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LATTICE DYNAMICS
AND PHASE TRANSITIONS

Determination of the Terminal Solid Solubility of Hydrogen in Hafnium by the Hydrogen Permeation Method

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Abstract—An approach proposed in this study, which is based on the hydrogen permeation method, has been used to determine the temperature dependence of the terminal solid solubility of hydrogen in iodide-refined hafnium GFI-1 in the temperature range from 350 to 550°C. The experiments were performed in the regime with maintaining a low constant saturation rate for a membrane sample, instead of the traditionally used regime with maintaining constant input pressure. This approach made it possible to obtain the values of terminal solid solubility under the conditions maximally close to equilibrium. It is shown that the obtained results are in good agreement with the few available data in the literature for the same temperature range.

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INTRODUCTION

Hydrogen embrittlement of structural materials, caused by hydride formation, is a widespread phenomenon, which significantly affects the performance characteristics of materials in various industries. This phenomenon may reduce significantly the yield stress, fatigue strength, and plasticity of materials. Hydrogen embrittlement occurs in several interrelated stages: hydrogen adsorption on the material surface, its diffusion into the lattice, formation of hydrides, and subsequent brittle fracture of the material under mechanical loads. The rates of these processes increase at higher temperatures and pressures; this circumstance makes the problem of hydrogen embrittlement especially urgent for heat- and corrosion-resistant materials, which are widely used in aviation, oil and gas industry, and chemical industry.

The research in this field is aimed at analyzing the kinetics and mechanisms of hydrogen embrittlement; developing methods for diagnosing and predicting this phenomenon; and designing new materials, stable to hydrogen impact. In particular, there is much interest in studying the influence of dopants and microstructural features of materials on their tendency to hydrogen embrittlement, as well as in developing methods of surface modification of materials, aimed at reducing the hydrogen adsorption ability. In this context, it is worth mentioning the metals important for modern technologies: titanium, zirconium, vanadium, and tantalum, as well as their alloys, which are subjected to formation of a brittle hydride phase during interaction with hydrogen-containing media. Study of the conditions of the phase transition between a solid hydrogen solution and a hydride phase is one of the key problems of the materials science of hydride-forming metals. These conditions can be characterized by such parameters as temperature and hydrogen concentration in a solution that is in equilibrium with a hydride phase. In an equilibrium system consisting of a solution and a hydride, the hydrogen concentration in the solution strictly depends on temperature. This concentration value is referred to as the hydrogen terminal solid solubility [1]. Nevertheless, this concept in somewhat idealized. Even when changing the concentration and/or temperature very slowly, the terminal solid solubility does not remain constant and depends strongly on the sample history. For example, the terminal solid solubility for hydride production at a certain temperature is higher than for hydride decomposition. The hysteresis manifesting itself at hydride production and decomposition is of fundamental nature, which is confirmed by the detailed analysis of scientific works [2]. Therefore, it is generally accepted to distinguish two main parameters: terminal solid solubility for hydride production, C_{tssp}, and terminal solid solubility for hydride decomposition, C_{tssd}. In this case, it is important which parameter (concentration or temperature) changes and what is the structural state of the material [3].

Experimental methods for determining the hydrogen terminal solid solubility vary in dependence of the physical principles, measured parameters, laboriousness, reliability of results, and type of samples studied [4]. It should be noted that the arsenal of methods and approaches aimed at determining the terminal solid solubility C_{tssp} under isothermal conditions for compact samples of technological metals and alloys is extremely limited. They include, in particular, such time-consuming and expensive methods as X-ray diffraction (XRD) and neutron diffraction, which require specialized equipment and highly qualified personnel.

In view of the aforementioned limitations, the development of a relatively simple and accessible technique, which can provide data on the terminal solid solubility under isothermal conditions for compact materials with a high degree of reliability, is an urgent and promising problem. Its solution may significantly expand the possibilities of scientific research and practical applications in metallurgy and gain a deeper insight into the physicochemical processes occurring in hydrogen–metal systems.

A methodology based on measurements of hydrogen permeation, which provided reliable C_{tssp} values for zirconium- and titanium-containing alloys, was described in detail in [4].

