

Features of Metallurgy of Titanium Hydride-Forming Alloys

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Received September 12, 2024; revised September 12, 2024; accepted September 20, 2024

Abstract—The article considers various aspects of metallurgical technologies to produce high-quality titanium-containing metal hydride (MH) alloys of the AB-, AB₂- and BCC-types with the prospect of developing foundations of their industrial-scale production using feedstock available in the Russian Federation, including a cheap mineral, ilmenite (FeO·TiO₂). The technologies of vacuum induction melting (VIM), vacuum arc melting (VAM) and self-propagating high temperature synthesis (SHS) were investigated and optimized. Dependence of the oxygen content, as the most harmful admixture for AB-type MH alloys, on the technological parameters of their preparation was constructed. The article also presents the data on the phase composition and hydrogen sorption performance of the selected titanium-containing alloys prepared by the developed technology.

Keywords: hydrogen energy, hydrogen storage alloys, titanium alloys, metallurgy

DOI: 10.1134/S0018143924701571

THEORETICAL ANALYSIS

Hydrogen energy technologies are based on the use of hydrogen as a universal, efficient and environmentally friendly energy carrier. The advantages of hydrogen include its environment friendliness, high efficiency of various energy conversion processes with its participation, as well as unlimited resources of raw materials for its production (water, natural hydrocarbons, biomass) [1, 2].

Along with the need to increase efficiency, service life, and reduce the cost of the main components of hydrogen energy systems (electrolyzers and fuel cells), solving problems related to the storage and transportation of hydrogen is a determining factor in their commercial competitiveness [3].

A promising solution is in the use of metal hydrides (MHs) which are characterized by a volume density of bound hydrogen up to 150 kg/m³ to be a promising alternative to traditional hydrogen storage methods. The advantages of MHs as hydrogen storage materials include compactness, safety, simplicity of design and operation, as well as the technological flexibility of the MH-based systems. The energy consumption for the decomposition of “low-temperature” MHs with the release of hydrogen gas is 20–30 kJ/mol H₂, accounting for about half of the energy required to release hydrogen bound in liquid organic hydrogen carriers (55–70 kJ/mol H₂). The main problem of creating

highly efficient metal hydride systems is the selection or purposeful development of MH materials whose properties maximally meet the technical requirements of the end user, primarily in terms of operating temperatures and hydrogen pressures. In addition, it is necessary to ensure the stability of hydrogen—sorption properties during repeated cycling, fast hydrogenation—dehydrogenation kinetics and high effective thermal conductivity of the metal hydride bed [4–6].

To date, the main factor constraining the commercialization of metal hydride energy technologies is the high cost of MH-based hydrogen storage systems. Currently, the widely studied nickel-based AB₅-type alloys of the system with rare-earth metals are used as the main MH material for commercial use. Giredmet JSC has worked out technological production routes and implemented low-tonnage smelting technologies from the charge materials produced in the Russian Federation. The alloys are supplied to the main research groups involved in the development of hydrogen energy technologies.

Reducing the cost of MH materials is possible when using the less expensive titanium—iron-based alloys of the AB-type. Even though research of the TiFe-based intermetallic compounds as hydrogen storage materials has been going on for more than 50 years, the intensity of work in this area has increased dramatically in recent years [7]. First of all, this is due to the need to identify the origin of signifi-

cant discrepancies in the hydrogen capacities of these materials (from 0.67 to 1.86 wt % H). The main disadvantage of the TiFe-based alloys is their sensitivity to the impurities in the solid phase, which, in turn, affects the hydrogen absorption properties. The harmful impurities are mainly oxygen and carbon, either contained in the feedstock or introduced during the smelting of the alloys [8]. Therefore, the issues of using charge materials and the choice of technological processes for the metallurgical production of these alloys are relevant now.

When developing new MH alloys, vacuum arc melting (VAM) methods are mainly used, due to smaller number of parameters affecting properties of the ingot, versatility of the melting technology, absence of interaction with lining materials, etc. [9, 10]. On the one hand, this universal technology enables one to quickly vary the compositions and to formulate a relatively simple alloy smelting technology. On the other hand, this technology is difficult to upscale. With an increase in the load weight above 1.0 kg, liquation inhomogeneities are observed in the ingot resulting in a poor quality of the final product.

The main industrially oriented method of smelting alloys with narrow confidence intervals of chemical composition is vacuum induction melting (VIM). To date, in the Russian Federation, furnaces with the possibility of smelting from 0.5 to 2000 kg per a load are operated. Basically, high-quality alloys can be prepared in the vacuum induction furnaces with the charge load of 25–300 kg [11].

Technologies for smelting alloys with a high content of metals having high affinity to oxygen (Ti, Zr, Hf, etc.) are implemented in vacuum induction furnaces with a cold crucible (VIM-CC) [12]. The main advantage of this smelting technology frequently used for the preparation of titanium-based hydrogen storage alloys [13] is in the absence of interaction of the melt with the ceramic lining. However, the VIM-CC technology also has a number of disadvantages including high energy intensity, poor mixing, presence of the overcooled zones in the melted load, strict safety requirements, as well as small melting volume (up to 50 kg).

Many worldwide research works in the field of metallurgy are devoted to the development of individual lining materials (crucibles or mixtures) directly used for the VIM-smelting of a pre-defined base alloy compositions, particularly, titanium alloys [8]. The high affinity of molten Ti to oxygen results in its interaction with the lining material. Methods of the VIM-smelting of Nitinol-type alloys in graphite crucibles are widely used, however, this crucible material is not suitable for TiFe smelting. Both titanium and iron have a high affinity to carbon forming carbides, and even minor impurities of carbon which form solid solutions in TiFe metallic matrix result in the

dramatic decrease of the reversible hydrogen sorption capacity [14].

In the development of the materials for VIM crucible lining, research is underway on using the coatings based on Y_2O_3 and ZrO_2 on the inner surface of the melting crucible [8, 15]. However, from the point of view of serial melting, this technology does not seem promising. The solution may be in the use of periclase crucibles based on MgO. The disadvantage of industrially produced in the Russian Federation periclase crucibles is their low resistance to temperature cycling during the melting process. The solution to this problem is in the addition of additives of Al_2O_3 , SiO_2 , etc. to the MgO base. However, these additives negatively affect the properties of Ti-based alloys melted in such crucibles [16].

