

Corrosion resistance of neodymium and dysprosium hydrides

Natalia Karakchieva, Galina Lyamina, Elena Knyazeva, Victor Sachkov, Irina Kurzina, Alina Pichugina, Alexander Vladimirov, Ludmila Kazantseva, and Anna Sachkova

Citation: [AIP Conference Proceedings](#) **1899**, 030008 (2017);

View online: <https://doi.org/10.1063/1.5009853>

View Table of Contents: <http://aip.scitation.org/toc/apc/1899/1>

Published by the [American Institute of Physics](#)

Corrosion Resistance of Neodymium and Dysprosium Hydrides

Natalia Karakchieva^{1,2,3, a)}, Galina Lyamina^{4, b)}, Elena Knyazeva^{4, c)}, Victor Sachkov^{1, d)}, Irina Kurzina^{1, e)}, Alina Pichugina^{1, f)}, Alexander Vladimirov^{1, g)}, Ludmila Kazantseva^{1, h)}, Anna Sachkova^{4, i)*}

¹National Research Tomsk State University, Lenin Avenue 36, 634050 Tomsk, Russian Federation

²Siberian Research Institute of Agriculture and Peat, Gagarin Street 3, 634050 Tomsk, Russian Federation

³Derzhavin Tambov State University, Internatsionalnaya Street 3, 392000 Tambov, Russian Federation

⁴National Research Tomsk Polytechnic University, Lenin Avenue 30, 634050 Tomsk, Russian Federation

^{a)} kosovanatalia@yandex.ru

^{b)} lyamina@tpu.ru

^{c)} knyazeva@tpu.ru

^{d)} itc@spti.tsu.ru

^{e)} kurzina99@mail.ru

^{f)} alina.com9@mail.ru

^{g)} fizickemsu@mail.ru

^{h)} lyudmilka-malinka@mail.ru

ⁱ⁾ Corresponding author: as421@yandex.ru

Abstract. This paper describes the methods of obtaining hydrides of rare earth elements such as dysprosium and neodymium. The properties and corrosion resistance of these elements are investigated. A synthesis method of monophasic dysprosium and neodymium dihydrides is presented. Synthesized dihydrides are agglomerates with an average size of 3-50 μm and are formed by crystalline grains of a nanometer size. BET specific surface area, morphology, elemental analyses and composition of samples have been studied. Corrosion stability in aqueous solutions of hydrochloric acid and sodium hydroxide were studied. It was determined that both hydrides undergo hydrolysis in acid and alkaline mediums. Neodymium hydride is more stable to corrosion than dysprosium hydride, which is proved by its longer exposure to aggressive medium to hydrides. The formation of insoluble /poorly soluble products of corrosion can make a significant contribution to the process of powder dissolution.

INTRODUCTION

The development of new generation materials with exceptional properties is currently among the major goals of material and engineering science [1-4]. Of special interest are advanced industrial materials based on rare earth elements [1]. One of the novel and promising lines of research in this field focuses on the application of materials with rare earth metals (REM) as potential precursors in additive manufacturing. Additive manufacturing has attracted a lot of attention [6-9]. This technology comprises a wide range of emerging technologies that fabricate three-dimensional objects directly from digital models through an additive process, typically by depositing and “curing in place” successive layers of a material [10]. Additive manufacturing or technologies of layer-by-layer synthesis, based on the methods of powder metallurgy and alloys [11], has become the most dynamically developing direction of/in engineering production [12,13], which makes it possible to manufacture products with gradient operational properties based on the physical processes of heterophase powder metallurgy [12,13].

Considerable effort is being directed toward developing new compositions of powder alloys, and investigating how the size of particles impacts on the properties of obtained products. This field is increasingly receiving interest from different manufacturing sectors including the sector of medical devices. Using advanced

manufacturing techniques can help achieve design flexibility, reduced processing costs, reduced waste, and the opportunity to fabricate easily custom-shaped details. Consequently, these techniques are likely to replace machining and casting of metal alloys in the manufacture of devices [9].

