ABSTRACT

for the degree of a Doctor of Philosophy (PhD) in specialty 6D072300 – "Applied Physics"

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Changes in the structural and phase state of the sorption-active material based on the Ti-Al-Nb system during thermal cycling

Currently, there is an increased interest in scientific, instrumental and technological aspects around the world in the global transition to hydrogen energy, where the key points are the technologies for production, storage, transportation and extraction of water.

In this regard, this paper is devoted to solving a serious and complex scientific problem related to the development of scientific and applied foundations for the creation of hydrogen storage materials based on the Ti-Al-Nb system for the purposes of safe storage and transportation of chemically pure hydrogen.

Relevance of the Research Topic

Currently, solid-state storage systems based on metal hydrides have shown great potential for storing hydrogen in large quantities. It is metal hydride systems that are the most attractive option for hydrogen storage and stand out for their reliable, compact, and multiply reversible properties. However, the technical and economic feasibility of hydrogen storage systems has not yet been realized, since none of the existing metal hydrides satisfies the main criteria for their practical use. This is mainly due to their low capacity, slow kinetics, and unacceptable hydrogen sorption/desorption temperatures.

The intermetallic alloy synthesis based on titanium in PM is one of the promising directions in obtaining materials for the safe storage of hydrogen. Currently, work is underway to study intermetallic compounds based on titanium aluminides with a high content of niobium, since the role of IMC of the Ti-Al-Nb system as structural materials is increasing every year. Herewith, these IMC of the Ti-Al-Nb system also have a good disposition to absorb hydrogen and can be considered as candidate materials for solving problems of hydrogen storage. The alloys in this system are usually of low density and therefore have a great advantage in achieving a potentially large hydrogen capacity. Among the titanium aluminides, IMC based on B2, Ti_2AlNb, Ti_3Al phases can contain and absorb a sufficiently large amount of hydrogen. In particular, intermetallic based on the Ti_3Al phase can absorb a large amount of hydrogen (4 wt.%). However, the use of such materials as hydrogen accumulators is hindered by their high temperature stability during desorption. The bcc-based phases (B2, Ti_2AlNb) that appear when Nb is added to Ti_3Al can have an even greater ability to absorb hydrogen, since weakly packed bcc structures usually outperform close-packed structures based on fcc and hcp in hydrogen absorption. This is facilitated by the formed nanoscale phases, which have a large number of voids filled with hydrogen atoms.

At the same time, use of alloys of the Ti-Al-Nb system for hydrogen storage requires a large amount of research aimed at studying IMC with a wide range of adjustable properties. The properties and structure of titanium-based IMC are directly dependent on the technological methods of their production, amount of the alloyed component, and ratio between the components in the initial charge. Herewith, there are no data in the scientific and technical literature on the cyclic stability of these materials during multiple sorption/desorption processes. For the technical application of metal hydrides and IMCs, stability of their properties during a long cycle, as well as thermal stability when exposed to elevated temperatures, is necessary. It is clear that depending on the content of alloyed elements, production technology and temperature conditions, it is possible to obtain various hydride systems with the required structure and phase state. However, the working life of metal hydrides and IMC for hydrogen storage can only be determined by simulation tests in the laboratory.

Goal of the Research: to establish patterns of IMC structural-phase state formation of the Ti-Al-Nb system during MA, SPS and thermo cycling sorption by hydrogen.

To achieve the goal, the following **tasks** were defined and solved:

1. Study formation of the phase composition and structure in the powder composition of the Ti-Al-Nb system at MA;

2. Develop a method for obtaining hydrogen storage materials from a powder composition of the Ti-Al-Nb system;

3. Figure out, how SPS affect the formation of the phase composition and structure of the mechanically activated powder composition of the Ti-Al-Nb system;

4. Study experimentally an effect of thermal-cycle process of hydrogen sorption/desorption on the structural-phase state of the IMC of the Ti-Al-Nb system.

Key Provisions for Defense:

1. Formation of the phase composition and structure of the powder composition of the Ti-25Al-25Nb (at. %) system during MA.

MA for 20 min. and 180 min. when accelerating 650 rpm. and 350 rpm accordingly, makes it possible to obtain a powder composition of the Ti-Al-Nb system with a developed defective structure, with macro- and micro-distortions, high specific surface area and reactivity;

2. Features of the structure and phase formation of mechanically activated powder compositions of the Ti-Al-Nb system depending on the temperature of the SPS.

SPS of mechanically activated powder compositions of the Ti-25Al-25Nb (at.%) system for 5 min. and at 1300 ºC leads to the formation of a continuous microhomogeneous, predominantly two-phase (O+B2) structure, with a high content of the orthorhombic NbAlTi2 phase;

3. Significant thermal stability of the structural-phase state and sorption properties of the two-phase (O + B2) alloy of the Ti-25Al-25Nb (at.%) system during thermal cycling.

The two-phase (O + B2) structure of the alloy of the Ti-25Al-25Nb (at. %) system as a result of multiple (10 cycles) high-temperature sorption / desorption processes (500/600 ° C) by hydrogen (1.91 wt.%) does not undergo significant change.

Scientific novelty of the research marks the first time that:

1. A method has been developed for producing hydrogen storage rechargeable IMCs of the Ti-Al-Nb system. The developed method is protected by the patent of the Republic of Kazakhstan No. 5809 dated 01/29/2021 Bull. No. 4;

2. Data have been obtained on the influence of particle sizes of elemental powders in the initial charge on the structure formation of titanium intermetallic compounds during MA and SPS;

3. The features of the formation of the structure and phase composition of the mechanically activated powder composition of the Ti-Al-Nb system during SPS are described and explained;

4. A two-phase (O + B2) alloy of the Ti-Al-Nb system has been obtained, which has a high thermal stability of the structural-phase state and sorption properties (1.91 wt.%).

