Progress report II on exothermic reaction in NdFe amorphous structure under hydrogenation.

V. Dubinko, Kharkov, 19.10.2016

1. Experimental setup

The Nd_xFe_y films produced by melt spinning (See the progress report I and Fig. 1) are defined as **NdFe10, NdFe20** and **NdFe45** with crystalline fraction **10%** , **20%** and **45%**, respectively.

In the progress report I, we have demonstrated that semi-crystalline films **NdFe45** did not absorb any significant amount of hydrogen as compared to the quasi-amorphous films of **NdFe10.**

In the present study**,** the films **NdFe10** and **NdFe20** have been hydrogenated under gradually increasing temperature in two different installations I and II, which differed mainly by the way of electric heating - pulsed (I) or simple AC (II). Both installations have been modernized to measure the **sample temperature** during the hydrogenation in addition to the hydrogen pressure in the reaction chamber.

a b

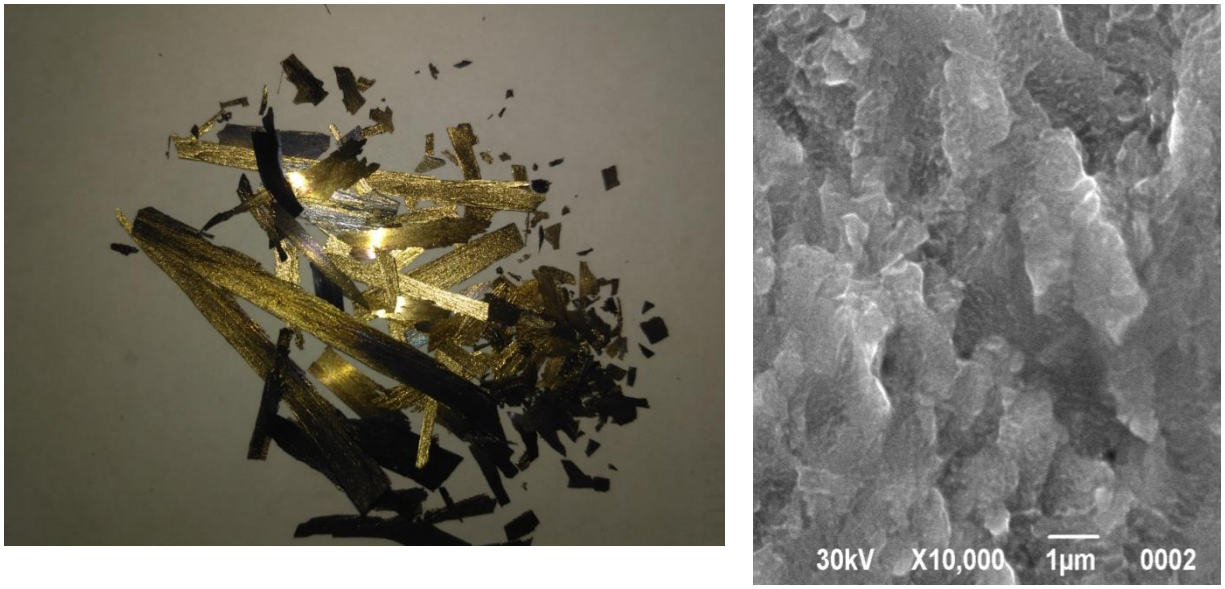

Figure 1. The appearance (a) and the surface microstructure (b) of Nd_xFe_y films 30 micron thick.

In both installations, the **NdFe10, NdFe20** films readily absorbed hydrogen up to a **loading ratio of ~1÷2 per metal atom**, while their thermal response to the loading depended crucially on the total mass of the films. A **fierce exothermic reaction** was detected, which resulted in the melting of the Cu foil, in which the films have been wrapped, **provided that the total mass of the films exceeded the critical value of ~ 1 gram**. Bellow the critical mass, the films absorbed hydrogen up to a similar loading ratio ~**1.5÷1.6** per metal atom *without a noticeable rise of their temperature*. The quantitative results of our experiments are presented below.

2. Installation I. Quartz reaction chamber of 300 ml volume with pulsed electric heating

Fig. 2 shows the evolution of the **NdFe20** temperature and H pressure (starting from ~100 kPa~1 bar) in time and the resulting appearance of the Cu foil with melted regions, which indicate that the maximum sample temperature was well above 1000 ^{o}C. The duration of the heating spike was about 140 seconds, while the maximum temperature (> 1000 ^{o}C) duration was too short to be measured by the thermocouple, which maximum registered temperature was 765 ^{o}C.