One more promising application of REM is obtaining special steels and alloys in nuclear engineering, microelectronics, and radio engineering. Additives on the base of REM, even in small amount, can significantly improve structural, plastic, resistant, and impact elasticity characteristics of materials [5, 14].

Production of high energy permanent magnets based on REM is one of the leading branches of world industry [15]. Ivanov notes [16] that the saturation of metallic materials (Nb, Dy, V etc.) with hydrogen can simplify their grinding. Moreover, using modifying additives as hydrides (e.g. heavy REM) in the composition of magnet alloys helps achieve even distribution of additives, which significantly improves the physical and operating characteristics of these materials.

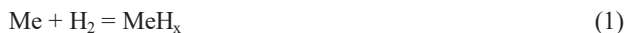
Due to the difficulties in the production of Nd, Pr and Dy from initial ore, technologies of magnet alloy processing are being developed to allow metal extraction. In these technologies, frequent use is given to hydrides and fluorides of REM. Consequently, the investigation of properties and methods for producing REM hydrides is an urgent problem, the solution of which will facilitate the development of technologies for the production of nanostructured alloys, ligatures, and other materials.

Of special attention is the investigation of how ambient conditions, especially humidity and ambient temperature, impact on the reliability and stability of initial compounds to predict properties in final product in operation. In this connection, the aim of this work is obtaining of rare earth metal hydrides, particularly hydrides of dysprosium and neodymium, and study their corrosion properties.

EXPERIMENTAL PART

Materials and Methods

Dysprosium and neodymium hydrides were synthesized in laboratory conditions according to the chemical equation:



The charge of metallic neodymium or dysprosium sample with mass $M=5$ g was placed into a quartz reactor (with volume $V=1$ liter) and subjected to annealing in a hydrogen flow with the use of an industrial hydrogen generator. The annealing was conducted according to the following scheme: first, the sample was heated to 370°C during 30 minutes at hydrogen flow rate of 0.5 L/min ; then, this sample was heated to 450°C during 90 minutes at hydrogen flow rate 1 L/min (rates of heating were about 12°C/min and 0.9°C/min respectively); and finally, it was kept at temperature 450°C during 60 minutes at hydrogen flow rate 2 L/min .

The composition of the obtained products was investigated by the X-ray diffraction analyses (XRD) using a Rigaku Miniflex 600 Diffractometer, and $\text{CuK}\alpha$ radiation. Typical runs were performed with a range of $10\text{--}90^\circ$ (2θ) with a step of 0.02° and the scanning speed of $2^\circ/\text{min}$. The identification of diffraction peaks and the calculation of coherent scattering areas were conducted with the JCPDS database.

The BET specific surface area of the obtained samples was measured by the automated Micromeritics 3Flex Surface Characterization Analyzer.

The surface morphology was studied with a Hitachi TM3000 Tabletop Scanning Electron Microscope at an accelerating voltage of 15 kW in conditions of charge reduction mode (electron gun pressure: 0.5 kPa , sample chamber pressure: $0.03\text{--}0.05\text{ kPa}$) equipped with a Bruker Quantax 70 EDS system for elemental analyses.

The corrosion stability of samples was tested by treating the samples in acid and alkaline aqueous solutions (0.1 M of HCl , NaOH), and then estimated through changing the mass of the substance (monitoring the mass loss of the samples). Mass changes were estimated with the time interval $\tau = 24\text{ h}$ (i.e. after 24 hours for 1st sample, after 48 hours for 2nd sample after 72 hours for 3rd sample, etc.). To increase the accuracy of measurements, nine parallel samples with mass = 0.2 g for each studied time interval have been studied.

