Anomalous Exothermic and Endothermic Data Observed by Nano-Ni-Composite Samples

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***Abstract* -- To study the anomalous heat effect of Ni-based binary-metal-nano-powder samples by gas-phase hydrogen isotope absorption/desorption, three kinds of samples CNZ, CNZ-II and NZ were tested for the temperature range 300-573 K. The highest excess heat power, ca. 2W/g-Ni was obtained with CNZ at 573 K. Peculiar H(D)-isotopic effect and sudden heat sink by abrupt H(D)-desorption were observed. The heat phenomenon looks happening on surface of nano-particle.**

***Index Terms* – Ni-based nano-particle, D(H)-gas absorption, excess heat, higher temperature, 2W/g-Ni**

I. INTRODUCTION

Gas-phase hydrogen isotope absorption/adsorption experiments have been performed since 2008 at Kobe University to elucidate the underlying mechanism of anomalously large heat release [1-5]. This paper reviews recent results by summarizing the observations of anomalous data on excess heat, D(H)-loading and abrupt desorption with endothermic heat sink in Ni-based-nano-composite samples under D(H)-gas charging at both room and elevated temperatures, done by Kobe-Technova group in 2012-2013.

Referring to our JCF12 paper [6] on Pd_1Ni_7/ZrO_2 samples, the optimum small fraction of Pd ad-atoms to Ni-core of binary Pd-Ni nano-particles would have made the Pd-Ni binary nano-particles very active catalyst for D(H)-gas adsorption/absorption at room temperature and would have caused very high D(H)/Ni loading ratio such as 3.0 and anomalously high dynamic sorption energy with enhanced isotopic effect for D-gas charging. We have considered that the effect of Pd ad-atoms may be taking place also by other element ad-atoms such as Cu. Our trial experimental procedure and results reported for Ni/ZrO_2, $Cu_{0.21}Ni_{0.21}/ZrO_2$ and $Cu_{0.08}Ni_{0.36}/ZrO_2$ samples (partially reported in our ICCF17 paper by Sakoh et al.[7]) will be summarized in this report. We have reanalyzed time-dependent data for speculating heat releasing mechanisms during the long (several weeks) lasted phase of D(H)-loading-into-nano-metal. It seems that competing process of D(H)-gas sorption and desorption at the surface of nano-powders would be attributed to the mechanism as discussed in this paper.

Burst-like heat peaks of η-values (in unit of eV per D(H)-take-in/out) were observed with anomalously high values reaching 600 eV/H-sorption, and with smaller η-values for isotopic D-sorption than H-sorption, at 573K. Integrated heat values for several-week runs were reached at the levels of ca. 800eV/atom-Ni for $Cu_{0.08}Ni_{0.36}/ZrO_2$ samples, which were about 10 times larger than those of Ni/ZrO_2 samples and about 4 times larger than those of $Cu_{0.21}Ni_{0.21}/ZrO_2$ samples, at temperatures of 523 to 573K.

In the pre-treatment runs at 573K, very anomalous abrupt desorption phenomenon with rapid decrease of loading ratio and heat-level (heat-sink phenomenon) were repeatedly observed for all nano-Ni composite samples. Observed heat-sink energy per D(H)-desorption was around 50-80 eV, which is too large to be explained by H(D)-bonding energy to any metal. Displacement/knock-on of plural Ni-atoms by a proton/deuteron desorption might cause ca. 40 eV per Ni-displacement for energy absorption. If so, we may speculate that vacancies/defects would be formed in Ni-core-lattice and multi-atomic H(D)-clusters would be trapped there in the post-pre-treatment D(H)-charging runs. (These clusters might be seeds to induce anomalous heat effect, which might be some nuclear origin, for further main runs of D(H) charging by elevating temperature above room temperature.)

After the pre-treatment, we took data by elevating temperature from 373K up to 573K. We did not observe the anomalous 'abrupt' heat sink events by desorption and did observe excess power showing rather monotonous evolution. We need further repeated experiments to conform the phenomenon.

No visible increase of neutron counts (by ^3He counter) over natural background has been observed until now. Very slight increase of gamma-ray counts (by NaI counter) was sometimes recorded, but we need spectral and heat-cross-correlation-based confirmation in further scaled-up experiments (See our report from A. Kitamura et al in this Conference [12]).

