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Peculiarities of hydrogen absorption by melt spun amorphous alloys $\text{Nd}_{90}\text{Fe}_{10}$

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A fierce exothermic reaction was detected in $\text{Nd}_{90}\text{Fe}_{10}$ films with sufficient degree of amorphous phase upon filling them with hydrogen or deuterium, which resulted in the melting of the samples and the Cu foil, in which the samples have been wrapped. Quantitative analysis have shown that the amount of heat produced in large $\text{Nd}_{90}\text{Fe}_{10}$ samples in our experiments is $80\div 100$ kJ per g of hydrogen, which cannot be explained by DSC data on the heat produced in small samples under different heating-cooling balance. Possible reasons for the discrepancy are discussed including low energy nuclear reactions taking place at the initial stage of hydride formation.

Keywords: hydrogen storage, amorphous alloys, exothermic reactions.

При гідруванні швидко загартованих плівок $\text{Nd}_{90}\text{Fe}_{10}$ з великим ступенем аморфізації виявлена сильна екзотермічна реакція, яка призводить до плавлення зразків і мідної фольги, в якій загорнуті зразки. Аналіз показав, що питома кількість тепла, що виділяється у великих зразках $\text{Nd}_{90}\text{Fe}_{10}$ в наших експериментах, на порядок перевершує питому кількість тепла, виробленого в невеликих зразках методом диференціальної калориметрії. Обговорюються можливі причини розбіжності, в тому числі, із залученням низькоенергетичних ядерних реакцій, що протікають на початковому етапі формування гідридів.

Ключові слова: зберігання водню, аморфні сплави, екзотермічні реакції.

При гидрировании быстро закаленных пленок $\text{Nd}_{90}\text{Fe}_{10}$ с большой степенью аморфизации обнаружена сильная экзотермическая реакция, которая приводит к плавлению образцов и медной фольги, в которую завернуты образцы. Анализ показал, что удельное количество тепла, выделяющееся в больших образцах $\text{Nd}_{90}\text{Fe}_{10}$ в наших экспериментах, на порядок превосходит удельное количество тепла, производимого в меньших образцах методом дифференциальной калориметрии. Обсуждаются возможные причины расхождения, в том числе, с привлечением низкоэнергетических ядерных реакций, протекающих на начальном этапе образования гидридов.

Ключевые слова: хранение водорода, аморфные сплавы, экзотермические реакции.

Introduction

The Nd-Fe alloys are known to readily absorb hydrogen, and this property is especially pronounced for melt spun $\text{Nd}_{80}\text{Fe}_{20}$ alloys that have amorphous structure and can absorb up to 2.4 wt% of hydrogen [1]. The interaction of hydrogen with amorphous metals has been studied extensively [2]. These studies were motivated by both scientific and technological interests, mainly the potential use of amorphous hydrides in hydrogen storage technology. The use of amorphous alloys as an alternative new energy storage material, however, still contains technical difficulties, in terms of limited hydrogen cycling ability, relatively high activation energy, fragileness of the host material after hydrogenation, which need further examinations.

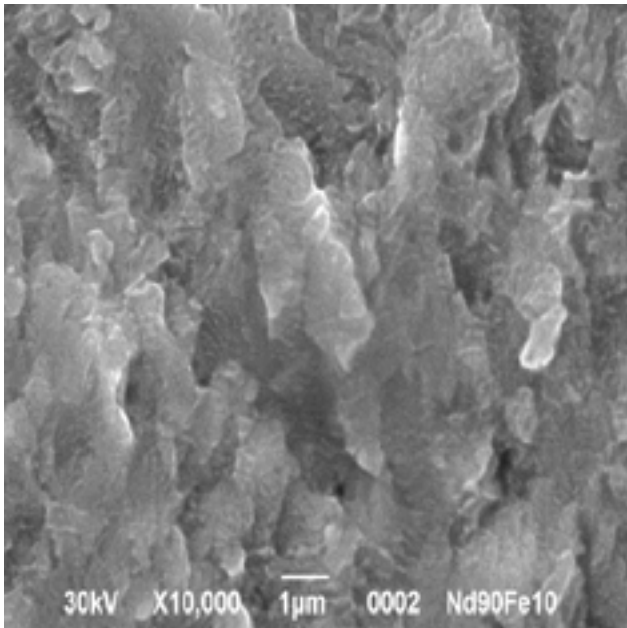
In this paper, we explore the kinetics and thermodynamics of hydriding of melt spun $\text{Nd}_{90}\text{Fe}_{10}$ alloys



