



Research Article

# 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. A peculiar H(D)-isotopic effect and sudden endothermic events caused by abrupt H(D)-desorption were observed. The heat phenomenon appears to be happening on surface of nano-particles.

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*Keywords:* D(H)-gas absorption, Excess heat, Higher temperature, 2W/g-Ni, Ni-based nano-particle

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## 1. 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 releases [1–5]. This paper reviews recent results by summarizing the observations of anomalous data on excess heat, D(H)-loading and abrupt endothermic desorption in Ni-based-nano-composite samples under D(H)-gas charging at both room temperature and elevated temperatures, done by Kobe–Technova group in 2012–2013.

Referring to our JCF12 paper [6] on Pd<sub>1</sub>Ni<sub>7</sub>/ZrO<sub>2</sub> 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 a very active catalyst for D(H)-gas

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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<sub>2</sub>, Cu<sub>0.21</sub>Ni<sub>0.21</sub>/ZrO<sub>2</sub> and Cu<sub>0.08</sub>Ni<sub>0.36</sub>/ZrO<sub>2</sub> 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 speculative heat releasing mechanisms during the long (several weeks) lasting phase of D(H) loading into nano-metal. It seems that competing processes of D(H)-gas sorption and desorption at the surface of nano-powders may be attributed to the mechanism as discussed in this paper.

Burst-like heat peaks of  $\eta$ -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  $\eta$ -values for isotopic D-sorption than H-sorption, at 573 K. Integrated heat values for several-week runs were reached at the levels of ca. 800 eV/atom-Ni for Cu<sub>0.08</sub>Ni<sub>0.36</sub>/ZrO<sub>2</sub> samples, which were about 10 times larger than those of Ni/ZrO<sub>2</sub> samples and about four times larger than those of Cu<sub>0.21</sub>Ni<sub>0.21</sub>/ZrO<sub>2</sub> samples, at temperatures of 523–573 K.

In the pre-treatment runs at 573 K, very anomalous abrupt desorption phenomena with rapid decrease of loading ratio and heat-level (an endothermic phenomenon) were repeatedly observed for all nano-Ni composite samples. Observed endothermic 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 the anomalous heat effect, which might be some nuclear origin, for further main runs of D(H) charging by elevating temperature above room temperature.)

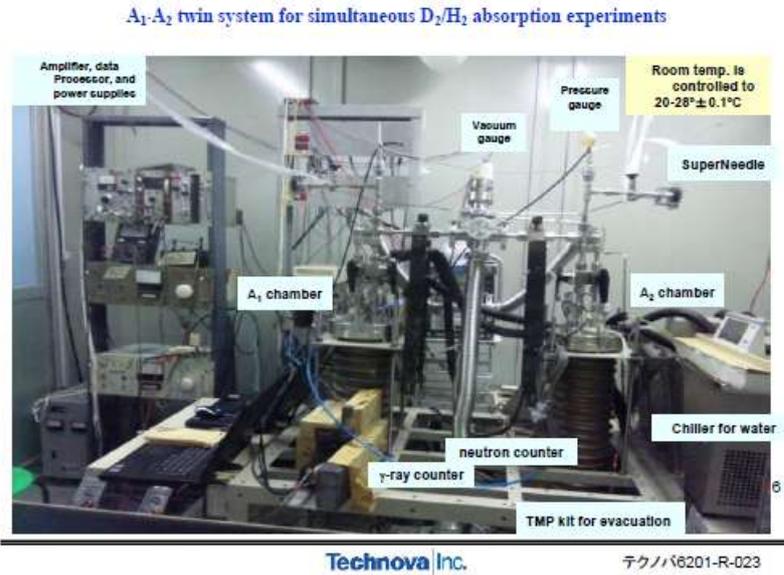
After the pre-treatment, we took data by elevating the temperature from 373 up to 573 K. We did not observe the anomalous ‘abrupt’ endothermic events by desorption and we did observe excess power showing steady, continuous evolution. We need further repeated experiments to conform the phenomenon.