Our research initiative is aimed at developing further this technique in order to apply it to hafnium, a metal whose chemical characteristics are similar to those of titanium and zirconium. Hafnium, being a fourth-group element of the periodic table, forms a metal hydride, which relates it to the aforementioned metals [5]. The phase diagrams for a binary system consisting of a metal and hydrogen are similar for titanium, zirconium, and hafnium [6]. Therefore, one can suggest that the hydrogen permeation method will also be efficient in the study of hafnium.

Along with the methodological importance, this work is of practical interest for the following reasons:

(i) hafnium enters the composition of some high-strength and heat-resistant alloys used in metallurgy, as well as in rocket and aviation industries [7];

(ii) there are prospects for replacing boron carbide with hafnium hydride as an efficient neutron absorber in the control and protection systems of nuclear power plants [8, 9]. To date, about 90% of all consumed hafnium is used specifically in this sphere;

(iii) hafnium is used in production of optical hydrogen sensors [10];

(iv) hafnium is one of the elements entering the composition of many promising high-entropy alloys for storing hydrogen in a bound form [11].

At the same time, the experimental studies devoted to determination of hydrogen terminal solid solubility in hafnium are very scarce.

Ogiyanagi et al. [12] performed measurements by differential scanning calorimetry under nonisothermal conditions on initially saturated samples. Because of the differences in the conditions of hydride production in [12] (constant concentration at a changing temperature) and the hydrogen permeation method (increasing concentration at a constant temperature), one would expect significant discrepancies in the obtained results.

For correct comparison of the obtained values of terminal solid solubility, the most appropriate study is [13], where the dependences of the equilibrium pressure on the hydrogen concentration in titanium, zirconium, and hafnium were measured at different constant temperatures by the Sieverts method; these data makes it possible to determine the temperature dependences of the hydrogen terminal solid solubility in these metals.

One of significant advantages of the used technique [4] is its simplicity and clearness. In addition, it allows one to perform measurements at a constant temperature, reproducing the operation conditions (often encountered in practice) for the units working in hydrogen-containing environments.

Based on the results and analysis of the numerical simulation of the hydrogen permeation of hafnium with allowance for the hydride formation, reported in one of our previous studies, we changed significantly the measurement protocol. The updated approach implies maintenance of a low constant saturation rate of the membrane, which should provide data on the terminal solid solubility close to equilibrium values.

We performed a series of experiments aimed at determining the temperature dependence of hydrogen terminal solid solubility in hafnium in the temperature range from 350 to 550°C. The obtained results were compared with the data in the literature. The comparative analysis confirmed high efficiency of the proposed technique and the adequacy of the C_{tssp} values determined with its aid, which proves its importance for further research in the fields of materials science and hydrogen power engineering.

EXPERIMENTAL

The technique used to determine the hydrogen terminal solid solubility in hafnium, which is based on the hydrogen permeation method, was described in detail in [4].

Briefly, its essence is as follows. Hydrogen is passed at a constant temperature through a membrane made of the studied material, and the input and output fluxes are measured. When the concentration of the hydrogen dissolved in the sample reaches the terminal solid solubility, a hydride phase metal starts being formed in the membrane bulk, which manifests itself in the character of permeating flux kinetics. If the conditions of the surface-limited regime of permeation are fulfilled, hydrogen is uniformly (to a certain extent) distributed over the membrane thickness (before the onset of hydride production), and its concentration at any point is equal to the concentration averaged over the entire sample. When reaching the terminal solid solubility, the hydrogen concentration in the solution phase ceases to increase, and, simultaneously, the output flux ceases to increase as well, because it is related to the dissolved hydrogen concentration. As a result, having determined the hydrogen concentration at which the output flux ceases to change, one can consider it as the hydrogen terminal solid solubility in the given material. Graphically, it can be presented as the ordinate of the intersection point of the asymptotics of the portions of the dependence of the permeating flux on the hydrogen concentration in metal: before it reaches a steady-state value (at the inflection point) and after the flux becomes steady (see below).