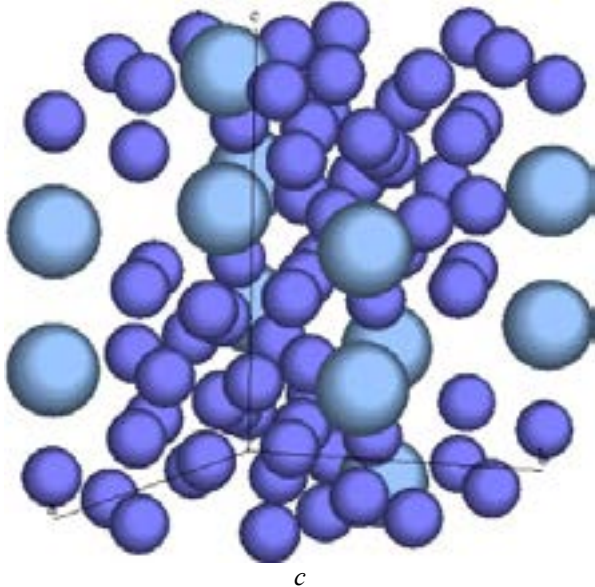
Fig. 1 Installation "Strychka" for fabrication of metal films with a complicated nonequilibrium structure.



a



b



c

Fig. 2 The appearance (a) and surface morphology (b) of the melt spun Nd90Fe10 films. (c) изменить на Fig. 2 The appearance (a), surface morphology (b) and unite cell (c) of the melt spun Nd90Fe10 films.

that have amorphous structure similar to that of $Nd_{80}Fe_{20}$ alloys investigated in [1].

Material fabrication and characterization

The melt spun $Nd_{90}Fe_{10}$ films have been produced in the installation “Strychka” (Fig. 1) by the deposition on a copper wheel rotating with a high speed that provides fast cooling at a rate up to 10^6 K/s. The rotation speed can be varied to obtain a required degree of disorder. The films are several cm in length, several mm in width and ~ 10 to 30 microns in thickness. Their appearance and surface morphology is shown in Fig. 2. One can see that the film surface is extremely rough containing a lot of micron size caverns, which is a common property of this type of materials.

The microstructure of the films consists of a combination between two crystalline phases Nd- α (low temperature hcp phase, $T < 683^\circ C$) and Nd- β (high temperature bcc phase) and amorphous phase Nd_2Fe_{17} , which is shown in Fig. 2c.

The unite cell of amorphous phase Nd_2Fe_{17} entering the initial microstructure of $Nd_{90}Fe_{10}$.

The lattice parameters of the crystalline phases and their relative fraction in respect to the amorphous phase changes slowly with time and is substantially different for the films produced in 2016, 2010 and 2008, as can be seen from the table 1.

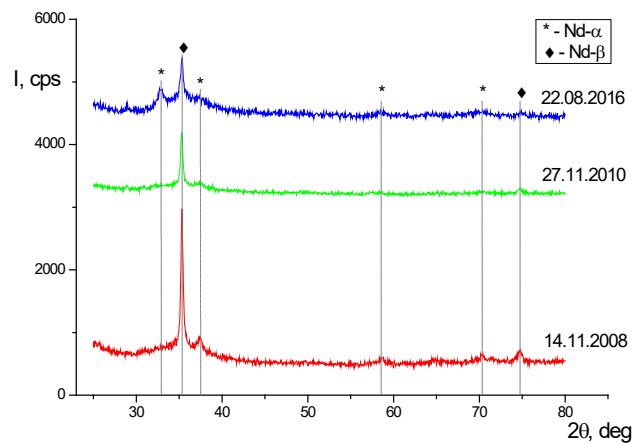


Fig. 3 Diffractograms of three films produced in different years, where the height of the diffraction peak corresponds to the crystalline fraction in a sample $X_c = 11\%$ (blue curve); 19% (green curve) and 47% (red curve).