II. EXPERIMENTAL APPARATUS AND PROCEDURE

In Photo-1, a view of experimental twin apparatus seen from a window of facility-cabin is shown. The A1 chamber is for H-gas loading experiments, and the A2 chamber is for D-gas loading experiments. We run simultaneously H- and D-gas charging with conditions as same as possible by the twin system. Calorimetry of this higher temperature experiment is made by the isoperibolic (isothermal) method, without using water-cooing of reaction chambers which are installed inside the A1/A2 outer evacuated thermal isolation chambers being always cooled with spiral water pipes wound the surface of A1/A2 chamber (see also Fig.1). The coolant water temperature is regulated to 24±0.1 C. The air temperature of the cabin is also regulated to 24±0.1 C by a spindle-type air conditioner installed outside the cabin.

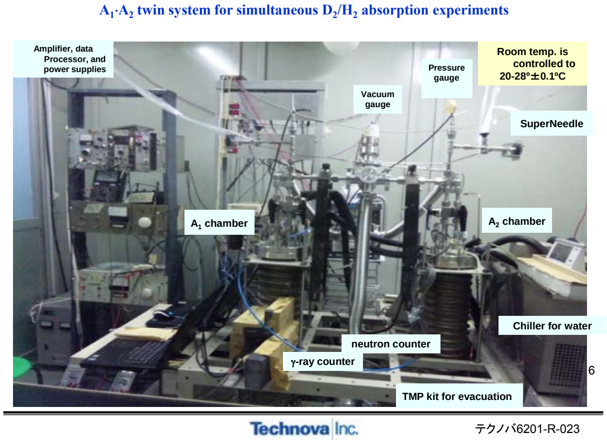


Photo-1: A window view of apparatus for the twin D(H)-gas loading experiment with metal-composite nano-powders

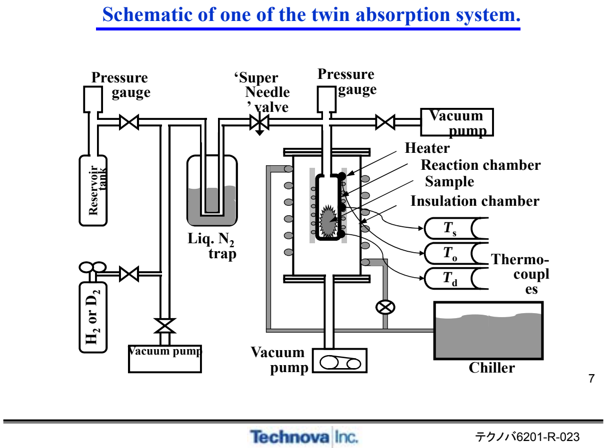
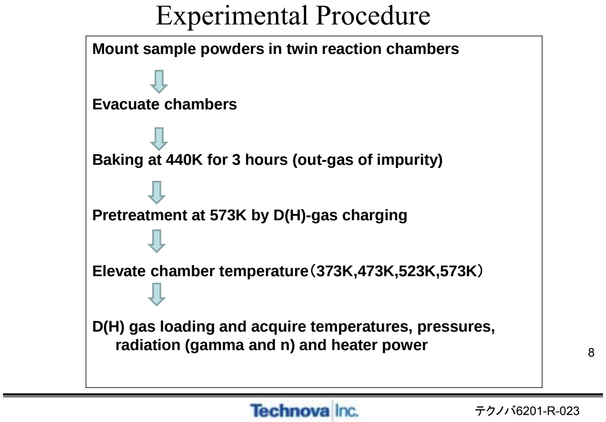


Fig.1: Schematic diagram of one system of the twin system for D(H)-charging experiments with metal nano-composite powders

The schematic diagram of one system of the twin system is shown in Fig.1.