No visible increase of neutron counts (by <sup>3</sup>He counter) over natural background has been observed until now. A 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]).

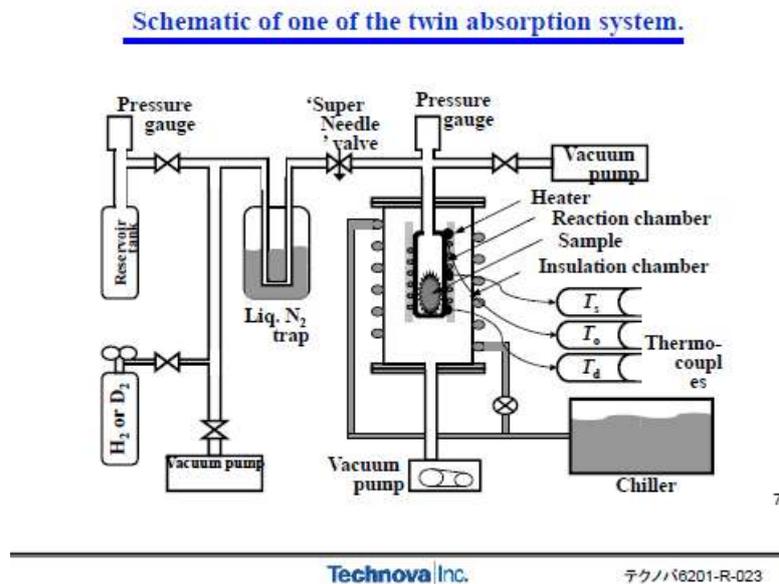
## 2. Experimental Apparatus and Procedure

In Fig. 1 (Photo 1), a view of experimental twin apparatus seen from a window of the room in our facility 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 similar as possible in the twin systems. Calorimetry of this higher temperature experiment is made by the isoperibolic (isothermal) method, without using water-cooling of reaction chambers which are installed inside the A<sub>1</sub>/A<sub>2</sub> outer evacuated thermal isolation chambers being always cooled with spiral water pipes wound the surface of A<sub>1</sub>/A<sub>2</sub> chamber (see also Fig. 2). The coolant water temperature is regulated to 24±0.1°C. The air temperature of the room is also regulated to 24±0.1°C by a spindle-type air conditioner installed outside the room.

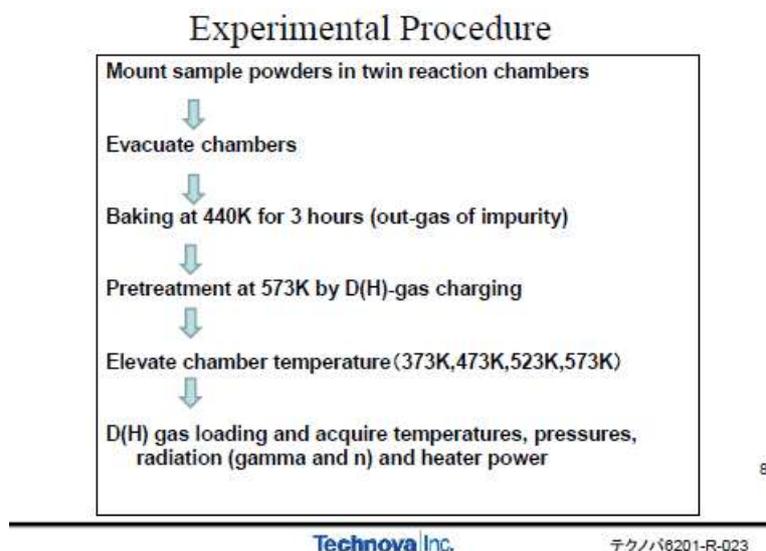
A schematic diagram of one of the systems of the twin system is shown in Fig. 2 The samples are put in the reaction chamber, and the outer chamber is evacuated for thermal insulation during hydrogen isotope absorption/adsorption. Sheath heaters with resistance of 37.9 and 53.8 Ω wound around the reaction chambers in the A<sub>1</sub> and A<sub>2</sub> 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 thermocouples are used to measure temperatures. Surface temperatures of a reaction chamber are monitored with these three K-type thermocouples (Ts, To and Td in Fig. 2). The calibration



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



**Figure 2.** Schematic diagram of one system of the twin system for D(H)-charging experiments with metal nano-composite powders.