Fig.3 shows X-ray diffractograms of three different films, where the height of the diffraction peak corresponds to the crystalline fraction in a sample. Let the integral intensity of diffraction lines of a crystalline phase be A_c , and the integral intensity of ‘disordered’ phase be A_d . Then the relative fraction of crystalline phase can be expressed as X_c :

$$X_c = \frac{A_c}{A_c + A_d} 100\%, \quad (1)$$

Table 1

Relative fraction and lattice parameters of crystalline phase in $Nd_{90}Fe_{10}$ films produced in different years and measured in 2016.

Production year	Phase	$X_c = \frac{A_c}{A_c + A_d} 100\%$	Lattice parameters, Å
2008	Nd-α	47	a = 3,659; c = 11,784
	Nd-β		a = 4,171
2010	Nd-α	19	a = 3,656; c = 11,804
	Nd-β		a = 4,170
2016	Nd-α	11	a = 3,658; c = 11,801
	Nd-β		a = 4,171

The samples in Fig. 3 correspond to $X_c = 11\%$; 19% and 47%, respectively, and in the following section, we describe the response of samples to a slow heating in the hydrogen atmosphere.

Kinetics and thermodynamics of the hydrogen absorption by the samples

Hydrogenation of samples with $X_c = 11\%$ and $X_c = 19\%$ was done under hydrogen pressure ranging from 0.2 to 3.4 bar and temperature increased gradually by electric heater. Active hydrogen absorption usually started slightly below or above 300 °C, and its rate and character depended on the hydrogen pressure. Above ~ 1 bar, hydrogenation was accompanied by a substantial heating of the samples, which resulted in the sample melting. An extreme example for the initial pressure of 3.4 bar is shown in Fig. 4. One can see an instant drop of pressure accompanied by a fierce

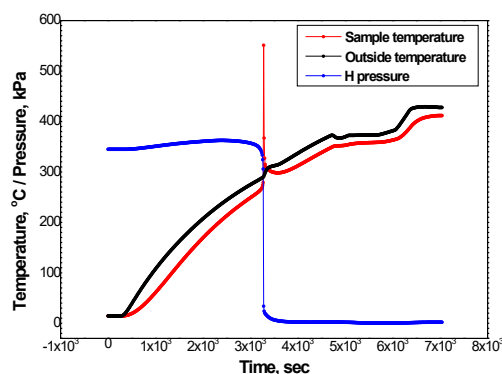


Fig. 4 $Nd_{90}Fe_{10}$ films with $X_c = 11\%$ of a mass 2.3713 g wrapped in a Cu foil of a mass 1.6225 gram. The loading ratio measured by the H pressure drop after hydrogenation was ~1.6 H per metal atom (~1.36 wt% H). ‘Outside temperature’ is measured at 2 mm distance from the external ceramic wall of the reactor.

exothermic reaction resulting in a sample heating spike. Duration of the heating spike was about 40 seconds, while the maximum registered temperature was 570 °C, which appears to be an underestimate.

Examination of the resulting appearance of the NdFe alloy, which has been wrapped in a Cu foil before the testing (Fig. 5.), shows that the alloy and the Cu foil have melted together around the thermocouple, which indicates that the maximum temperature was higher than 1000 °C, since the melting temperature of $Nd_{90}Fe_{10}$ is 685 °C and the melting temperature of Cu is 1085 °C.

XRD analysis of the hydrogenated material has shown that all the amorphous phase has transformed into two crystalline hydride phases, fcc NdH_2 and hcp $Nd_2Fe_{17}H_{4.6}$ shown in Fig. 6.