A SALD-7101 Laser Diffraction Particle Size Analyzer from Shimadzu was used to measure the size of powder particles. This analyzer allows measuring particle size distribution in the range from 0.01 to $300\ \mu\text{m}$. For this purpose, the powder sample was placed into a mixing chamber with dispersion liquid (hydrochloric acid solution with a concentration of 0.1 M), and dispersed for 120 min. using an ultrasonic device. The measurements were performed in a flow-type cell with a 15-minute time interval.

For estimation of particle size distribution an equivalent spherical size (diameter) was used, which is defined as the diameter of a sphere with the same weight as a real particle. Microscope metalgraphic EU METAM PB 21-1 was used to observe the changes in the metal surface.

Error estimation in mass change of samples after acid and alkaline treatment was calculated as a variation coefficient (Sr , %) according to the following equation:

$$Sr = \frac{SD}{m_{av}} \cdot 100\% , \quad (2)$$

where SD is standard deviation and m_{av} is an average sample mass.

RESULTS AND DISCUSSION

Structure and morphology characterization of dysprosium and neodymium hydrides

Figures 1(A) and 1(B) present X-ray diffraction data on the synthesized samples of dysprosium and neodymium hydrides. According to the XRD analyses, the samples represent monophasic products identified as DyH₂ (Figure 1A) and NdH₂ (Figure 1B). Both have crystallographic characteristics (Table 1).

TABLE 1. Crystallographic characteristics of synthesized dysprosium and neodymium hydrides. CSR - coherent-scattering region.

Composition	a = b, nm	c, nm	CSR, nm	PDF-ICDD*
NdH ₂	5.4617	10.7566	5–16	00-054-0458
DyH ₂	5.1949	5.1949	6–62	03-065-4122

*PDF (Powder Diffraction File) – file in database according to ICDD (The International Centre for Diffraction Data)

The scanning electron microscopy shows that both samples are composed of irregular shape particles in the form of debris with the size of 3-50 μm for NdH₂ and 3-30 μm for DyH₂. This debris form agglomerates. The BET surface area of the NdH₂ and DyH₂ samples consists of 9.02 m^2/g and 0.34 m^2/g , respectively.

The elemental analysis of the obtained hydrides showed that the NdH₂ sample contains 98±1 % *weight* of Nd, and the sample DyH₂ contains 99±1 % *weight* of Dy, which is in a good agreement with the molecular formula of compounds.

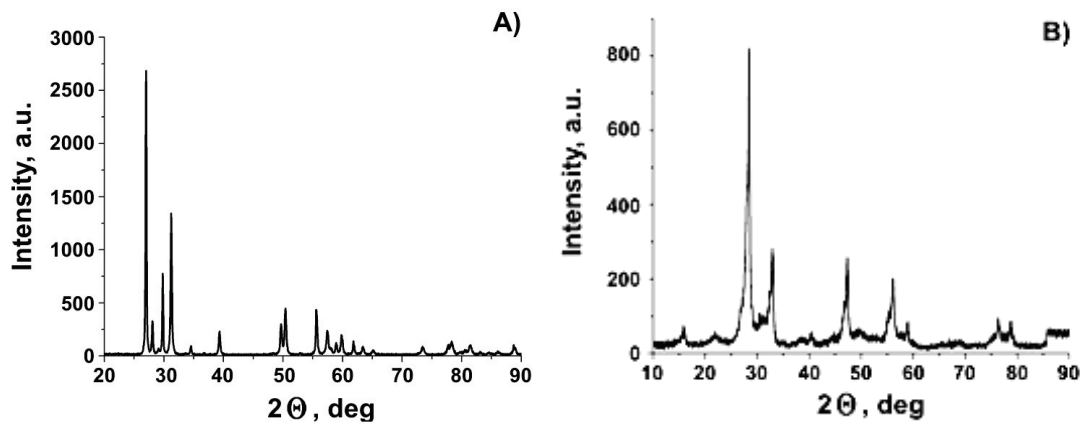


FIGURE 1. XRD patterns of synthesized samples: A) NdH₂; B) DyH₂

Corrosion stability

Corrosion stability of NdH₂ and DyH₂ were investigated in acid and alkaline aqueous solutions of HCl and NaOH with concentration $C=0.1\text{ M}$. Figure 2 shows the results of mass change measurements in the powder samples. The treatment time was $\tau = 24\text{ h}$ and τ varied from 0 to 9.