This work is aimed at the search of technological solutions for the smelting of hydrogen-accumulating alloys on the basis of titanium, particularly, TiFe intermetallic, from local charge materials, while preserving high requirements to the functional properties of the final product in its use in hydrogen energy technologies.

EXPERIMENTAL

The studied series of alloys was prepared according to two main technological routes.

The first one includes the methods of traditional melting from pure charge components: vacuum induction melting (VIM) and vacuum arc melting (VAM) in a controlled atmosphere.

The influence of variation of lining and charge materials with micro-alloying with mischmetal (Mm), as well as of the smelting technological modes on the content of impurities (oxygen and carbon) in the alloy was studied on the TiFe equiatomic composition using VIM and VAM technologies.

For the VIM technology, an optimal composition of the lining mixture based on periclase (MgO) was additionally developed. Several studies were conducted in which the composition of the mixture and the technology of in situ crucible formation varied.

Different grades of charge components for the smelting were varied including:

- Iron (Fe)—ARMKO Type 1 (TU 00187895-103-2019), Fe electrolytic (CAS 7439-89-6).
- Titanium (Ti)—TG-90 (GOST 9853.9-96), TI-1 (TU48-4-282-73).
- Mischmetal Mm—Ce36La (TU 48-4-280-9).

Fused magnesite PPPL96 (TU 14-8-448-83), CaO (GOST 8677-76), ZrO_2 (GOST 21907-76), Y_2O_3 (CAS: 1314-36-9) and other modifying additives were used as a basis for experiments with the lining materials.

The vacuum induction melting of alloys and the study of the effect of the lining materials interaction

Table 1. Starting charge materials for SHS

Material	Regulatory document	Components, wt %							
		TiO ₂	FeO* Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	Cr ₂ O ₃	MnO ₂	ZrO ₂	total impurities
Concentrate ilmenite (FeTiO ₃)	TU 07.29.19-010-58914756-2020	61.9	28.3	3.5	2.2	1.8	1.0	0.8	2.2–4.5
Scale of ferrous metals (Fe ₃ O ₄ ·Fe ₂ O ₃ ·FeO)	TU 0783-110-00187895-2008	–	92.8	<1.0	0.05	0.08	0.6	0	4.0–7.2

with liquid metal were carried out in an induction furnace with the load capacity up to 1.5 kg (Fe). The design of this furnace allows the introduction of the charge material into the melt in the required sequence. In this regard, the effect of the refining process of the base component (Fe) before the introduction of Ti and mischmetal through the dispensing system (feeder) was additionally studied.

The melting was carried out in the furnace chamber after pre-evacuation to 0.25 Pa and pre-heating the charge materials in the crucible to $T = 800\text{--}900^\circ\text{C}$ and 3 minutes-long hold for the outgassing. It was followed by the melting itself which was carried out in two different modes:

(a) All the charge materials loaded in the crucible were brought to complete melting due to increase of the power supplied to the inductor. The melting pool was kept at the maximum power for 2 minutes to allow induction stirring. Then the chamber was filled with high-purity argon (TU 20.11.11-006-45905715-2017) at the pressure up to 33 kPa, and the melt was casted into a steel mold of the circular cross section.

(b) Initially, the alloy base (Fe) was loaded into the crucible while the remaining charge materials (titanium, mischmetal) were placed into the feeder. After raising the power and complete melting of Fe, the vacuum refining of the melt was carried out. Then the furnace chamber was filled with the high-purity argon, and the remaining charge materials were supplied to the melting pool from the feeder. Similarly to the mode (a), the melt was kept for 2 min and casted into the mold.

Vacuum arc melting was carried out in a laboratory arc-melting furnace with a non-consumable tungsten electrode. The design of the crystallizer (water-cooled hearth) allows the melting in one smelting cycle of up to 4 samples of different compositions, up to 100 g in weight each. The alloys were produced in the pre-evacuated and filled with argon (pressure up to 120 kPa) furnace chamber. The charge materials listed above, as well as zirconium (TU 95-46-97), ERX-0 chromium (GOST 5905-2004), VEL-2 vanadium (TU 48-4-335-86), Mn998 manganese (GOST 6008-90), and DNK-0 nickel (TU 1732-122-48200234-2011) were used for the vacuum arc melting.

The second route was centrifugal SHS metallurgy (SHS-M) [17] with the possibility of synthesizing alloys from pure oxide raw materials (TiO₂, FeO, Fe₃O₄, Al₂O₃, etc.). Complex reductive synthesis takes place during SHS due to aluminio- and aluminio-calcio-thermic reactions. This work is focused on the study of the possibility of obtaining the MH alloy from ilmenite concentrate (FeO·TiO₂) of the Tugansk deposit and wastes from metallurgical production, in order to minimize the cost of the product. The alloys were synthesized on a radial centrifugal unit under the influence of high gravity from 1.0 to 300.0 g. A description of the general scheme of this centrifugal installation is presented in [18]. Table 1 shows the composition of the feedstock. A distinctive feature of the technology is the use of available oxide raw materials. After synthesis at 2100–3500°C, phase separation of the target metal product from the slag, based on the difference in their densities, occurs due to the application of centrifugal forces [18].

The varied technological parameters of experimental series of melts of the TiFe intermetallic (50/50 at %, or 53.8/46.2 wt %) are presented in Table 2.

For the quantitative elemental analysis, a Finnigan Element GD glow discharge mass spectrometer, an inductively coupled plasma atomic emission spectrometer iCAP 6300, and a spectrum analyzer with double focusing of the Nir–Johnson geometry (all from Thermo Fisher Scientific, Germany) were used. The contents of non-metallic impurities were determined using two instruments manufactured by LECO, USA, viz: SC844 (carbon and sulfur) and ONH836 (oxygen, nitrogen, and hydrogen) analyzers.

Microstructural studies were performed by scanning electron microscopy (SEM) using a FEI Quanta FEG 250 microscope equipped with the EDAX Octan Elect EDS system.

The X-ray diffraction (XRD) analysis of the alloy samples was performed using powder diffractometer (AERIS/Malven PANalytical B.V.); CuK α radiation, Bragg angle range $2\theta = 15^\circ\text{--}90^\circ$. The patterns were further processed using GSAS software.

