. Takahashi and A. Kitamura.

25.) After about 350000s from the beginning of D₂ intake the temperature abruptly increased and the wire was broken. We observed that the pressure decreased, because some problems to the reactor gas tight, but at times of 80000s before. The SEM observations showed fusion of a large piece of wire. The shape was like a ball. Further analyses are in progress.

26.) Starting from July 10, 2012, we used the second wire (#2), stored in the plastic bag.

27.) In the meanwhile, we improved the overall detection of external temperatures and added 3 other thermometers. The main thermometer was moved from the original position, close to the end of the wire, to the centre.

28.) The results were qualitatively similar to the first wire, although at lower intensity. The starting temperature of loading, from the value of 125°C of the wire #1, increased to about 160°C. In particular, the wire was not able to withstand direct heating conditions. We think that the surface was partially obstructed from something (plastic?).

29.) On July 23 we made de-loading and on July 24 we made loading again by: dynamic vacuum conditions, 220°C internal reactor temperature, power at Ni-Cr, 50000s duration.

30.) The results seem largely improved about: speed of loading (time of the drop of R/Ro from 1 to 0.85 of only 2000s), time necessary to get anomalous heat (less than 6 hours). The experiments are in progress as to-day, July 26, 2012.

31.) The experiment will be stopped on July 28 to package and “shipping” the reactor to USA (National Instruments Meeting at Austin-Texas) and later-on to Korea (ICCF17 Conference at Daejeon).