The samples are put in the reaction chamber, and the outer chamber is evacuated for thermal insulation during hydrogen isotope absorption/adsorption. Sheath heaters with resistance of 37.9 Ω and 53.8 Ω wound around the reaction chambers in the A_1 and A_2 systems, respectively, are used for sample heating in the cases of baking preconditioning runs and D(H)-gas charging absorption runs at elevated temperatures. Alumel-chromel thermo-couples are used to measure temperatures. Surface temperatures of a reaction chamber are monitored with these three K-type thermo-couples (Ts, To and Td in Fig.1). The calibration curve of heat-power vs. reaction chamber-surface temperature was obtained for the average of three TC data as a function of input heater-power by sheath heaters, under He-gas charged condition instead of D(H)-gas. Correction of difference in convection heat removal components between D(H)-gas and He-gas was done by using the difference of specific heat data of D(H)-gas and He-gas. Variation of heater input power was monitored in every second and used for correction: this correction was less than ±0.5 W for a month long runs of experiment. A slight change of cabin temperature gave a slight effect (less than ±0.2W) on power level data of reaction chamber and was used for correction. We have done such corrections for power level determination as much as we could consider. The accuracy of excess heat-power level is estimated to be good with error bar of less than ±0.5 W.

The standard procedure of gas-charging experiment is shown in Fig.2. The D(H)-gas charging was started with 0.9-0.6 MPa pressure of source cylinder (reservoir tank) and fed through the super-needle valve with several scc/m initial flow rates adjusted for the A1/A2 chambers.



Experimental Procedure

Mount sample powders in twin reaction chambers

⇩

Evacuate chambers

⇩

Baking at 440K for 3 hours (out-gas of impurity)

⇩

Pretreatment at 573K by D(H)-gas charging

⇩

Elevate chamber temperature（373K,473K,523K,573K）

⇩

D(H) gas loading and acquire temperatures, pressures, radiation (gamma and n) and heater power

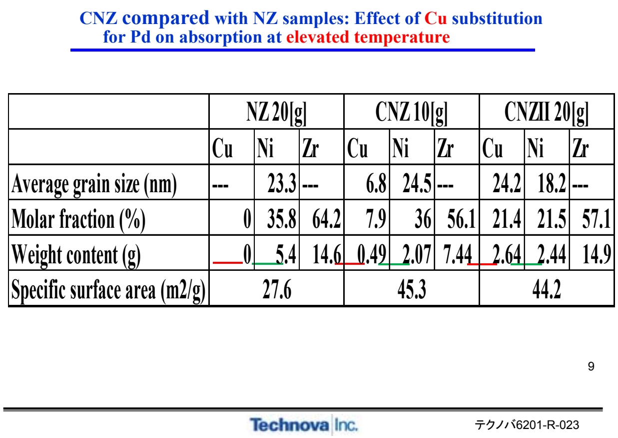
Fig.2: Standard procedure of D(H)-gas charging experiments with nano-metal composite powders

We have used three kinds of Ni-based nano-composite samples for this series of experiments. Specification data of three samples are shown in Table-1.

By the X-ray diffraction spectroscopy (XRDS) and the transmission-type electron microscope (TEM) picture analysis, initial particle sizes are around 24 nm for Ni-particles similarly for NZ, CNZ and CNZ-II samples. The particle size of Cu-particles was around 7 nm for CNZ and around 20 nm for CNZ-II. Used sample-weights were 20g, 10g and 20 g, respectively for NZ, CNZ and CNZ-II samples. We have assumed that only Ni-component is active to H(D)-absorption and relevant excess heat effect. Net weights of Ni components were 5.4g, 2.07g and 2.44g, respectively for NZ, CNZ and CNZ-II samples.

After some runs of H(D)-charging, we will speculate the formation of shell-core structured binary Cu-Ni nanoparticle [11], and we need to wait for TEM image for post-run samples.

Table-1: Specification data of NZ, CNZ and CNZ-II samples



CNZ compared with NZ samples: Effect of Cu substitution for Pd on absorption at elevated temperature

	NZ 20[g]			CNZ 10[g]			CNZII 20[g]		
	Cu	Ni	Zr	Cu	Ni	Zr	Cu	Ni	Zr
Average grain size (nm)	---	23.3	---	6.8	24.5	---	24.2	18.2	---
Molar fraction (%)	0	35.8	64.2	7.9	36	56.1	21.4	21.5	57.1
Weight content (g)	0	5.4	14.6	0.49	2.07	7.44	2.64	2.44	14.9
Specific surface area (m2/g)	27.6			45.3			44.2		

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III. RESULTS AND DISCUSSION

A. Comparison of base-temperature dependence of excess heat for Ni-base three samples

In Figs. 3 through 5, we show the results of observed excess heat-power data, respectively for NZ, CNZ-II and CNZ samples. D(H)-gas pressure data and D(H)/Ni dynamic loading ratio data are also included in figures.