Research Object:

Powder composition of Ti-Al-Nb system after high-energy treatments and multiple sorption/desorption.

Research Subject:

The IMC formation features of Ti3Al, Ti2AlNb, Nb2Al and B2 in powder composition of the Ti-Al-Nb system during their MA and following SPS, and also effect of thermal-cycle processes of sorption/desorption on structural and phase states and IMC properties of the Ti-Al-Nb system.

Research Methods:

To analyze the structure and phase state of the studied samples, methods of metallographic study using optical, scanning, and transmission electron microscopy, as well as X-ray diffraction analysis were used. To determine the elemental composition, the method of X-ray spectral microanalysis was used. Operational properties of the IMC were defined using VIKA experimental unit. This unit is designed to study materials by thermal desorption method in the temperature range from 20 °C to 1500 °C.

Relevance of Research:

1. The application of technological methods of preliminary MA with subsequent SPS, as well as experimental results on the study of the behavior of the IMC of the Ti-Al-Nb system in thermocyclic sorption / desorption processes can be used directly in the implementation of practical activities in the direction of research on the development of a method for obtaining hydrogen-intensive materials based on titanium aluminides;

2. The data obtained during the implementation of R&D as part of the dissertation work can be used to explain the nature of structural transformations while forming composites under nonequilibrium conditions, namely, under conditions of rapid heating and cooling, implemented during high-energy processing of powder compositions. They will also provide additional knowledge on the technology of creating new structural materials with a set of optimal properties used in hydrogen energy, automotive and aerospace industries.

3. Experimental results of the study will be used directly in the implementation of practical activities in the direction of research to develop a method for obtaining

hydrogen-intensive materials based on titanium aluminides at the National Nuclear Center of the Republic of Kazakhstan when performing research work on the following topics:

– "Development of technologies for the production and storage of hydrogen for the development of alternative energy in the Republic of Kazakhstan" within the framework of program-targeted financing of scientific, scientific and technical programs for 2021-2023, IRN BR10965284;

– "Study of the influence of various temperature-time parameters of heat treatment on the formation of a set of properties of alloys based on orthorhombic titanium aluminide" as part of the Scientific and Technical Program "Development of nuclear and energy projects in the Republic of Kazakhstan" for 2021-2023, IRN BR09158470.

Author`s Personal Contribution:

The author was directly involved in setting research objectives, personally analyzed patent searches and literature data, participated in experiments and analytical work, and performed statistical processing of the results. The analysis of the obtained results and the formulation of the main conclusions were conducted jointly with scientific consultants.

Relation of Work to Research Programs:

The work was cnducted within the framework of an interstate project and a state budget research program, where the author participated as a responsible executor:

– Interstate project on hydrogen energy (Agreement internal No.14.627.21.0003) The Federal State Unitary Enterprise "Central Research Institute of Structural Materials "Prometey" (FSUE "CRI SM "Prometey", Saint Petersburg, Russia), The State Scientific Institution "Powder Metallurgy Institute" (SSI PMI, Minsk, the Republic of Belarus) and the Republican State Enterprise "National Nuclear Center of the Republic of Kazakhstan", (RSE NNC RK, Kurchatov, RK).

– Budget program "Development of Nuclear and Energy Projects", specific "Applied Scientific Research of a Technological Nature in the Field of Nuclear Energy" on the topic "Research of advanced materials based on the Ti-Al-Nb system for storing and transporting hydrogen" (State registration number - 0118RK01124) for 2018 -2020.

Degree of Result Reliability:

It is ensured by the use of well-tested experimental methods and research methods, a large amount of experimental data and their statistical processing. The main results of the dissertation are published in publications recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, as well as in peer-reviewed foreign scientific journals included in the database of ThomsonReuters and Scopus companies, and in collections of materials from international and domestic conferences.

Approbation of the Work Results:

The materials of the work were reported at 5 scientific and technical conferences and workshops, including:

1. XIV International Scientific and Practical Conference “The Future of Nuclear Energy” (2018, Obninsk);

2. 14th International Conference “New Materials and Technologies: Powder Metallurgy, Composite Materials, Protective Coatings, Welding”, (2020 Minsk);

3. International Conference “Advanced Materials Manufacturing and Research: New Technologies and Methods” (2021, Ust-Kamenogorsk);

4. International Scientific and Practical Conference of the Russian and International Engineering Academies, (2021, St. Petersburg);

5. IX International Conference “Semipalatinsk Test Site : Legacy and Prospects for the Development of Scientific and Technical Potential” (2021, Kurchatov).

In addition, the main results were reported and discussed at meetings of the Scientific and Technical Council of the Republican State Enterprise “National Nuclear Center of the Republic of Kazakhstan”, as well as at monthly and quarterly scientific workshop for doctoral students of the Department of Technical Physics of D. Serikbayev EKSU and S. Amanzholov EKU.

Publications:

The main results of the dissertation were published in 7 publications, including 3 foreign scientific publications included in the Scopus and Web of Science database, in 3 publications recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, 6 materials of International conferences and in 1 utility model patent of the Republic of Kazakhstan.

Structure and Scope of Dissertation:

The paper is presented on pages 122, consists of introduction, 5 sections, conclusion and a list of references. It contains 48 figures, 19 tables and the list of references with 131 items.