Figure 2 (curves 1) shows that in acid media both powders underwent corrosion, and as a result each sample lost from 45% to 65% of their mass within the predetermined time. For the NdH₂ sample, weight loss equaled 0.112g from the initial mass of 0.2 g, and for DyH₂ the mass loss was 0.127 g from the initial - 0.2 g. Thus, the powder sample of NdH₂ demonstrated considerably higher corrosion stability at the final stage of measurements as compared to the DyH₂ sample.

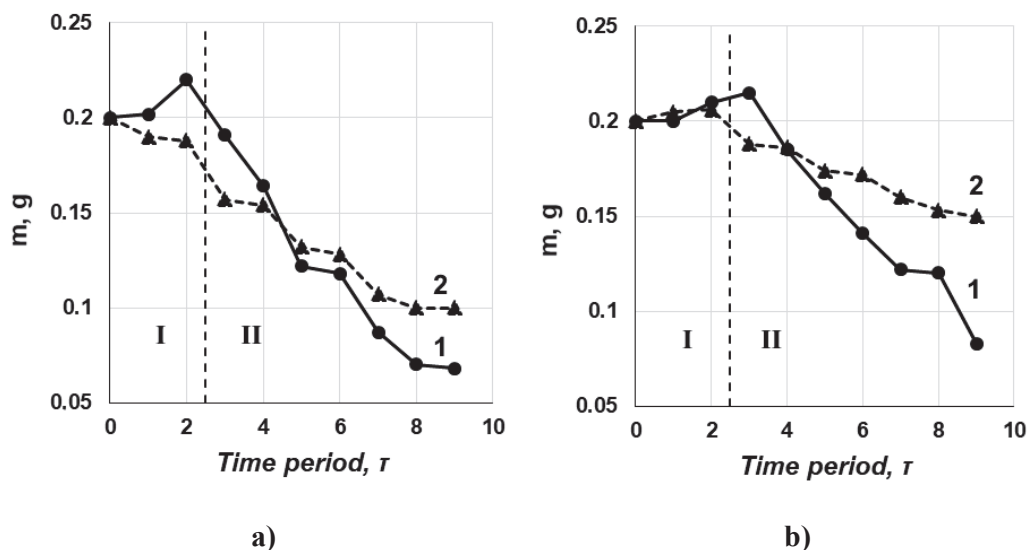


FIGURE 2. Mass change measurements of powder samples DyH₂ (a) and NdH₂ (b) in aqueous solutions of 0.1M of HCl (1) and 0.1M of NaOH (2). 0 – 0h; 1 – 24h; 2 – 48h; 3 – 72 h; 4 – 96h; 5 – 120h; 6 – 144h; 7 – 168h; 8 – 192h; 9 – 216h

In alkaline media (Figure 2, curves 2), the tendency remained the same and became even more profound. On the 9th day of treatment, the neodymium hydride lost about 0.05 g of its initial weigh of 0.2 g whereas for the dysprosium hydride sample weight loss was twice as much (0.095 g of 0.2 g).

As shown in Figure 2, the curves of powder dissolution both in acid and alkaline media can be conditionally divided into two areas: I – sample mass increase, which corresponds to the formation of oxide film; II – active dissolution. Figures 2a and 2b show that such a tendency in acid medium is more profound than in alkaline medium.