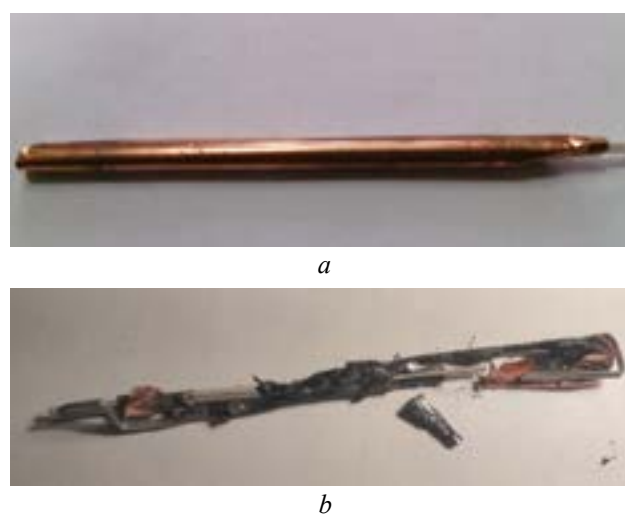


Fig. 5 $Nd_{90}Fe_{10}$ films with $X_c = 11\%$ of a mass 2.3713 g wrapped in a Cu foil of a mass 1.6225 gram before (a) and after (b) hydrogenation at a rate shown in Fig. 4.

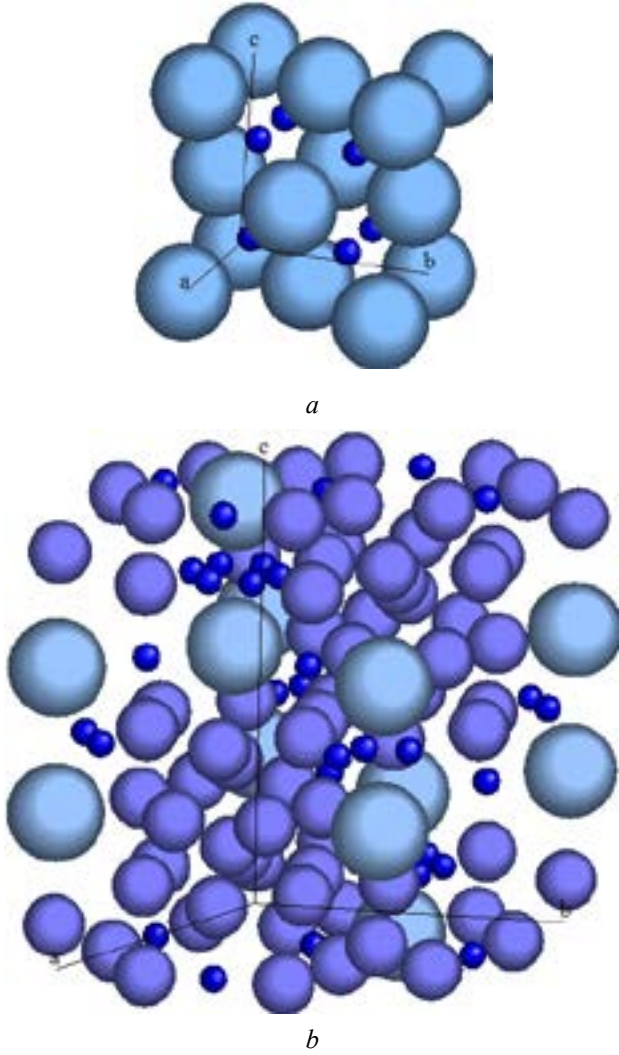


Fig. 6 Unit cells of fcc NdH₂ (left) and hcp Nd₂Fe₁₇H_{4.6} (right) phases. NdH₂ is a dominating phase containing a majority of absorbed hydrogen. *изменить на* Fig. 6 Unit cells of fcc NdH₂ (a) and hcp Nd₂Fe₁₇H_{4.6} (b) phases. NdH₂ is a dominating phase containing a majority of absorbed hydrogen.