Hydrogen sorption properties of the alloys were studied using H-Sorb 2600 gas sorption analyzer (Bei-

Table 2. Variable technological parameters of the experimental melts

#	Method	Crucible type	Charge materials (CM)	CM loading	Notes
1	VIM	MgO + X ₁ *	Fe-ARMKO Ti-TG-90	All into crucible	–
2			Fe electrolytic Ti-TG-90	Fe–crucible Ti-feeder	High purity Fe
3			Fe-ARMKO Ti-TI-1		High purity Ti
4		MgO + X ₂ **	Fe-ARMKO Ti-TG-90	All into crucible	–
5			Fe-ARMKO Ti-TG-90	Fe–crucible Ti-feeder	–
6			Fe-ARMKO Ti-TG-90	Fe–crucible Ti, Mm-feeder	+1% Mm (LaCe)
7		Al ₂ O ₃	Fe-ARMKO Ti-TG-90	All into crucible	–
8			Al ₂ O ₃ + AlN		AlN deposited onto inner surface of the crucible
9	VAM	Copper (crystallizer)	Fe-ARMKO Ti-TG-90	All into load	–
10			Fe-ARMKO Ti-TG-90		Pre-melting of Ti (O getter) in the furnace chamber
11			Fe-APMKO Ti-TI-1		High purity Ti
12	SHS-M	Steel	TiO ₂ , FeO, Fe ₃ O ₄ , Al ₂ O ₃	–	Reducing agent Al
13			–	–	Reducing agent Al + Ca
14			FeO·TiO ₂ + scale	–	Reducing agent Al + Ca

* X₁—mixture MgO + CaF₂, SiO₂ and Al₂O₃ + binder.

** X₂—CaCO₃, Y₂O₃, ZrO₂, etc. + binder.

jing CI-Ultrametris Technology, China) by the measurement of the pressure–composition isotherms (PCI; hydrogen absorption and desorption) after 3–4 activation cycles which included exposure in hydrogen at the starting pressure of 50 atm (5.0 MPa) and the ambient temperature (22–25°C) followed by vacuum heating to 300–400°C. The PCI's were taken in the pressure range 0.5–90 atm (0.05–9.0 MPa) and the ambient temperature. After taking H₂ desorption isotherm which exhibited significant residual hydrogen concentration in the sample, the temperature-programmed H₂ desorption (TPD) was carried out at P(H₂) = 0.1–4 atm (0.01–0.4 MPa), T = 20–450°C, heating rate 5°C/min.

RESULTS AND DISCUSSION

Preparation of the Alloys

The first stage of the experimental study was in the development of optimal composition for the lining

mixture resistant to the elements contained in titanium-based alloys and in the development of a process for in situ producing the crucible in the melting inductor, without application of industrially used process for producing and sintering crucibles, their packing into inductor, etc.

The manufacturing of the melting crucible is based on the use of cheap and locally available periclase mass (MgO + MgCO₃). As a result of calcination at the temperature above 1000°C, magnesite loses most (92–94%) of carbon dioxide and transforms into a chemically active powder—caustic magnesia. Magnesia calcinated at temperatures up to 1500–1650°C is characterized by weak chemical activity and high (up to 2800°C) refractoriness.

Figure 1 shows a diagram of the in situ preparation process of the melting unit by packing the mass of the prepared mixture and heating the crucible of the required geometry with a graphite block to the calcination temperatures (1500–1650°C). In doing so, it is

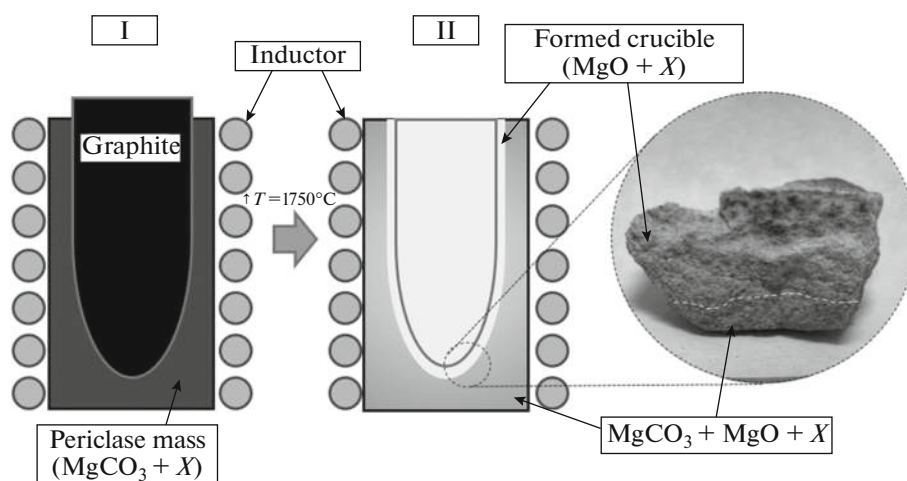


Fig. 1. Schematics of preparation of the melting unit using the periclase mass. I—Packing of the crucible, II—in situ formation of the crucible on the basis of MgO.

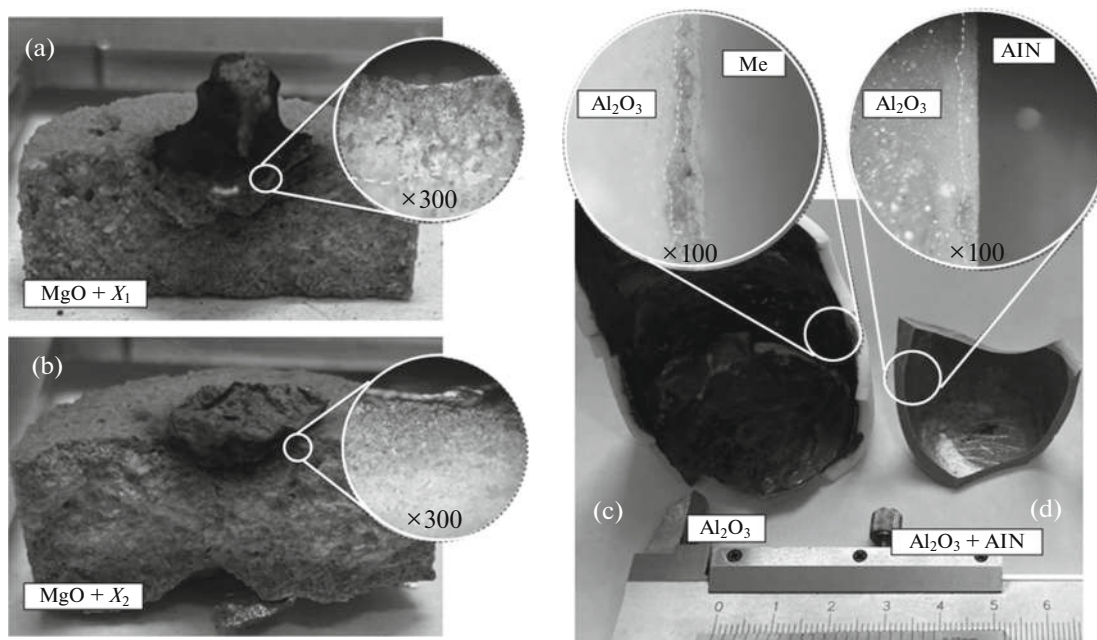


Fig. 2. Evaluation of the interaction of TiFe alloy with ceramic materials.