At room temperature for base-temperature, we have observed no visible increase of D(H)/Ni-dynamic loading ratios and neither detectable excess heat-power.

A common trend for the three kinds of samples is: excess heat-power level becomes visible for higher base-temperatures than 473 K (200 C), and becomes larger as base-temperature increases (up to 573 K, data were taken). And excess heat-power levels are largest for CNZ sample, data for CNZ-II sample is next high and the data for NZ sample (namely without Cu) is the lowest.

Another common trend is the evolution of larger excess heat-power levels for H-gas charging than those for D-gas charging. This trend is astonishing, but other research groups as Piantelli et al [8] and Celani et al [9] have claimed to observe the same effect. We have thought traditionally deuteron-induced cold fusion, especially for Pd-D systems at room temperature of base-temperature, is the easiest happening nuclear effect in condensed matter. Why the reversed effect has happened for H-loading is of a new great mystery. The author has discussed on some plausible reasons [10] by the recovery time (annealing) difference of damaged structures of nano-powders between the D-induced nuclear heat-source as by the 4D/TSC fusion events and the H-induced nuclear heat-source as by the 4H/TSC weak/strong (WS) fusion events. Released energy (47.6 MeV) by 4D fusion is one order larger than that (7.72 MeV) by 4H/TSC WS fusion [10-11]. Therefore the lattice-damage by atom-displacement may be two orders of magnitude larger for D-system in Ni than that for H-system. For seeing more discussions about the damage recovery effect, please see the author's paper in JCMNS Vol.9 [11].

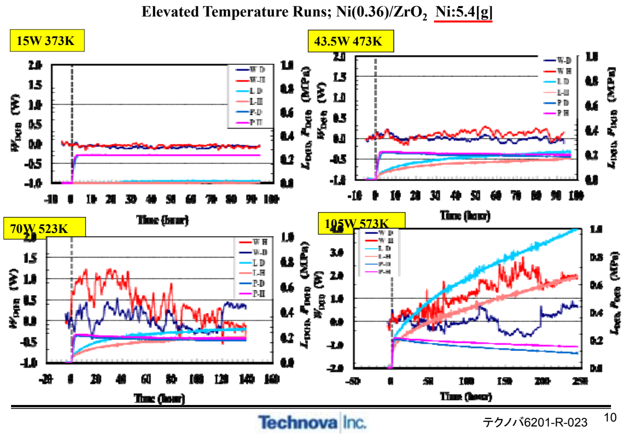


Fig.3: Base-temperature dependence of excess heat-power taken for NZ sample. Here W denotes excess-power (red for H and blue for D), p pressure and L loading ratio.

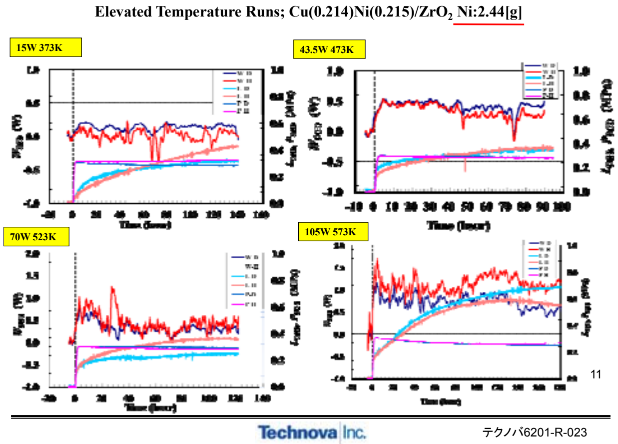
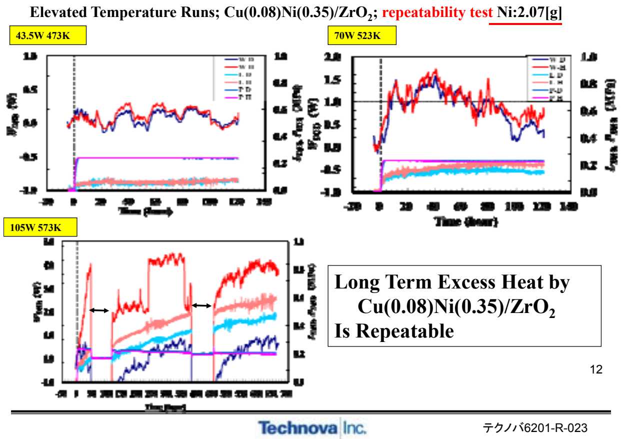