The coefficients of variation (*Sr*, %) were estimated for the mass change of powder samples after their treatment in corrosion media (acid and alkali). The coefficients of variation for parallel experiments were changed at an interval of 9 to 22%. Also, the analyses of coefficients for the first and ninth samples revealed the following tendency: the experimental error is lower if a powder sample is treated in corrosion medium for one day rather than nine days (Table 2). This is apparently connected with the formation of insoluble or poorly soluble products of corrosion, which have a significant impact on the process of powder dissolution.

TABLE 2. Change in mass of powder dysprosium and neodymium hydrides samples after acid/alkaline treatment.

Powder composition	Sample number	HCl (0.1 M)		NaOH (0.1 M)	
		Sample mass, g	Coefficient of variation, %	Sample mass, g	Coefficient of variation, %
DyH ₂	1	0.205	9	0.193	9
	9	0.073	22	0.106	14
NdH ₂	1	0.199	9	0.202	8
	9	0.088	19	0.150	10

Optical images of the powder samples of dysprosium and neodymium hydrides (before acid/alkaline treatment; after 216-hour treatment in 0.1 M HCl aqueous solution; after 216-hour treatment in 0.1 M NaOH aqueous solution) were taken.

As shown, it is observed significant amount of oxidized forms on surface of samples which were treated in acid medium. Also, the morphology characteristics of dysprosium and neodymium hydrides differ from each other. Particles of neodymium hydride powder are agglomerated into large aggregates, while powder of dysprosium hydride is less agglomerated and covered with a thick oxide film. To investigate the corrosion process, observations how the particle (aggregates) size changing occurs in solutions were done. For this purpose, laser diffraction was used to measure particle size distributions during the first 120 minutes after placing the powder into acid medium.

Figure 3 presents how an average equivalent spherical diameter (d_{av} , μm) of powders changes in solution of 0.1M HCl. Using ultrasound in the analysis prevents the formation of oxidation products that weakly adhere to a particle surface.

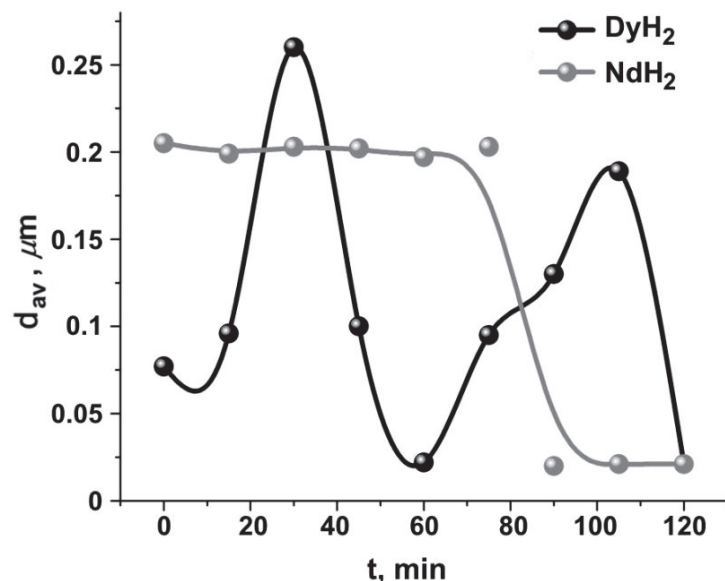


FIGURE 3. Changing of equivalent spherical diameter (d_{av} , μm) of dysprosium and neodymium hydrides powder in aqueous solution of $0.1M$ HCl

Figure 3 shows that the size of dysprosium hydride particle is unstable in solution. This is typical of agglomeration-deagglomeration processes, which appear when oxidation products are either formed or removed from a surface. Neodymium hydride particles, conversely, have a constant size for a long time, and only in the 80th minute of their stay in aggressive medium under ultrasound influence, they start to decrease in size. In alkaline medium at optical images is seen that neodymium hydride powder is changed slightly in comparison with dysprosium hydride, which is covered with thick layer of hydrolysis products in alkaline medium.