possible to obtain a “working layer” (10–20 mm) on the inner surface of the crucible. The remaining layer of the non-sintered mixture is a protective barrier in case of crucible cracking during alloy smelting.

Focusing on the composition of industrially produced crucibles based on magnesite mass, the use of an MgO packing mixture with a small (up to 3.0%) addition of binders (CaF_2 , SiO_2 and Al_2O_3) was initially tested. Figure 2a shows a photo of metal interaction (TiFe alloy 50/50 at %) with crucible material. Note the presence of a transition region of the metal–ceramic layer. The melt interacts with the crucible

material destroying it with the formation of non-metallic inclusions, thus reducing the quality of the resulting metal.

By introducing certain modifying additives (CaCO_3 , ZrO_2 , etc.) including the ones which contain rare-earth metal (Y_2O_3) and other binding components in a total amount not exceeding 5.0 wt %, the problem of excluding the addition of CaF_2 , SiO_2 and Al_2O_3 into the periclase mixture ($\text{MgO} + \text{X}_2$) is solved, while maintaining the shaping, heat resistance and thermal cyclicality of the resulting crucibles. Figure 2b shows photograph of the sample illustrating the inter-

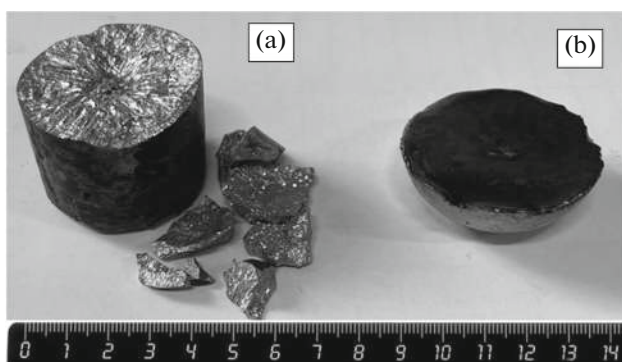


Fig. 3. TiFe ingots prepared by VIM (a) and VAM (b) methods.

action of the alloy with the $\text{MgO} + \text{X}_2$ mixture which forms the boundary layer during the melting. The absence of metal interaction with the lining leads to improvement of the quality of the resulting metal.

Additionally, the melting of the TiFe (50/50 at %) alloy in a standard corundum-core crucible was carried out as the reference point (Fig. 2c). The use of corundum Al_2O_3 -based crucibles is not recommended for smelting these types of materials. However, applying a special aluminum nitride (AlN) coating of the inner surface of the crucible (Fig. 2d) during the preparation of the melting unit reduced the interaction of the alloy with the crucible.

In this way, a series of alloys were prepared by vacuum induction melting with variable parameters, according to Table 2. The ingots (Fig. 3a) had a characteristic metallic shade with a brittle character of the fracture. The weight of the ingots was of 0.6 ± 0.02 kg.

Example of the sample prepared by the arc melting is shown in Fig. 3b. The samples looked like hemispheres reproducing geometry of the cell where the charge was melted. The weight of the VAM samples was 0.25 ± 0.02 kg.

In addition to the TiFe alloys, several alloys of AB_2 - and BCC-types were prepared by VAM technology from the high-purity metals. On-going further studies are focused on optimizing the routes of VIM melting of these alloys from technical-grade feedstock.

The next way to prepare the TiFe alloy was its synthesis by the method of SHS metallurgy. Experimental syntheses from pure oxides (TiO_2 , FeO , Fe_3O_4 , Fe_2O_3 , etc.) allowed us to establish the possibility of preparing the alloys of the required composition, as well as to work out the main modes of the reduction reaction. With the resulting equiatomic Ti/Fe ratio, the total amount of impurities in the alloy was 0.11 wt %, excluding non-metal impurities. The residual Al content was below 0.04 wt %. The analysis of the TiFe alloy ingot prepared from ore raw materials (Fig. 4) shows the possibility of obtaining the material in this way. The main parameter determining the quality of the final alloy will be the presence of impurities in the starting materials. In particular, this kind of ilmenite concentrate ($\text{FeO} \cdot \text{TiO}_2$) contains a high content (up to 1.8 wt %) Cr_2O_3 which is also involved in the reduction reaction and results in a noticeable Cr content (up to 0.6 wt %) in the final alloy. The total amount of impurities was 0.93 wt %. However, it is certainly of interest to study the effect of these impurities on the hydrogen absorption/desorption performance.

Characterization of the Alloys: Non-metallic Impurities

The common factor for the comparison of the prepared materials was the content of oxygen as the main harmful non-metallic impurity affecting the practical properties of the alloy [16]. The diagram (Fig. 5) shows the values of the oxygen impurity content depending on the technological parameters of the alloys' preparation. The diagram can be divided into three main sectors—methods for the alloys preparation: VIM, VAM and SHS-M. The varied parameters included lining materials (VIM), charge materials