Fig.4: Base-temperature dependence of excess heat-power taken for CNZ-II sample. Here W denotes excess-power (red for H and blue for D), p pressure and L loading ratio.



Long Term Excess Heat by Cu(0.08)Ni(0.35)/ZrO$_2$ Is Repeatable

Fig.5: Base-temperature dependence of excess heat-power taken for CNZ sample. Here W denotes excess-power (red for H and blue for D), p pressure and L loading ratio.

The largest heat-power level in this series of experiments was ca. 2W/g-Ni by CNZ sample at 573 K. The integrated value (total excess heat) was ca. 800 eV/Ni-atom. It is too large to explain by known chemical heat source for used materials [6-7].

B. *Dynamic H(D)-sorption/desorption energy data*

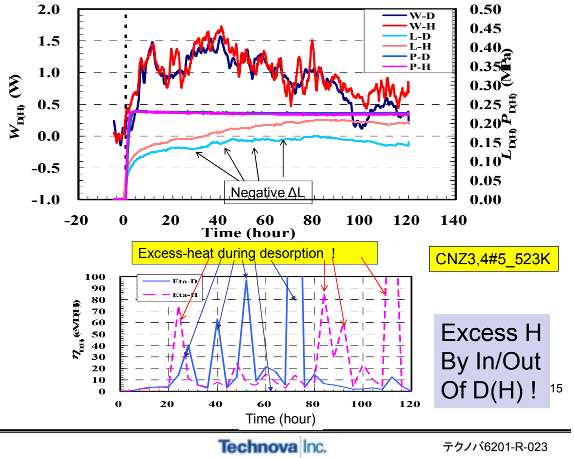


Fig. 6: Data of dynamic H(D)-sorption/desorption energy for CNZ

Next, we discuss time resolved parameters. The time-resolved specific sorption energy, or differential heat of hydrogen uptake, $\eta_{D(H)}$, is defined as the output energy per one hydrogen isotope atom absorbed/adsorbed [2];

$$\eta(t) \equiv \frac{\int_{t}^{t+\Delta t} W_{\text{true}}(t)\,dt}{L(t+\Delta t)-L(t)} \qquad (1)$$

The formula holds for H(D)-desorption too.

Typical calculated values of $\eta_{D(H)}$ data for CNZ sample are shown in Fig.6 and Fig.7, respectively for base-temperature of 523 K and 573 K.

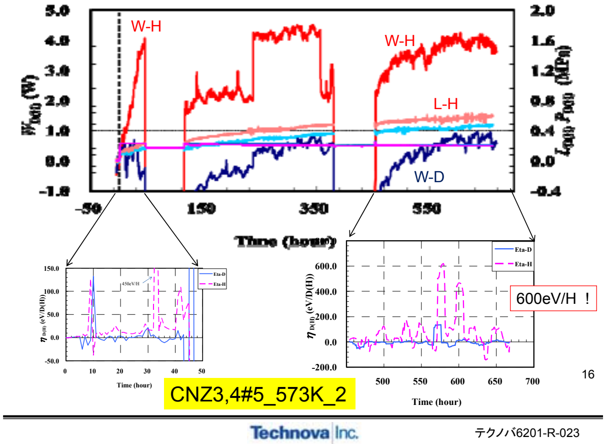


Fig.7: Data of dynamic H(D)-sorption/desorption energy for CNZ sample at 573 K

We have observed 'burst-like' data of η-values as seen in Figs. 6 and 7. The largest η-value is ca. 600 eV/H. It is anomalously large value, in the sense of chemistry or solid state physics. We need to consider possible mechanisms to release such large free energy by some nuclear processes such as discussed in our papers [9-11].