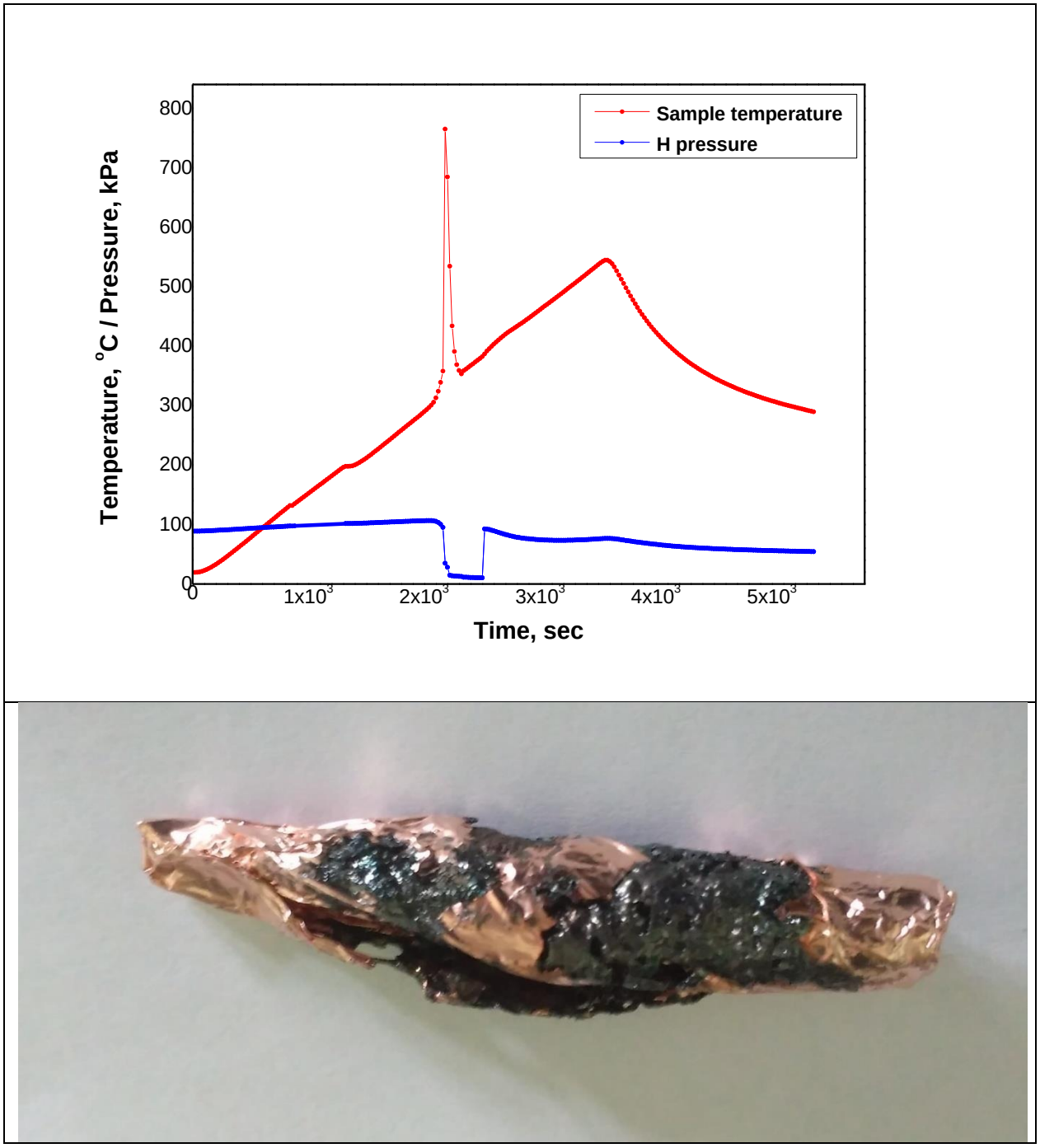

Figure 2. NdFe20 films of a mass **2.1795 g** wrapped in a Cu foil of a mass 0.813 gram. The loading ratio measured by the H pressure drop and weight increase after hydrogenation was ~**1.8 H per metal atom (**~1.5 wt%H).