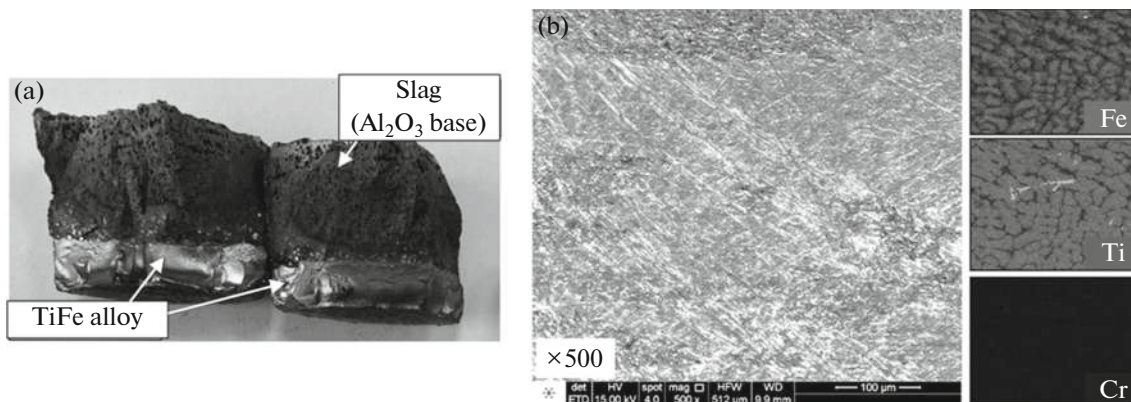


Fig. 4. SHS-M ingot of the alloy on the basis of TiFe (50/50 at %) prepared from the ore feedstock (a) and SEM images of its microstructure (b).

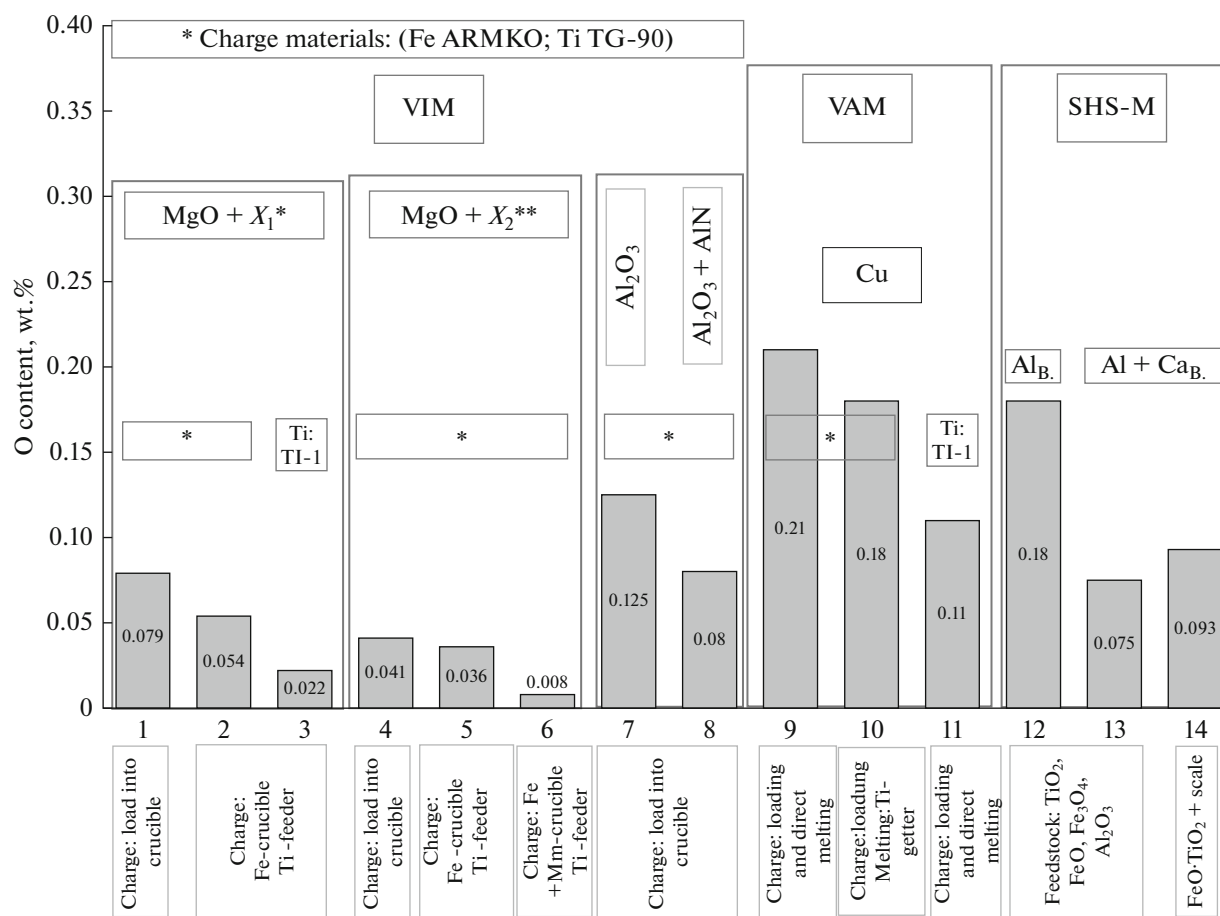


Fig. 5. Influence of technological routes of the melting of equatomic TiFe alloy on the oxygen content in the ingot.

(VIM and VAM) and sequence of their loading into the melting zone (VIM), as well as pre-melting of titanium getter (VAM). For SHS-M, the reducing agent and the feedstock were varied.

Analysis of the data presented in Fig. 5 allows us to conclude that the content of oxygen impurity in the TiFe alloy strongly depends on the technological factors of its preparation.

The reference sample melted in corundum crucible (Al₂O₃; No. 7 in Fig. 5) contains 0.125 ± 0.005 wt % of the oxygen impurity. Coating of the inner surface of this crucible with aluminum nitride (Al₂O₃ + AlN; No. 8 in Fig. 5) results in the decrease of the oxygen content to 0.080 ± 0.002 wt %.

During the VIM smelting of TiFe alloys in the MgO + X₂ mixture without additives of CaF₂, SiO₂ and Al₂O₃ traditionally used in industrial crucibles, significant discrepancies in the oxygen content were observed. Under the same melting conditions (No. 1 and No. 4 in Fig. 5), the oxygen content is decreased from 0.079 to 0.041 wt %. Applying the technological operation of vacuum refining of iron before entering titanium results in the decrease of the oxygen content from 0.079 to 0.054 wt % (No. 1 and No. 2 in Fig. 5).