**Figure 3.** Standard procedure of D(H)-gas charging experiments with nano-metal composite powders.

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 every second and used for correction: this correction was less than  $\pm 0.5$  W for a month long runs of experiment. A slight change of room temperature gave a slight effect (less than  $\pm 0.2$ W) 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  $\pm 0.5$  W.

The standard procedure for the gas-charging experiment is shown in Fig. 3. 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 s/m initial flow rates adjusted for the  $A_1/A_2$  chambers.

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. Based on 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 20, 10 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 5.4, 2.07 and 2.44 g, respectively, for NZ, CNZ and CNZ-II samples.

After some runs of H(D)-charging, we plan to speculate about the formation of shell-core structured binary Cu–Ni nanoparticle [11]. We need to wait for TEM images of post-run samples to do this.

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

	NZ20 (g)			CNZ10 (g)			CNZII20 (g)		
	Cu	Ni	Zr	Cu	Ni	Zr	Cu	Ni	Zr
Average grain size (nm)	–	23.5	–	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)	–	5.4	14.6	0.49	2.07	7.44	2.64	2.44	14.9
Specific surface area (m <sup>2</sup> /g)		27.6			43.5			44.2	

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

### 3. Results and Discussion

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

In Figs. 4–6, 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 we did not detect 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 the base-temperature increases (up to 573 K, data were taken).

Excess heat-power levels are largest for CNZ sample, data for CNZ-II sample is next higher, 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 occurring nuclear effect in condensed matter. Why the reversed effect has happened for H-loading is of a new great mystery. One of us (Takahashi) has discussed some plausible reasons [10] for 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 more discussions about the damage recovery effect, please see Ref. [11].

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].

#### 3.2. Dynamic H(D)-sorption/desorption energy data

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];

$$\eta(t) \equiv \frac{\int_t^{t+\Delta t} W_{\text{true}}(t) dt}{L(t + \Delta t) - L(t)}. \quad (1)$$

The formula holds for H(D)-desorption too. Typical calculated values of  $\eta_{D(H)}$  data for CNZ sample are shown in Figs. 7 and 8, respectively, for base-temperature of 523 and 573 K.

We have observed ‘burst-like’ data of  $\eta$ -values as seen in Figs. 7 and 8. The largest  $\eta$ -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. 7, 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.

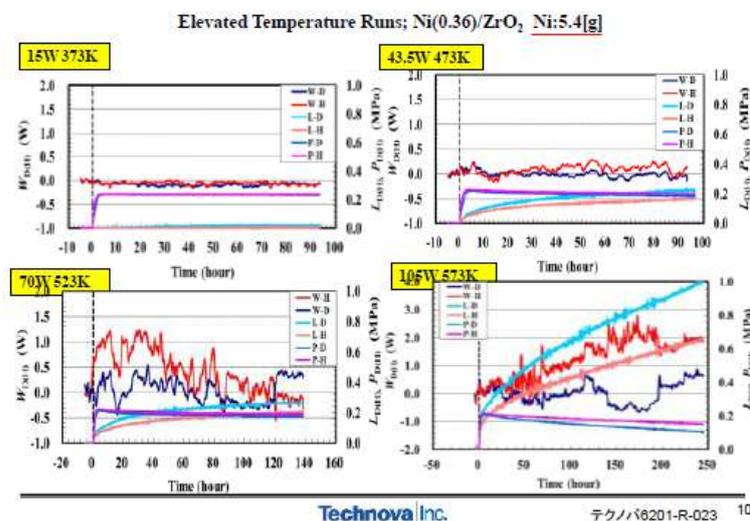
### 3.3. Abrupt endothermic events caused by H(D)-desorption

Typical data is shown in Fig. 9 for the CNZ-II sample. In the pretreatment runs at 573 K (see Fig. 3), we have observed an anomalous phenomenon of abrupt burst-like D(H)-desorption and corresponding endothermic reaction with anomalously large amplitudes for all three of the samples.