3. Installation II. Ceramic chamber of 100 ml volume with AC heating

This installation allows an automatic control of temperature both **inside** the sample package wrapped in the Cu foil and **outside** the ceramic reaction chamber at ~ 2 mm distance from the wall. Fig. 3 shows the evolution of the **NdFe10** temperature, outside temperature and H pressure (starting from ~340 kPa~3.4 bar) in time and the resulting appearance of the NdFe alloy and the Cu foil **melted together** around the thermocouple, which indicates that the maximum temperature was even higher than in the installation I. Duration of the heating spike was about 40 seconds, while the maximum temperature (> 1000 ^{o}C) duration was too short to be measured by the thermocouple, which maximum registered temperature was 570 ^{o}C.

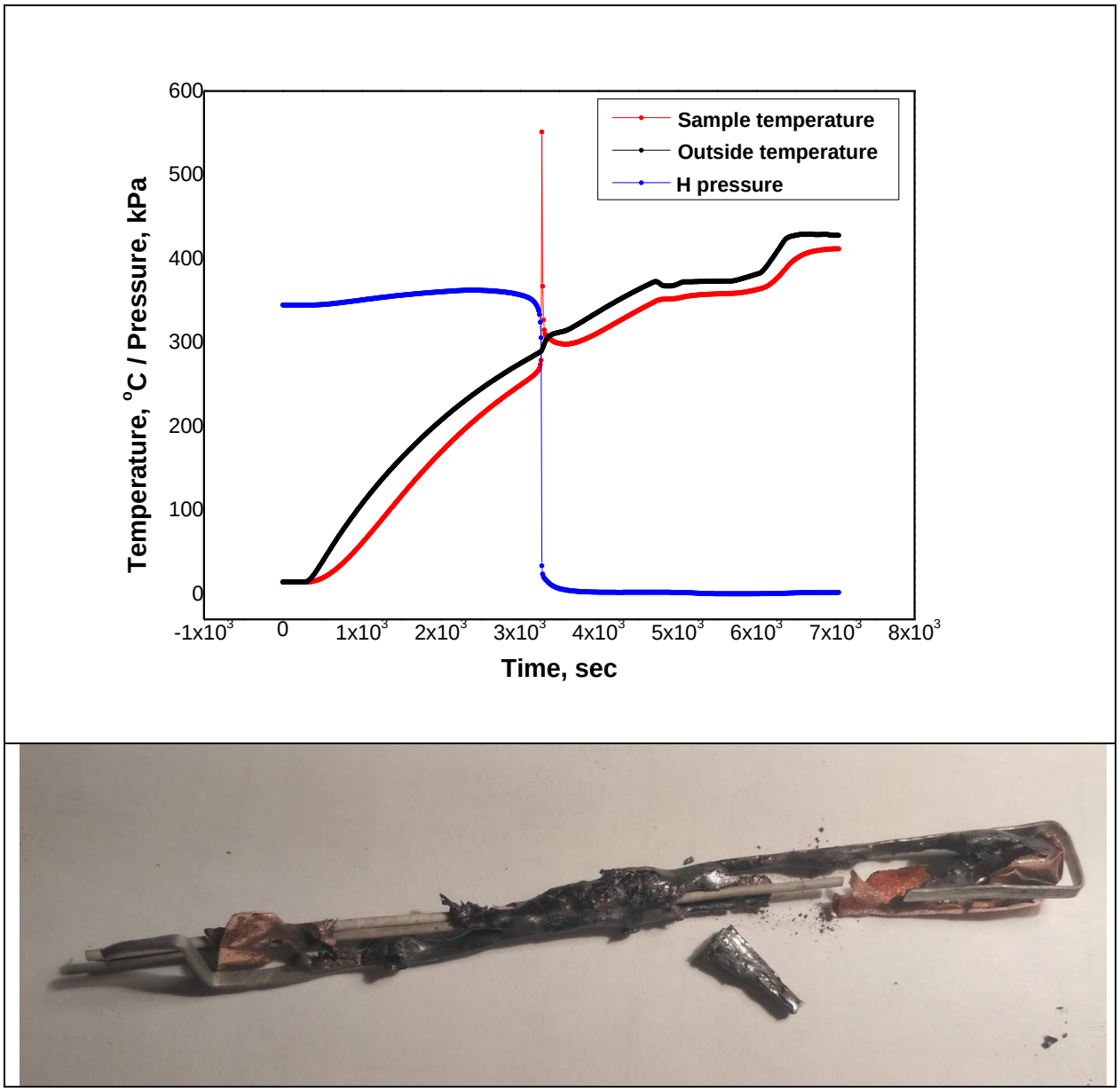

Figure 3. NdFe10 films of a mass **2.3713 g** wrapped in a Cu foil of a mass 1.6225 gram. The loading ratio measured by the H pressure drop after hydrogenation was ~**1.6 H per metal atom (**~1.36 wt%H).