When using pure “iodide” titanium (TI-1) the oxygen content decreases from 0.054 to 0.022 wt % (No. 2 and No. 3 in Fig. 5). The lowest content of the oxygen impurity in the alloy melted using technical-grade titanium (TG-90) was observed when minor amounts (1–2 wt %) of mischmetal were added to the charge. In this case, the amount of oxygen in the alloy was even lower than the one for the alloy prepared using expensive high-purity TI-1 titanium (0.008 against 0.022 wt %; No. 6 and No. 3 in Fig. 5).

In alloys prepared using VAM technology, higher oxygen contents were observed due to the technological features of alloy smelting and the lack of the possibility of refining the charge materials during melting. Nevertheless, the use of pure “iodide” titanium (TI-1) results in the decrease of the oxygen content from 0.21 to 0.110 ± 0.002 wt %.

The carbon content in all the alloys prepared by VIM and VAM technologies was 0.010 ± 0.005 wt %.

In the alloy samples synthesized by SHS-M technology, the oxygen contents were similar to the ones observed for the alloys prepared by induction (VIM) and arc (VAM) melting routes. It shows the possibility to use this technology for the preparation of Ti–Fe

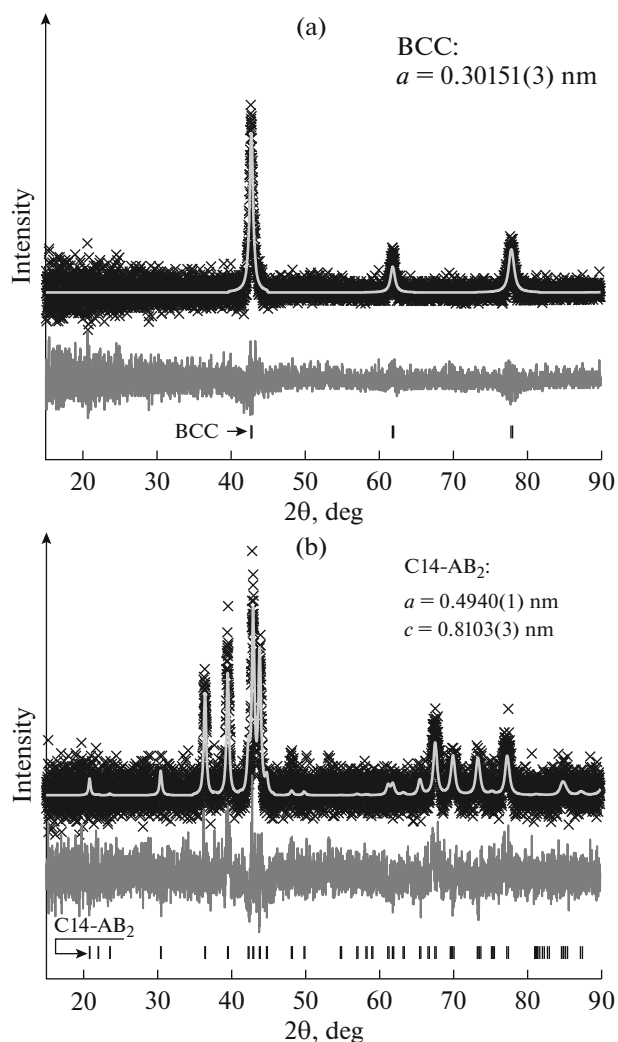


Fig. 6. XRD patterns of the alloys $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Cr}_2\text{-V}$ (a) and TiZrMnFeCrNi (b).

alloys. In the alloy synthesized from industrially manufactured oxides (No. 13 in Fig. 5) and using the complex reducing agent Al–Ca, the minimum value of oxygen content is observed, 0.080 ± 0.005 wt %. It is especially worth noting the direction of the preparation of these materials from an ore concentrate of natural origin—ilmenite ($\text{FeO}\cdot\text{TiO}_2$), with an oxygen content of 0.090 ± 0.005 wt % in the final product. Carbon contents in samples prepared from the oxide and ore raw materials were 0.010 ± 0.005 and 0.020 ± 0.005 wt %, respectively. Evaluation of the application potential of the SHS-M technological approach requires additional studies which should include carrying out the synthesis at presence of various additional modifiers.

For the AB_2 - and BCC-type titanium alloys prepared using VAM technology the oxygen content was lower than the one for the arc-melted TiFe. For example, the contents of oxygen impurity in the equatomic

TiZrMnFeCrNi alloy (high-entropy AB_2) and $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Cr}_2\text{-V}$ alloy (BCC, 50 at % V) was found to be 0.098 ± 0.03 and 0.088 ± 0.05 wt %, respectively; the corresponding contents of carbon impurity were of 0.018 ± 0.002 and 0.005 ± 0.002 wt %.

Characterization of the Alloys: Phase Composition and Hydrogen Sorption

According to the XRD analysis, the TiFe-based alloys contained the major phase of TiFe intermetallic, space group $Pm\bar{3}m$ (221), with the lattice period a varying between 0.298 and 0.299 nm, in a good correspondence with the literature data [19]. The impurity phases mainly included TiFe_2 (C14 Laves phase) and oxygen-containing intermetallic $\text{Ti}_4\text{Fe}_2\text{O}_{1-x}$ (η -phase) formed during oxygen-induced disproportionation of TiFe [16]. Addition of mischmetal deoxidizer to the charge was shown to decrease oxygen content in the alloy and, accordingly, to reduce the content of TiFe_2 which does not form hydride at the experimental conditions. In turn, the hydrogen absorption performance of the mischmetal-doped alloys is significantly improved. Additional factors strongly affecting the hydrogen sorption properties of the TiFe-based alloys were found to be Ti/Fe atomic ratio and content of the η -phase known as efficient hydrogenation catalyst [16]. The details are presented in the separate publication [20]. More detailed analysis of the interrelation of the preparation routes (Fig. 5), phase-structural and morphological features, as well as hydrogen sorption properties of the TiFe-based alloys is on-going; the results will be published in a due course.

As it can be seen from Fig. 6, both BCC (a) and AB_2 (b) alloys are single-phase. The value of the lattice period of the BCC phase ($a = 0.3015$ nm) is similar to the reference data for the BCC-V ($a = 0.3024$ nm [21]), and the lattice periods of C14-TiZrMnFeCrNi ($a = 0.494$ nm, $c = 0.810$ nm) are in very good correspondence with the published data for the intermetallic of the same composition ($a = 0.493$ nm, $c = 0.809$ nm [22]). Both alloys are easily activated: hydrogen absorption begins after evacuation at the ambient temperature, and the reproducible hydrogen absorption kinetics are achieved after the first vacuum heating to 300°C .