The amount of heat produced by hydrogenation

The energy required for heating the Nd₉₀Fe₁₀ films and Cu foil from 270 to 1100 °C and for melting the Cu foil is given by

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

$$\Delta T = 830 \text{ K}, \quad (2)$$

where $m_{NdFe} = 2.3713 \text{ g}$, $m_{Cu} = 1.6225 \text{ g}$ and

$$C_{NdFe} = 0.214 \frac{\text{J}}{\text{g} \cdot \text{K}}, \quad C_{Cu} = 0.385 \frac{\text{J}}{\text{g} \cdot \text{K}}$$

are the

masses and the heat capacities of NdFe films and Cu foils, respectively, $Q_{Cu}^{melt} = 207 \text{ J/g}$ is the latent heat of melting of Cu.

The energy required to heat the walls of ceramic (Al₂O₃) chamber tube around the samples from 295 to 308 °C is given by

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

$$\Delta T = 13 \text{ K}, \quad (3)$$

where $m_{Al_2O_3} = 93.5 \text{ g}$ and $C_{Al_2O_3} = 1105 \text{ J/(g} \cdot \text{K)}$

are the mass and the heat capacity of the Al₂O₃ 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:

$$\Delta Q_{tot} = \Delta Q_{NdFe+Cu}(830 \text{ K}) + \Delta Q_{Al_2O_3}(13 \text{ K}) = 1263 \text{ J} + 1322 \text{ J} = 2585 \text{ J}, \quad (4)$$

Dividing this heat by the amount of absorbed hydrogen that caused the reaction, 0.031 g, one obtains a specific heat of hydrogen absorption as

$$Q_H = 2585 \text{ J} / 0.032 \text{ g} = 80170 \text{ J/g}, \quad (5)$$

which will be compared with a direct DSC measurements in the following section.

Differential scanning calorimetry of Nd₉₀Fe₁₀

Differential scanning calorimetry (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. The temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time.

Fig. 7 shows the results of heating the small Nd₉₀Fe₁₀ 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 °C and a larger endothermic peak at 676 °C. The former corresponds to the crystallization of amorphous phase of Nd₉₀Fe₁₀, while the latter corresponds to the melting of Nd₉₀Fe₁₀ alloy.

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

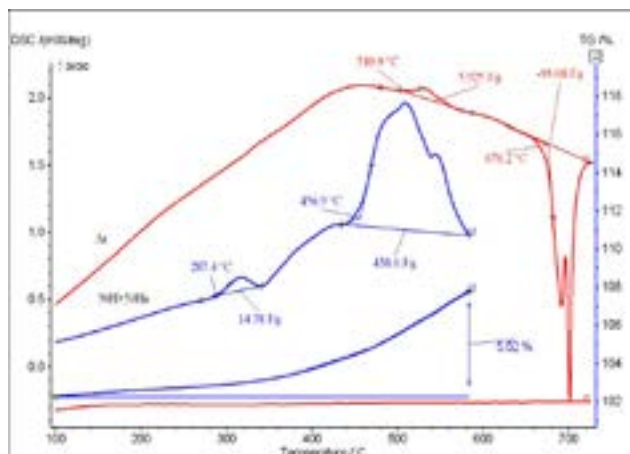


Fig. 7 DSC of $Nd_{90}Fe_{10}$ samples in the Ar (11.9 mg; heating rate 20 K/min - red curves) and H/He atmosphere (18.8 mg; heating rate 10 K/min - blue curves).

second reaction *per gram of absorbed hydrogen*: $Q_1 = 1500$ J/g and $Q_2 = 9800$ J/g.

Thus, a specific heat of hydrogen absorption in a DCS experiment is given by $Q_1 + Q_2 = 11300$ J/g, which is almost an order of magnitude less than 80170 J/g estimated in our hydrogenation experiments. It means that the underlying reactions taking place in our experiments should be different from those taking place in a DSC installation.