From Fig. 3 and its enlarged section (Fig. 4) one can see an increase of the temperature outside the ceramic reactor resulting from the exothermic reaction induced by H absorption in NdFe films.

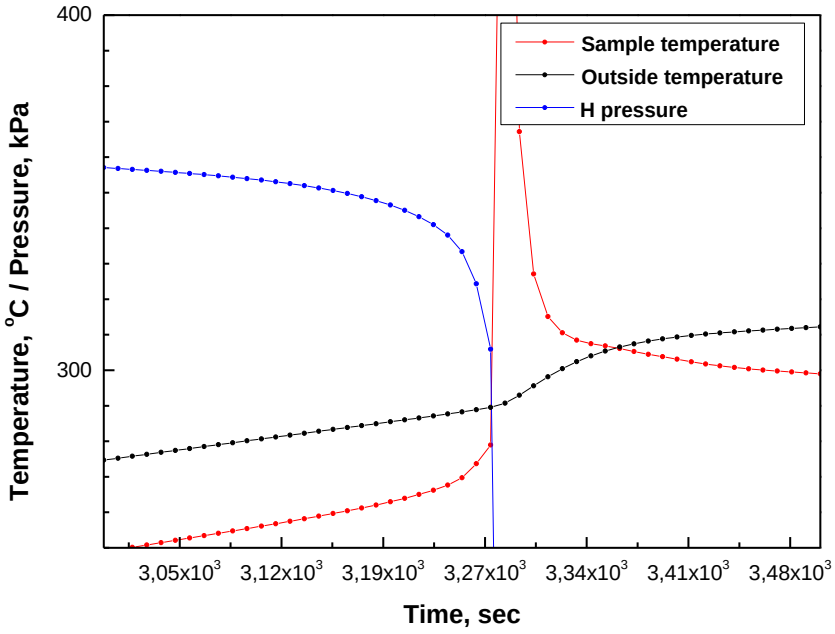

Figure 4. Enlarged segment of the Fig. 3 showing the response of the temperature outside ceramic reactor to the exothermic reaction induced by H absorption in NdFe films.

These data allow us to evaluate the amount of heat produced by the reaction as follows. The energy required for heating the NdFe films and Cu foil from 270 to 1100 °C and for melting the Cu foil is given by

$$\Delta Q_{NdFe+Cu}(\Delta T) = C_{NdFe} m_{NdFe} \Delta T + C_{Cu} m_{Cu} \Delta T + Q_{Cu}^{melt} m_{Cu} = 1263 \text{ J}, \ \Delta T = 830 \text{ K}, \quad (1)$$

where $m_{NdFe} = 2.3713$ g, $m_{Cu} = 1.6225$ g and $C_{NdFe} = 0.214 \dfrac{J}{g \cdot K}$, $C_{Cu} = 0.385 \dfrac{J}{g \cdot K}$ are the masses and the heat capacities of NdFe films and Cu foils, respectively, $Q_{Cu}^{melt} = 207$ J/g is the latent heat of melting of Cu.

The energy required to heat the walls of ceramic (Al_2O_3) chamber tube around the samples from 295 to 308 °C is given by

$$\Delta Q_{Al_2O_3}(\Delta T) = C_{Al_2O_3} m_{Al_2O_3} \Delta T = 1322 \text{ J}, \ \Delta T = 13 \text{ K}, \quad (2)$$

where $m_{Al_2O_3} = 93.5$ g and $C_{Al_2O_3} = 1105 \dfrac{J}{g \cdot K}$ are the mass and the heat capacity of the Al_2O_3 tube surrounding the samples (the tube inner diameter 10 mm, outer diameter 20 mm, the sample length 100 mm).

So the **minimum amount** of heat produced by the observed reaction (*without account of the heat dissipation*) can be estimated as **2585 J** given by the sum:

$$\Delta Q_{tot} = \Delta Q_{NdFe+Cu}\left(830\ \mathrm{K}\right) + \Delta Q_{Al_2O_3}\left(13\ \mathrm{K}\right) = 1263\ \mathrm{J} + 1322\ \mathrm{J} = 2585\ \mathrm{J}\,, \qquad (3)$$

4. Hydrogenation of NdFe films with subcritical masses in the installations I and II

Fig. 5 shows the hydrogenation kinetics of NdFe20 and NdFe10 films with masses *below 1 g* in installations I and II, respectively. In the former case, the heating was done at a constant rate of ~10 K per min, while in the latter case the outer temperature was kept constant at 383 ^{o}C, where the H absorption rate was maximal. After draining the 100 ml chamber of hydrogen, a new H portion was pumped in, which was partly absorbed by the samples up to a saturation.