Figure 7 shows the hydrogen absorption and desorption isotherms for the TiZrMnFeCrNi AB_2 -type alloy. The alloy exhibits reversible hydrogen storage capacity close to 1 H/M ($180 \text{ N cm}^3/\text{kg}$ or 1.7 wt % H) and hydrogen equilibrium pressures (H_2 desorption) between 0.15 and 1.0 MPa at the room temperature that makes it promising for the hydrogen storage applications. The PCI data are in line with the

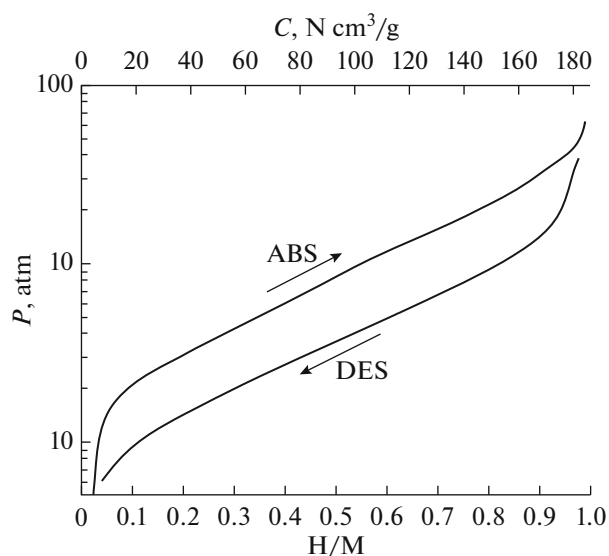


Fig. 7. Hydrogen absorption (ABS) and desorption (DES) isotherms at $T = 22^\circ\text{C}$ for the AB_2 -type TiZrMnFeCrNi alloy.

literature ones [22], however, in our case significant plateau slope was observed as distinct to the flat plateau in [22]. The origin of the deviation appears to be in compositional inhomogeneity of the ingot prepared in our work using VAM technology.

The room-temperature PCI curves for the BCC alloy $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Cr}_2\text{-V}$ (50 at % V) are presented in Fig. 8a. The isotherms exhibit typical behavior for the BCC alloys based on vanadium [23] including high absolute hydrogen storage capacity which approaches $340 \text{ N cm}^3/\text{g}$. About $220 \text{ N cm}^3/\text{g}$ of the absorbed hydrogen can be desorbed at $P(\text{H}_2) \geq 0.1 \text{ MPa}$ that corresponds to the phase transition from the “dihydride” MH_{2-x} to “monohydride” MH_{1-x} . The remaining hydrogen can be removed partially during heating the sample to 450°C at $P(\text{H}_2) = 0.1\text{--}0.4 \text{ MPa}$ (see TPD curve in Fig. 8b), or completely, after 1 hour long heating the sample to $375\text{--}400^\circ\text{C}$ in vacuum. Disadvantages of the BCC alloy as a hydrogen storage material include very high hysteresis (Fig. 8a), as well as specific mechanical properties of the alloy (combination of high strength and ductility) which make difficult its preparation for the loading into hydrogen storage containment, as distinct from the brittle hydrogen storage intermetallics of AB, AB_2 and AB_5 types [6].

Easy activation and satisfactory hydrogen storage performances of titanium alloys of the AB_2 and BCC types have their origin in the low content of non-metallic impurities in these alloys even in the case of applying not optimal in this respect upscaled vacuum

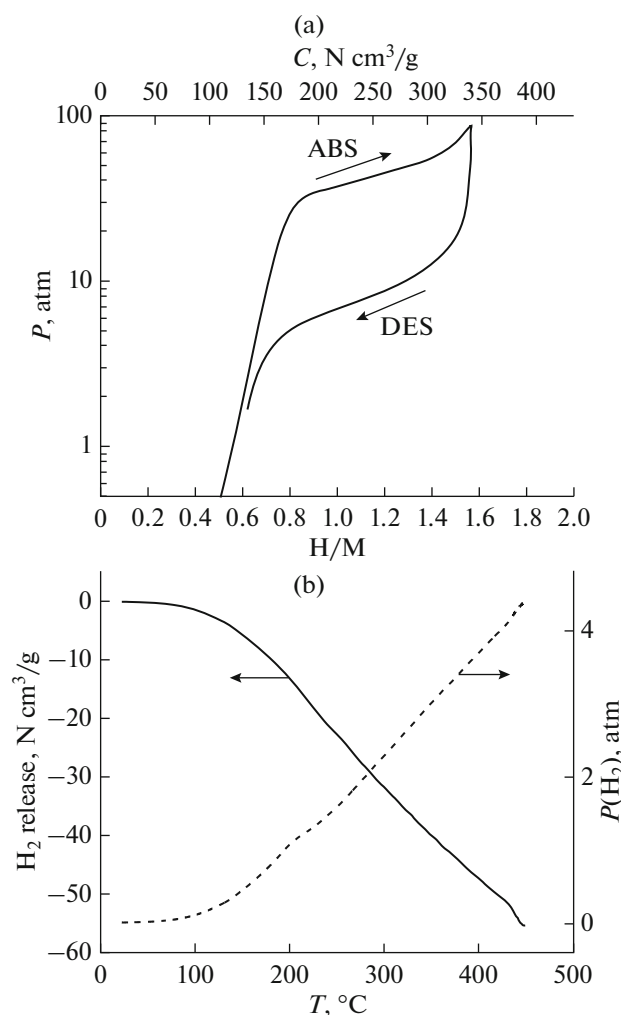


Fig. 8. Hydrogen absorption (ABS) and desorption (DES) isotherms at $T = 25^\circ\text{C}$ (a) and TPD curve (b) for the BCC alloy $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Cr}_2\text{-V}$.

arc melting route (see examples for TiFe in Fig. 5; series 9–11). Further works in this direction should be focused on the optimization of the VIM and SHS-M technologies for the semi-industrial-scale preparation of these alloys. Special attention should be paid to the AB_2 -type hydrogen storage alloys which appear to be less sensitive to oxygen contamination than the AB-type ones [24, 25].