Deuterium absorption by $Nd_{90}Fe_{10}$ mixed with Cu powder

In this experimental setup, we used deuterium atmosphere and attempted to prolong the deuterium absorption stage and avoid melting of the samples by mixing a powder produced from $Nd_{90}Fe_{10}$ with Cu powder and packing the mixture in a Cu tube. In this way, deuterium access to $Nd_{90}Fe_{10}$ was delayed, and the heat produced under hydrogenation in 1.722 g of $Nd_{90}Fe_{10}$ was distributed over all the material of the mixture and the tube with a total mass of 14.372 g. As a result, the sample temperature T_s did not exceed the furnace temperature T_f by more than 5 °C even during the most active deuterium absorption stage that lasted 40 min (Fig. 8), and the overall time when $T_s > T_f$ was about 15 min. Taking into account the heat balance, one can estimate the total produced heat as 2190 J and the specific heat of hydrogen absorption as 102100 J/g, which is close to our estimate 80170 J/g of the specific heat produced under hydrogenation of pure $Nd_{90}Fe_{10}$ samples.

Discussion

Specific heat produced per one gram of absorbed hydrogen or deuterium in our reactor conditions seems to be much higher than that in DSC installation, which means that the underlying reactions should be different. We have tested samples with a mass in the gram range, while DSC samples were ~ 10 mg, which could imply different heating-cooling balance affecting the reaction route.

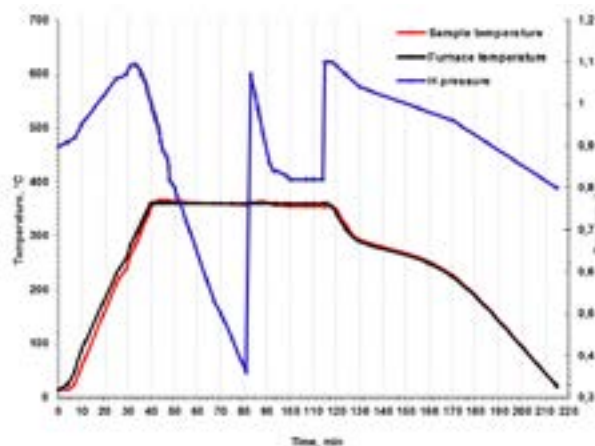


Fig. 8 $Nd_{90}Fe_{10}$ powder with $X_c = 11\%$ of a mass 1.7222 g mixed with Cu powder of a mass 2.2526 g, wrapped in a Cu foil of a mass 0.43955 g and packed in a Cu tube of a mass 9.565 g. The loading ratio measured by the weight gain after D absorption was ~ 1.1 H per metal atom (~ 1.834 wt% D).

One of the possible reasons for abnormal heat production is known to be the low energy nuclear reactions (LENR) that take place in heavily deuterated palladium [3] or hydrogenated nickel [4] under nonequilibrium conditions. These reactions can be triggered by localized anharmonic vibrations (LAVs) created at sufficiently high temperatures at special places of the disordered lattice [5-9]. Another driving mechanism of the LAV creation is irradiation that can displace atoms from equilibrium positions far enough to induce anharmonic vibration mode [10]. In view of that, it is desirable to fill the alloys with hydrogen or deuterium or the H-D mixture directly under irradiation and to measure their response to such combined treatment.

Conclusions and outlook

A fierce exothermic reaction was detected in $Nd_{90}Fe_{10}$ films with sufficient degree of amorphous phase upon filling them with hydrogen or deuterium, which resulted in the melting of the samples and the Cu foil, in which the samples have been wrapped.

Quantitative analysis have shown that the amount of heat produced in $Nd_{90}Fe_{10}$ samples in our experiments cannot be explained by DSC data on the heat produced in small samples.

One of the possible explanations of this discrepancy is based LENR taking place *at the initial stage of hydride formation*, when 80-90% of amorphous phase in the films produced LAVs [5-10] that triggered LENR. Subsequently, the amorphous phase transforms to crystalline hydrides where the LAVs do not form, which stops the LENR. Upon cooling, various hydride phases are observed by X ray analysis: NdH_2 (fcc) and $Nd_2Fe_{17}H_{4.8}$ (hcp).

In order to initiate LENR, it is desirable to make the

hydrogenation directly under irradiation and to measure the response to such combined treatment. This problem needs further investigations.

The Nd-Fe 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. There is a need to re-investigate some of these materials with a due control of the heat production under hydrogenation and external triggering.

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.

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