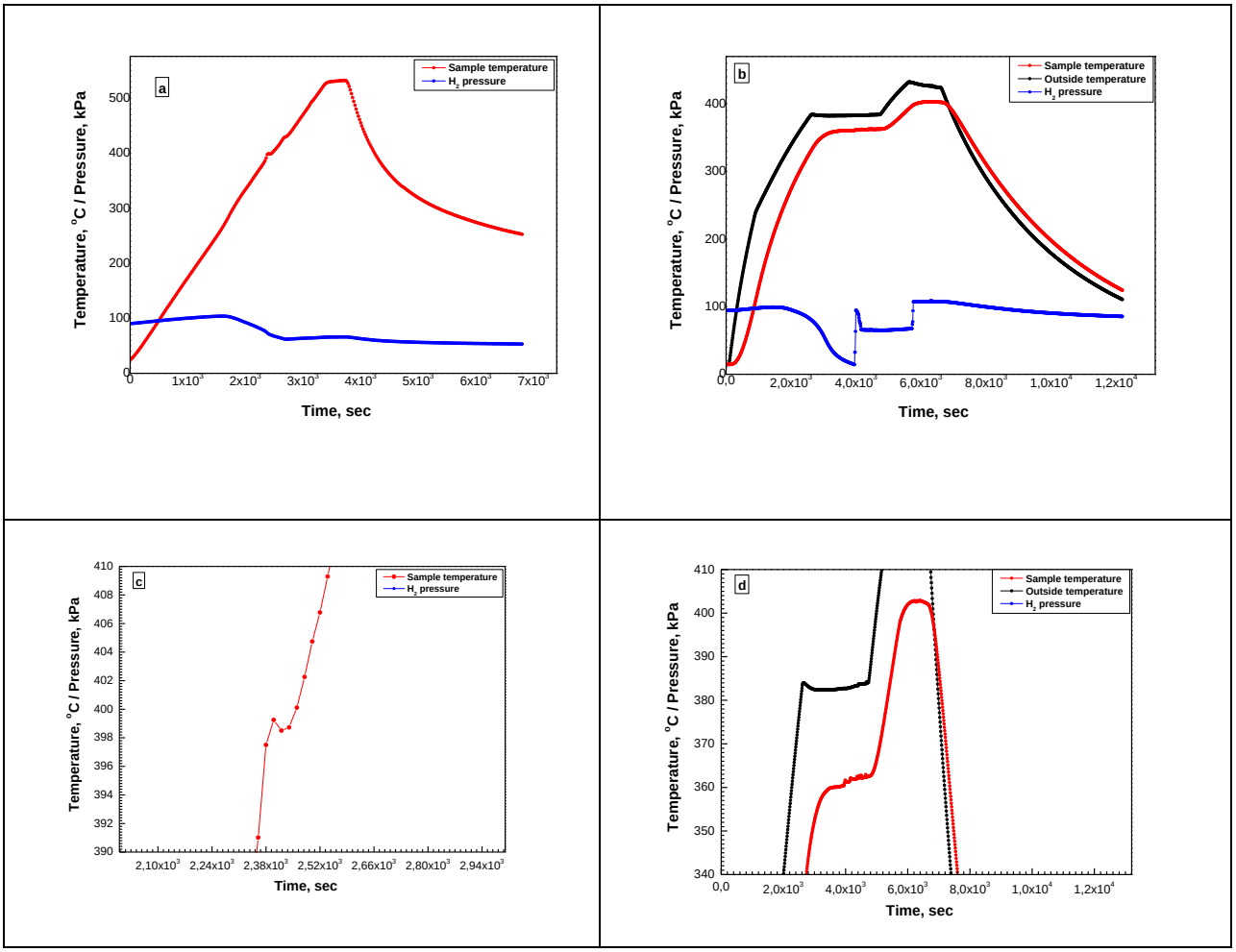

Figure 5. (**a**) NdFe20 films of a mass **0.8243 g** wrapped in a Cu foil of a mass 0.524 g and hydrogenated in the installation I. The loading ratio measured by the H pressure drop and weight increase after hydrogenation was ~**1.6 H per metal atom (~**1.37 wt%H). (**c**) Enlarged segment of the Fig. (**a**) showing the sample temperature increase by ~**5 K** in response to the H absorption. (**b**) NdFe10 films of a mass **0.6687 g** inserted in a ceramic tube of a mass 9.4668 g and hydrogenated in the installation II. The loading ratio measured by the weight increase and H pressure drop after hydrogenation was ~**1.5÷2 H per metal atom (~**1.3÷1.7 wt%H). (**d**) Enlarged segment of the Fig. (**b**) showing the sample temperature increase by ~**3 K** in response to the H absorption.