CONCLUSIONS

Three metallurgical technologies including: vacuum induction melting (VIM), vacuum arc melting (VAM), and self-propagating high-temperature synthesis combined with centrifugal metallurgy (SHS-M), have been studied experimentally regarding possibility of their optimization in the upscaled manufacturing of titanium-containing hydride-forming alloys

from feedstock available in the Russian Federation. It was found that the main factor negatively influencing on the target hydrogen storage performances of the final product is its contamination with non-metallic impurities, first of all, oxygen.

The oxygen contamination is most critical for TiFe-based alloys altering their phase composition and, in turn, worsening the hydrogen sorption performance.

It was shown that the content of oxygen impurity in the TiFe alloys strongly depends on the technological factors of their preparation. Conversely, the titanium alloys of BCC and AB₂ types are less prone to the oxygen contamination and exhibit hydrogen sorption properties promising for their use in hydrogen storage applications.

As a result of analysis of experimental data on the preparation of TiFe alloys (50/50 at %) using the applied technologies and determination of oxygen content in the final product, the following outcomes have been achieved:

- Optimal compositions of lining mixtures based on MgO have been developed for VIM, with a possibility to in situ prepare the melting crucible from the cheapest industrially produced in Russia magnesite (MgCO₃). It will allow to exclude the use of conventional ceramic crucibles which yield poor-quality final product.

- Adding minor amounts of mischmetal deoxidizer was suggested to significantly improve the quality of the product prepared using VIM technology. The content of oxygen in the alloy melted from technical-grade charge components with mischmetal additive was found to be lower than for the alloy prepared from the expensive high purity raw materials without mischmetal.

- Optimal operation protocol for VIM technology including sequence of placing the charge components into the melting pool has been developed.

- It was found that a decrease of the oxygen content in the alloys melted using VAM technology can be achieved by pre-melting of titanium getter and/or by the use of pure charge materials.

- Optimal reducing agent on the basis of calcium and aluminum mixture has been identified for the SHS-M technology of the alloys' preparation from the cheap and locally available feedstock including oxide wastes of ferrous metallurgy and/or ilmenite mineral.

Results of this study contribute into implementation of hydrogen energy technologies in Russia via development of efficient metallurgical routes for the manufacturing of hydrogen storage alloys from inexpensive locally available raw materials.

FUNDING

The work on the development of the VIM and VAM technologies including preparation and characterization of the BCC and AB₂ alloys was carried out under the support from the Ministry of Science and Higher Education of the Russian Federation (Megagrant, Agreement no. 075-15-2022-1126, signed on July 1, 2022).

The results explicitly related to TiFe were generated under financial support of the grant of the Russian Science Foundation no. 23-13-00418, <https://rscf.ru/project/23-13-00418/>.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

REFERENCES

1. Filippov, S.P. and Yaroslavtsev, A.B., *Russ. Chem. Rev.*, 2021, vol. 90, p. 627.
2. Qureshi, F., Yusuf, M., Arham, K.M., et al., *Fuel*, 2023, vol. 340, p. 127574.
3. Amirthan, T. and Perera, M.S.A., *J. Nat. Gas Sci. Eng.*, 2022, vol. 108, p. 104843.
4. Bellosta von Colbe, J., Ares, J.R., Barale, J., et al., *Int. J. Hydrogen Energy*, 2019, vol. 44, p. 7780.
5. Hirscher, M., Yartys, V.A., Baricco, M., et al., *J. Alloys Compd.*, 2020, vol. 827, p. 153548.
6. Lototsky, M.V., Tarasov, B.P., and Yartys, V.A., *J. Energy Storage*, 2023, vol. 72, p. 108165.
7. Lototsky, M.V., Davids, M.W., Fokin, V.N., et al., *Therm. Eng.*, 2024, vol. 71, p. 264.
8. Fashu, S., Lototsky, M., Davids, M.W., et al., *Mater. Des.*, 2020, vol. 186, p. 108295.
9. Mitchell, A. and Tripp, D.W., *SAMPE Quart.*, 1989, vol. 20, p. 38.
10. Arun, S., Radhika, N., and Saleh, B., *Vacuum*, 2024, vol. 226, p. 113314.
11. Linchevsky, B.V., *Vakuumnaya metallurgiya stali i splavov* (Vacuum Metallurgy of Steel and Alloys), Moscow: Metallurgiya, 1970.
12. Chronister, D.J., Scott, S.W., Stickle, D.R., et al., *J. Miner. Met. Mater. Soc.*, 1986, vol. 38, no. 9, p. 51.
13. Nagase, I. and Shimizu, T., *Denki-Seiko* (Electr. Furn. Steel), 2003, vol. 74, no. 4, p. 233.
14. Lee, S.-M. and Perng, T.-P., *Int. J. Hydrogen Energy*, 2000, vol. 25, p. 831.
15. Davids, M.W., Martin, T.C., Fursikov, P.V., et al., *J. Phys. Energy*, 2024, vol. 6, p. 035005.
16. Davids, M.W. and Lototsky, M., *Int. J. Hydrogen Energy*, 2012, vol. 37, p. 18155.
17. Sanin, V.V., Filonov, M.R., Yukhvid, V.I., et al., *Russ. J. Non-Ferrous Met.*, 2016, vol. 57, no. 2, p. 124.
18. Sanin, V.V., Ageev, M.I., Martynov, D.A., et al., *Deform. Razrush. Mater.*, 2024, no. 9, p. 2.

19. Melnyk, G. and Tremel, W., *J. Alloys Compd.*, 2003, vol. 349, p. 164.
20. Tarasov, B.P., Shamov, I.D., Melnikov, S.A., and Lototsky, M.V., *High Energy Chem.*, 2024, vol. 58, Suppl. 4, p. S539.
21. Kuentzler, R. and Khan, H.R., *Phys. Lett. A*, 1985, vol. 113, p. 89.
22. Edalati, P., Floriano, R., Mohammadi, A., et al., *Scr. Mater.*, 2020, vol. 178, p. 387.
23. Lototsky, M.V., Yartys, V.A., and Zavaliy, I.Y., *J. Alloys Compd.*, 2005, vols. 404–406, p. 421.
24. Davids, M.W., Lototsky, M., and Pollet, B.G., *Adv. Mater. Res.*, 2013, vol. 746, p. 14.
25. Davids, M.W., Martin, T., Lototsky, M., et al., *Int. J. Hydrogen Energy*, 2021, vol. 46, p. 13658.

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