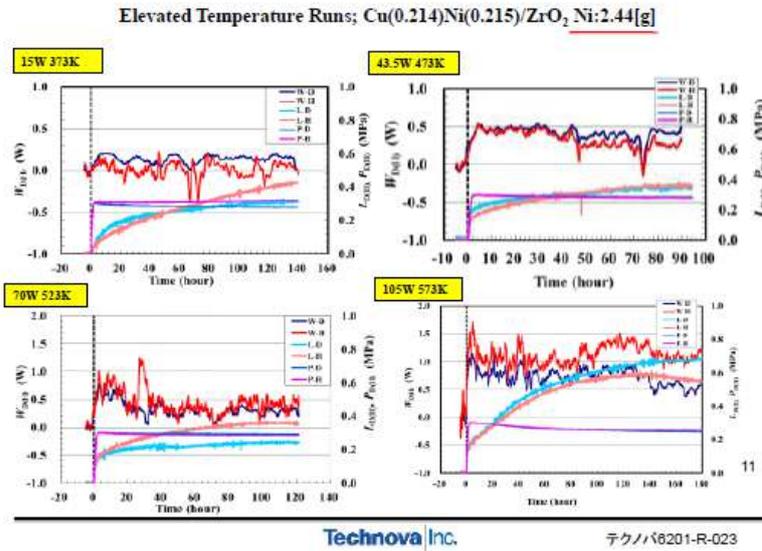
In the latter runs at 573 K or lower temperatures, the evolution of excess heat-power level was observed continuously and persistently and the abrupt endothermic events were not observed. What is the reason for such a drastic change of D(H)-absorption/excess-heat episodes from the initial pretreatment run to the final long lasting persistent excess heat runs? When the abrupt desorption happened, average  $\eta$ -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 in these circumstances.

One event that might be considered would 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. Figure 10 is a speculative image of a plausible process.

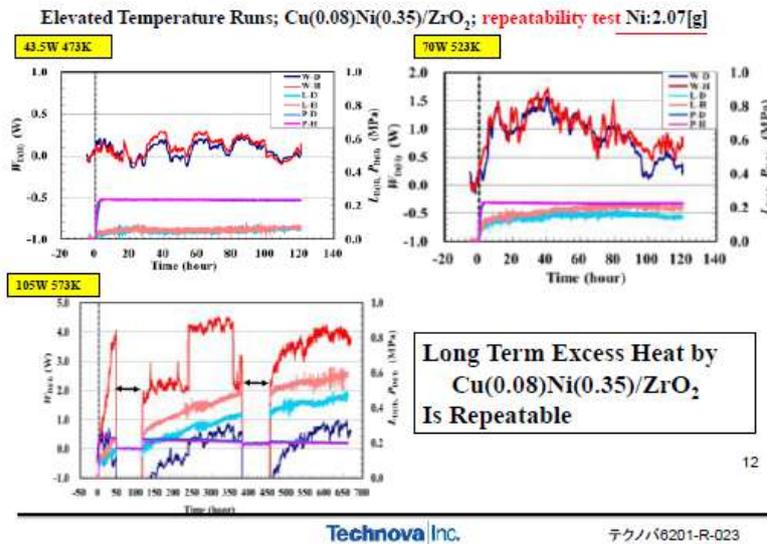
Why do samples after the pretreatment become ‘gentle’ for persistent excess heat generation? We have no definite answer yet. We might consider that two separate nano-particles of Cu (6.8 nm, initially) and Ni (24.5 nm, initially)