In spite of the high loading ratio of H to metal (**1.5÷1.6**), comparable with those measured for supercritical amounts of NdFe, the amount of heat produced by the samples with subcritical masses was almost undetectable. Enlarged fragments of the sample temperature evolution (Figs. 5, **c** and **d**) show the temperature increase ranging between 3 and 5 K in response to the hydrogenation that resulted in the fragmentation of the films into small pieces (Fig. 6, **a**) similar to those formed after hydrogenation of supercritical amounts of NdFe (Fig. 6, **b**).

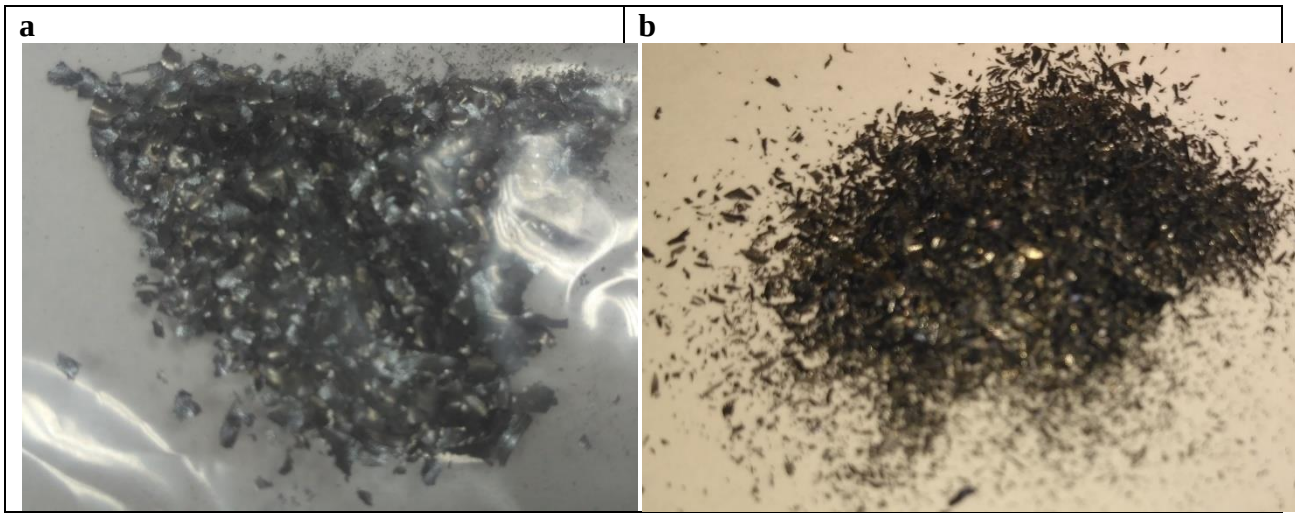

Figure 6. Fragmentation of the NdFe films into small pieces after hydrogenation of subcritical (**a**) and supercritical (**b**) amounts of NdFe.

In order to measure directly the amount of heat produced during the hydrogenation of NdFe and to understand better its kinetics, the fresh NdFe10 samples were sent for a precise calorimetric analysis by the Differential Scanning Calorimetry method to the Physisc&Technology Institute of Metals and Alloys (Kiev). The results are presented in the following section.

5. Calorimetry of NdFe10 films under hydrogenation in DCS installation

Differential scanning calorimetry or **DSC** is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time (*similar to the conditions in our installations I and II*).

Fig. 7 shows the results of heating the small NdFe10 samples (**11.9** and **18.8** mg) in the pure Ar atmosphere (red curves) and in the mixed atmosphere of H and He (blue curves). In the first case, the lower red curve shows zero weight gain, which means that Ar is not absorbed by the sample, as expected. The upper red curve shows one small exothermic peak at 510 ^{o}C and a larger

endothermic peak at 676 ºC. The former corresponds to the crystallization of amorphous phase of NdFe, while the latter corresponds to the melting of NdFe alloy.