CONCLUSIONS

In this work, the method of neodymium and dysprosium hydride production has been described. The obtained hydrides were investigated for such properties as BET surface area, morphology, and elemental composition. The X-ray diffraction analyses and the Scanning Electron Microscopy showed that the synthesized compounds contain no extrinsic phases and represent agglomerates with the size from 3 to 30 μm and from 3 to 50 μm for dysprosium and neodymium hydrides, respectively.

The neodymium and the dysprosium hydrides were examined for their corrosion stability in acid ($0.1M$ HCl) and alkaline ($0.1M$ NaOH) solutions. Both hydrides in both mediums (acid and alkaline) are hydrolyzed; however, NdH₂ is more stable to corrosion than DyH₂. This is especially evident through a more prolonged interaction with the corrosion medium. The degree of hydrolyses in HCl for NdH₂ powder accounts for $\approx 55\%$, and for DyH₂ $\approx 65\%$. In the acid medium, powder corrosion goes through the passivation stage, which is accompanied by the consolidation of particles in the case with the neodymium hydride.

In an alkaline medium the tendency is preserved ($\approx 25\%$ and 48% mass loss for NdH₂ and DyH₂, respectively), which indicates that in this medium the corrosion stability of hydrides is more profoundly expressed.

ACKNOWLEDGEMENTS

The results were obtained within the framework of the state task of the Ministry of Education and Science of the Russian Federation, project No. 10.3031.2017 / 4.6.

REFERENCES

1. D N. Brown, *IEEE Trans. Magn.* **52**, 1 (2016).

2. N. Kosova, V. Sachkov, I. Kurzina, A. Pichugina, A. Vladimirov, L. Kazantseva and A. Sachkova, *IOP Conf. Ser.: Mater. Sci. and Eng.* **112**, 012039-1–012039-5 (2016).
3. B. P. Bewlay, S. Nag, A. Suzuki and M. J. Weimer, *Mater. High Temp.* **33**, 549–559 (2016).
4. S. Ferrari, M. C. Mozzati, M. Lantieri, G. Spina, D. Capsoni and M. Bini, *Sci. Rep.* **6**, 27896 (2016).
5. K. P. Belov, *Soros Educ. J.* **1**, 94–99 (1996), (In Russian).
6. P. Sun, Z. Z. Fang, Y. Xia, Y. Zhang and C. Zhou, *Powder Technol.* **301**, 331–335 (2016).
7. S-L. Lu, H-P. Tang, M. Qian, Q. Hong, L-Y. Zeng and D. H. StJohn. *J. Cent. South Univ.* **22**, 2857–2863 (2015).
8. Boyer R .R, Williams J C, Wu X, Clark L P. *Titanium Powder Metal. Sci. Technol. Appl.* 497–514 (2015).
9. A. T. Sidambe. *Mater.* **7**, 8168–8188 (2014).
10. S. L. N. Ford, *J. Int. Commer. Econ.* (Published electronically, September 2014). <http://www.usitc.gov/journals>.
11. E. A. Shestakova, R. M. Yanbaev, F. M. Yanbaev and A. Y. Galdina, *The II International Conference "Additive Technology: Present and Future"*Part.1, Moscow, Russia, (2016) (In Russian),.
12. T. J. Horn and O. L. Harrysson, *Sci. Prog.* **95**, 255–282 (2012).
13. V. I. Kotlyarov, V. T. Beshkarev, V. E. Kartcev, V. V. Ivanov, A. A.O. Gasanov, et.al., *The II International Conference "Additive Technology: Present and Future"*(In Russian), Part.1, Moscow, Russia, (2016).
14. A. Simon., *Angewandte Chemie – Int. Ed.* **51**, 4280–4286 (2012).
15. V. Sofronov, Z. Ivanov, Y. Makaseyev and T. Kostareva, *Key. Eng. Mater.* **683**, 345–352 (2016).
16. C. B. Magee, J. Lui and C. E. Lundin, *J. Less-Common Met.* **78**, 119–138 (1981).