Another interesting feature of dynamic heat release is: as seen the data shown in Fig.6, exothermic bursts are taking place for both of dynamic change of D(H)-sorption and D(H)-desorption, and especially exothermic (not endothermic) bursts happened for D(H)-dynamic desorption. This phenomenon depicts that the excess heat generating events are taking place at around surfaces of Ni or Cu-Ni-binary nano-particles. Our theoretical prediction based on the surface mesoscopic catalysis effect to induce D(H)-cluster fusion [9-11] might match to the observed fact. However, we need further confirmation study from various angles based on future experiments using various kinds of nano-powders.

C. *Abrupt heat sink by abrupt H(D)-desorption*

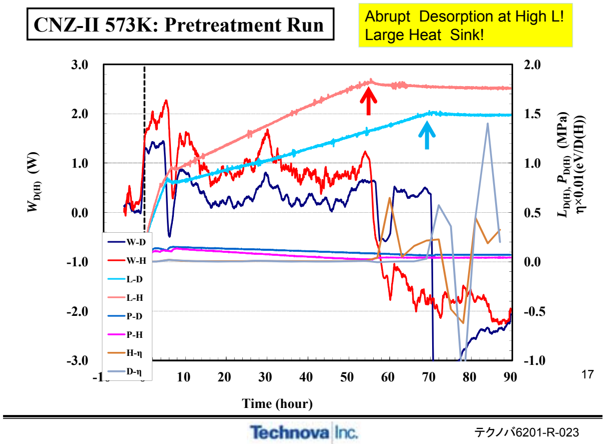


Fig.8: Abrupt heat sink data with abrupt H(D)-desorption observed in the initial pretreatment run of CNZ-II sample (see points of arrows and data around time 10 hrs). Here P notes pressure, L loading and W excess power

Typical data is shown in Fig.8 for CNZ-II sample. In the pretreatment runs at 573 K (see Fig.2), we have observed an anomalous phenomenon of abrupt burst-like D(H)-desorption and corresponding heat-sink with anomalously large amplitudes for all of the three samples.

In the latter runs at 573 K or lower temperatures, the evolutions of excess heat-power level were observed rather monotonously and persistently and the abrupt heat sink data were not observed. What is the reason of such drastic change of D(H)-absorption/excess-heat episodes from the initial pretreatment run to the final long lasting persistent excess heat runs? When the abrupt desorption happened, average η-values were ca. -50 to -80 eV/H(D)-desorption. We consider the highest possible H(D)-bonding energy to metal atom is on the order of a few eV, so that -50 eV/H(D) is too large to explain by the H(D)-absorption/desorption energy. Some peculiar events should happen there.

One considerable happening might be a single or plural Ni-atoms kick-out (displacement) induced by the abrupt H(D)-desorption, for we know from the radiation damage study of hot-fusion materials that metal atom displacement energy from lattice is on the order of 40 eV.

We may draw a speculative image as Fig.9 on a plausible process.

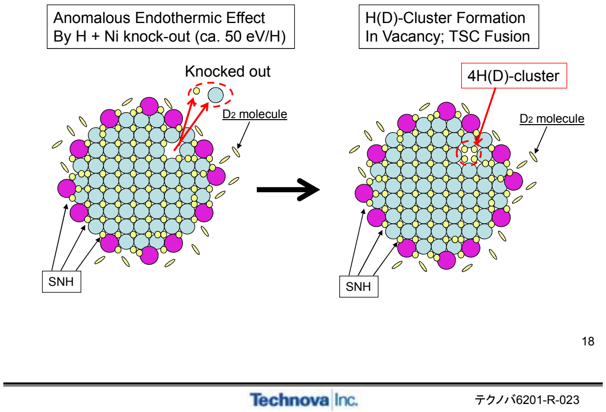


Fig.9: An image of plausible mechanism for the abrupt heat-sink with H(D) and Ni-atom kick-out. Here smaller circles with green color depict Ni atoms, and purple larger circles do Cu atoms.

After the kick-out of Ni-atom, a void/vacancy forms to attract transient H(D)-cluster, like 4H(D)/TSC, formation (see right figure of Fig.9). Such a void formation might be a mechanism of plausible candidate active sites for nuclear reactions.