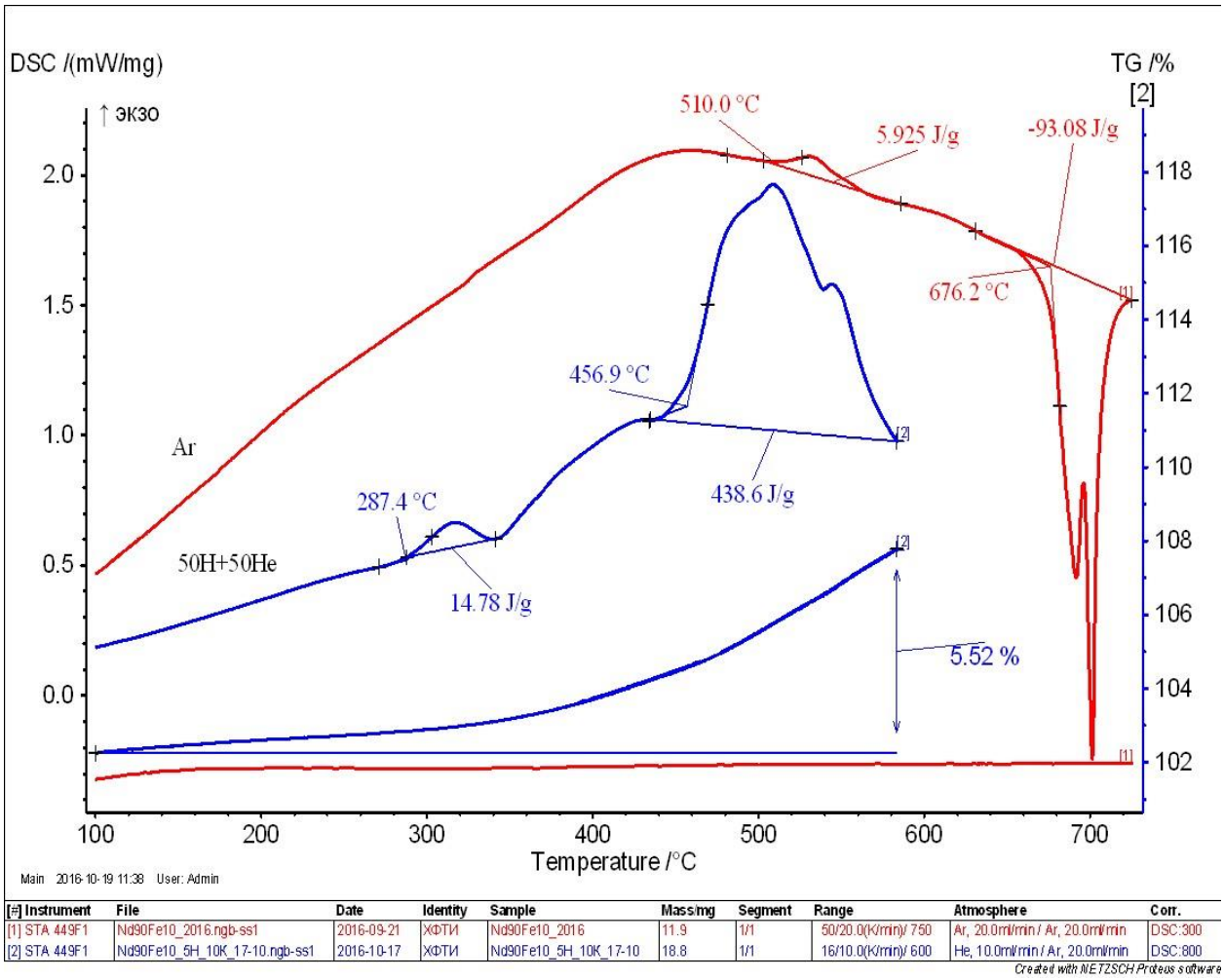

Figure 7. DSC of NdFe10 samples in the Ar (11.9 mg; heating rate 20 K/min - red curves) and H/He atmosphere (18.8 mg; heating rate 10 K/min - blue curves).

The lower blue curve shows the weight % increase of the sample due to the H absorption, which amounts to ~1wt% at the temperature of the first exothermic peak on the upper blue curve (14.78 J/g) and to 5.52 wt% at the temperature of the second and much more powerful exothermic peak (438.6 J/g). From these data, one can evaluate the amount of heat released in the first and in the second reaction per gram of absorbed hydrogen: Q_1 = 1500 J/g and Q_2 = 9800 J/ g.

5. Discussion

Based on the calorimetric data on the H absorption by NdFe10, one can evaluate the amount of heat that is **expected to be produced** by 2.3713 g of NdFe10 in the installation II at the absorption ratio 1.36 wt% measured by the H pressure drop during H absorption (see Fig. 3).