**Figure 4.** 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.



**Figure 5.** 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.



**Figure 6.** 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.

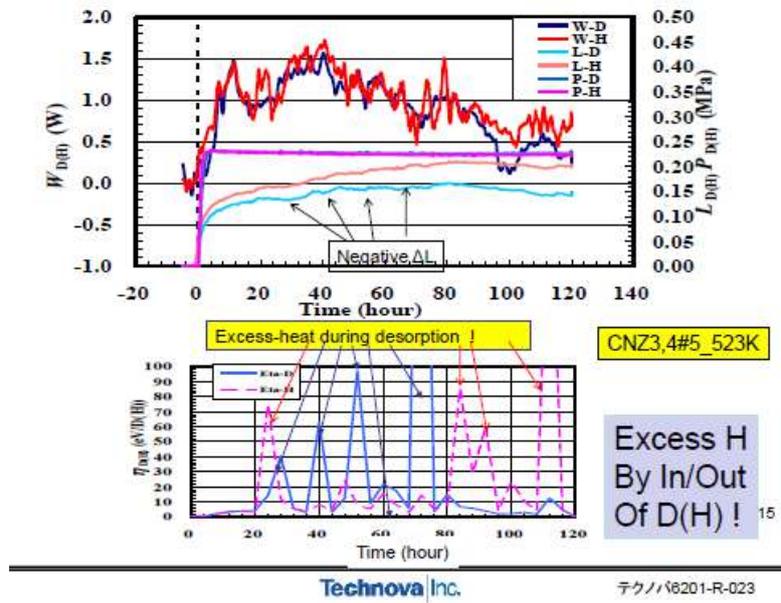


Figure 7. Data of dynamic H(D)-sorption/desorption energy for CNZ.

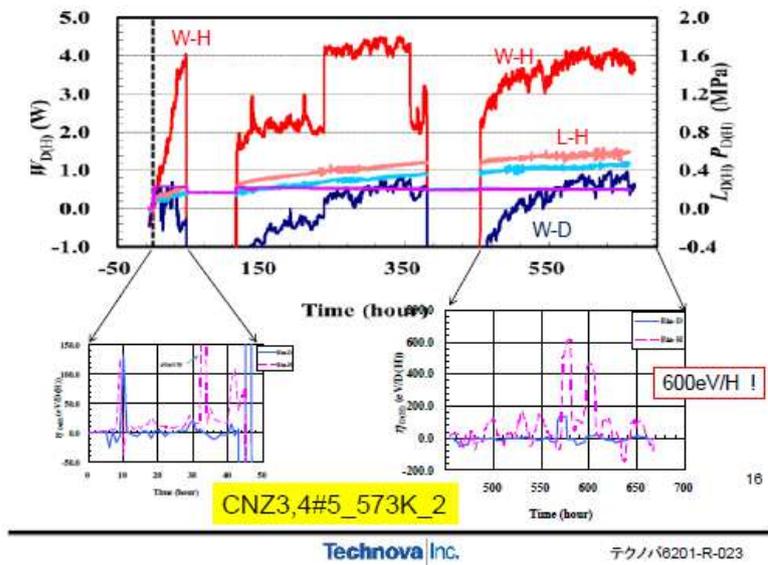
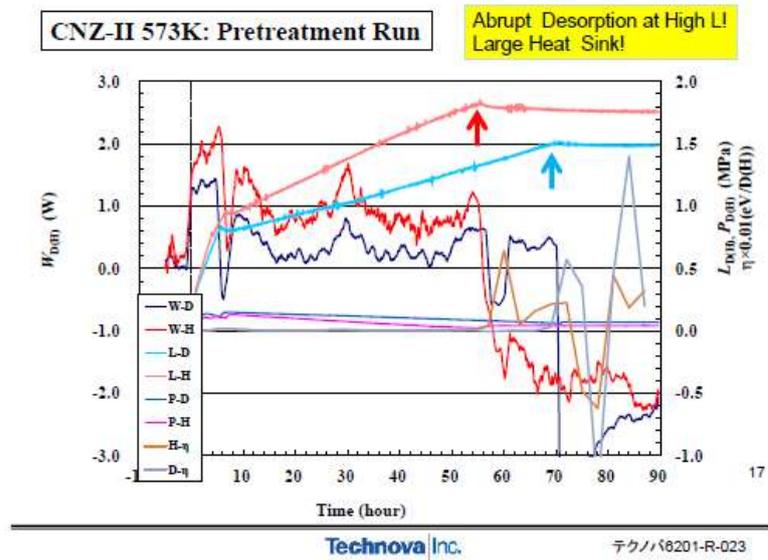
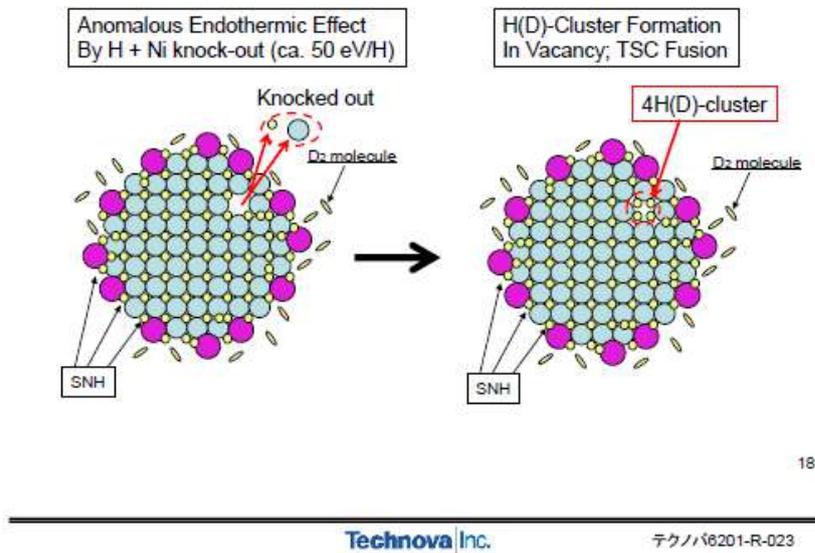