Why do samples after the pretreatment become 'gentle' for persistent excess heat generation? We have no definite answer yet. We might consider that two separate nano-particles of Cu (6.8nm, initial) and Ni(24.5nm, initial) might merge to make a Ni-core/Cu-outer shell structure as drawn in right figure of Fig.9 to be a strong mesoscopic catalyst[11].

IV. CONCLUSION

Present 3 kinds of Ni-nano-composite samples gave anomalous and long-lasting excess heat data at elevated base-temperature (523K,573K) conditions.

Cu·Ni·Zr nano-composite samples gave several fold larger heat level than Ni·Zr nano-composite sample.

Cu additive seems working as strong catalyst for Ni-core particle to absorb D(H)-gas and releasing anomalously large excess heat. However, the reason why H-gas loading gave much larger heat-level than D-gas loading is yet to study. It is interesting mystery.

The 8% Cu-added Ni-nano sample showed ca. 4 fold larger heat level per g-Ni than that of 21.4% Cu-added Ni-nano sample and such data were repeatedly observed.

In pretreatment runs, anomalous abrupt desorption/endothermic effect was repeatedly observed for all of the three kinds of samples. The mechanism of such abrupt change is interesting, but is yet to study.

At 573K, η-values were anomalously large as100～600 eV/H, and integrated heat was 800 eV/atom-Ni for CNZ samples. This seems to conclude the existence of non-chemical reaction heat, but the explanation by definite nuclear mechanism is yet to study.

Further confirmation experiments about the presently observed anomalous exothermic and endothermic phenomena are expected by using some scaled-up devices.

REFERENCES

[1] A. Kitamura, T. Nohmi, Y. Sasaki, A. Taniike, A. Takahashi, R. Seto, Y. Fujita; Phys. Lett. A **373** (2009) 3109–3112.

[2] A. Kitamura, Y. Miyoshi, A. Taniike, A. Takahashi, R. Seto and Y. Fujita; J. Condensed Matter Nucl. Sci. **4** (2011) 56-68.

[3] A. Kitamura, Y. Miyoshi, H. Sakoh, A. Taniike, A. Takahashi, R. Seto and Y. Fujita; J. Condensed Matter Nuclear Science, **5** (2011) pp.42-51.

[4] H. Sakoh, Y. Miyoshi, A. Taniike, A. Kitamura, A. Takahashi, R. Seto and Y. Fujita; Proc. 12th Meeting of Japan CF Research Society, JCF12 (2012) 10-18.

[5] A. Takahashi, A. Kitamura, Y. Miyoshi, H. Sakoh, A. Taniike, R. Seto, and Y. Fujita; 16th Int. Conf. Condensed Matter Nuclear Science, Chennai, India, 2011; Session of New Energy Technology, 241st ASC National Meeting, Mar. 2011.

[6] Y. Miyoshi, H. Sakoh, A. Taniike, A. Kitamura, A. Takahashi, R. Seto, Y. Fujita, T. Murota and T. Tahara: Proc. JCF-12 (2012) 1: visit http://jcfrs.org/file/jcf12-proceedings.pdf

[7] H. Sakoh, Y. Miyoshi, A. Taniike, A. Kitamura, A. Takahashi, R. Seto, and Y. Fujita; 17th Int. Conf. Condensed Matter Nucl. Sci., Daejeon, Korea, Aug. 2012.

[8] F. Piantelli, et al.: "Some results from the Nichenergy laboratory", presentation at the 10th Int. Workshop, Siena, April 2012 (see ISCMNS web site

[9] F. Celani, et al: Cu-Ni-Mn wires with improved submicrometric surfaces used as LENR device by new transparent dissipation-type calorimeter, Proc. ICCF17, to be published

[9] A. Takahashi: JCMNS, Vol.9 (2012) 108

[10] A. Takahashi: Nuclear products of cold fusion by TSC theory, Proc. ICCF18, to be published

[11] A. Takahashi, et al: Mesoscopic catalyst and D-cluster fusion, Proc. JCF11 (2012)47-53; http://jcfrs.org/file/jcf11-proceedings.pdf

[12] A. Kitamura , A. Takahashi , R. Seto , Y. Fujita , A. Taniike and Y. Furuyama: A Mass-Flow-Calorimetry System for Scaled-up Experiments on Anomalous Heat Evolution at Elevated Temperatures, Proc. ICCF18, to be published