The low temperature reaction with Q_1 = 1500 J/ g would have resulted in production of Q_1×2.3713×0.0136 = **48 J** of energy that could heat 2.3713 g of NdFe and 1.6225 g of Cu by **31**

K in the adiabatic regime (with no dissipation of energy). Taking into account a probable heat dissipation, this could explain the appearance of small ~**3÷5 K** peaks in the experiments with *subcritical masses* of NdFe (Fig. 5).

The high temperature reaction with Q_2 = 9800 J/ g would have resulted in production of Q_2×2.3713×0.0136 = **315 J** of energy that could heat 2.3713 g of NdFe and 1.6225 g of Cu by **266 K** in the adiabatic regime. However, this is evidently not sufficient to explain the observed heating of the *large* samples up to the melting point of the Cu foil *etc.* (Fig. 3) that required at least **2585 J**, which is an order of magnitude more than the amount of heat expected from the DSC examination of *small* NdFe samples.

6. Conclusions and outlook

A **fierce exothermic reaction** was detected in NdFe films with sufficient degree of amorphous phase, which resulted in the melting of the Cu foil, in which the films have been wrapped, provided that the total mass of the films exceeded the critical value of ~ 1 gram. Bellow the critical mass, the films absorbed hydrogen up to a similar loading ratio ~1.5÷1.6 per metal atom *without a significant rise of their temperature*.

Quantitative analysis have shown that the amount of heat produced in NdFe samples with *supercritical* mass cannot be explained by DSC data on the heat produced in *subcritical* NdFe samples.

Based on the obtained results, we may presume that the observed *abnormal heating* was due to much more powerful reaction such as LENR taking place <u>at the initial stage of hydride formation</u>, when 80÷90% of amorphous phase in the films produced LAVs [1-7] that triggered LENR. Subsequently, as the temperature grows sharply beyond 1000 C, it results not only in the melting of the copper foil (Cu melting point under normal conditions is 1085 C), but also in the crystallization and subsequently melting of the $Nd_xFe_yH_z$ structure (at ~500 C and ~700 C, respectively), which destroys LAVs and stops the LENR. Upon cooling, the material recrystallizes in the form of various hydride phases observed by X ray analysis: NdH_2 (fcc) and $Nd_2Fe_{17}H_{4.8}$ (hcp).

In order to prolong LENR, we need to control the film temperature so that it would be **self-sustaining** (that may explain the need for a critical mass), and on the other hand it would not **run away** and destroy the reaction structure as it did in our experiments so far. <u>This problem needs further investigations.</u>

The NdFe structure explored in the present study may be not the only one that could provide the necessary conditions for the LAV induced LENR. In spite of a huge body of investigations of materials connected to the *hydrogen storage problem*, they have not been focused on the

investigation of the *energy production* under hydrogenation. In the cases when abnormally large enthalpies of hydride formation have been reported, the samples have been destroyed by the reaction, similar to case under investigation in this report. We need to re-investigate some of these materials with a due control of the heat production under hydrogenation.

Among the promising candidates to be investigated are the Ti-Zr-Ni melt-spun alloys that can take various structures ranging from amorphous to quasi-crystalline, Laves phase, etc., which can store large amounts of hydrogen and provide the necessary conditions for the LAV excitation in the hydrogen subsystem.

References

1. V.I. Dubinko, P.A. Selyshchev and F.R. Archilla, *Reaction-rate theory with account of the crystal anharmonicity*, **Phys. Rev**. **E** 83 (2011**),**041124-1-13
2. V.I. Dubinko, *Low-energy Nuclear Reactions Driven by Discrete Breathers*, **J. Condensed Matter Nucl. Sci.**, 14, (2014) 87-107.
3. V.I. Dubinko, *Quantum tunneling in gap discrete breathers*, **Letters on Materials**, 5 (2015) 97-104.
4. V.I. Dubinko, *Quantum Tunneling in Breather 'Nano-colliders'*, J**. Condensed Matter Nucl. Sci**., 19, (2016) 1-12.
5. V. I. Dubinko, D. V. Laptev, *Chemical and nuclear catalysis driven by localized anharmonic vibrations*, **Letters on Materials** 6 (2016) 16–21.
6. V. I. Dubinko, *Radiation-induced catalysis of low energy nuclear reactions in solids***, J. Micromechanics and Molecular Physics**, 1 (2016) 165006 -1-12.
7. V. Dubinko, D. Laptev, K. Irwin*, Catalytic mechanism of LENR in quasicrystals based on localized anharmonic vibrations and phasons,* presented at ICCF20, https://arxiv.org/abs/1609.06625