Figure 8. Data of dynamic H(D)-sorption/desorption energy for CNZ.



**Figure 9.** Data showing abrupt endothermic H(D)-desorption observed in the initial pretreatment run of CNZ-II sample (see points of arrows and data around time 10 h). Here  $P$  denotes pressure,  $L$  loading and  $W$  excess power .



**Figure 10.** An image of plausible mechanism for the abrupt endothermic reaction with H(D) and Ni-atom kick-out. Here smaller circles with green color depict Ni atoms, and purple larger circles depict Cu atoms. .

might merge to make a Ni-core/Cu-outer shell structure as drawn in right figure of Fig. 10 to be a strong mesoscopic catalyst [11]. However, this is speculative.

#### 4. Conclusion

The present three kinds of Ni-nano-composite samples gave anomalous and long-lasting excess heat data at elevated base-temperature (523, 573 K) conditions. Cu–Ni–Zr nano-composite samples gave several fold larger heat level than Ni–Zr nano-composite sample. A Cu additive seems to work as a strong catalyst for Ni-core particle to absorb D(H)-gas and releasing anomalously large excess heat. However, we have not yet studied why H<sub>2</sub> gas loading produced much more heat than D<sub>2</sub> gas loading. It is an 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, an anomalous abrupt desorption/endothemic effect was repeatedly observed for all of the three kinds of samples. The mechanism of such an abrupt change is interesting, but has not yet been studied. At 573 K,  $\eta$ -values were anomalously as large as 100–600 eV/H, and integrated heat was 800 eV/atom-Ni for CNZ samples. This seems to indicate the existence of non-chemical reaction heat, but there is still no explanation by definite nuclear mechanism. Further confirmation experiments about the presently observed anomalous exothermic and endothermic phenomena are expected, using scaled-up devices.

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