Samples in the form of round membranes were cut by a laser from a 0.35-mm-thick hafnium iodide (GFI-1) sheet. The sample diameter was 15 mm, and the region available for hydrogen permeation had a diameter of 10 mm.

The experiments were performed using a design of quick-clamp seal for membrane samples in a diffusion cell, the draft of which is presented in Fig. 1. Membranes were sealed between two small flanges using copper spacers. The use of external threaded rods, installed outside the high-temperature zone, made it possible to maintain the connection tightness even in the thermal cycling regime.

Sample preparation. It is known that the fourth-group transition metals, such as titanium and zirconium, actively interact with oxygen air even at room temperature, forming dense continuous oxides on the surface, which impede dissociation of hydrogen on the surface and, as a consequence, its subsequent permeation into the material. Hafnium, belonging to the same group, quite expectedly demonstrates similar behavior.

The first experiments with hafnium revealed that, without any treatment of the hafnium membrane surface, surface oxides reduce the permeating flux to values indistinguishable at the noise level of the recording system (10^{12} $H_2/(cm^2\ s)$) at temperatures up to 500°C and hydrogen pressures at the membrane input side up to 50 Torr.

Hence, it is necessary to remove oxides from the surface of studied membranes in order to increase the rate of adsorption–desorption processes on the membrane surface.

In the first stage, we compared three surface preparation techniques:

(i) cleaning of the input and output membrane surfaces by argon ions;

(ii) cleaning by argon ions with subsequent deposition of a protective catalytic coating on the processed surface (on both membrane sides);

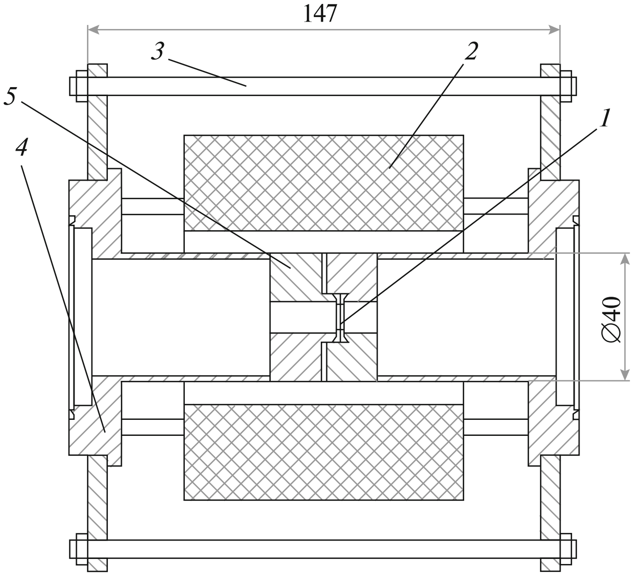

Fig. 1. Draft of quick-clamp fixing of membrane samples: (*1*) sample, (*2*) external heater, (*3*) threaded rods, (*4*) flanges, and (*5*) diffusion cell.

(iii) abrasive surface treatment (on both membrane sides).

The first two versions were implemented using equipment of the Resource Center "Physical Methods of Surface Investigation" (Saint-Petersburg University Research Park).

A technological ion source KLAN-103M was used for ion etching.

After the ion cleaning, the samples were placed in argon-filled containers without contact with air and then transported to the diffusion cell for carrying out hydrogen permeation experiments.

The samples intended for depositing catalytic coatings were preliminarily subjected to similar cleaning by argon ions, after which, without any contact with air, a bilateral nickel coating was deposited on them; the interaction of this coating with hydrogen has been studied well. It retains stably high hydrogen adsorption rate even after a long-term contact with air.

A coating was deposited by magnetron sputtering in a Kepler 450 system. Its thickness was calculated (proceeding from the process parameters) to be 5 μm.

Abrasive treatment of membranes was performed directly before placing them in the diffusion cell, using P100 grit cloth-backed abrasive paper. The time from the end of surface cleaning to the pumping onset for both membrane sides was no longer than 120 s.

Based on a comparison of the hydrogen permeability (at $T = 450°C$ and constant saturation flux) of the samples subjected to three types of surface preparation, the following conclusions were drawn (Fig. 2):

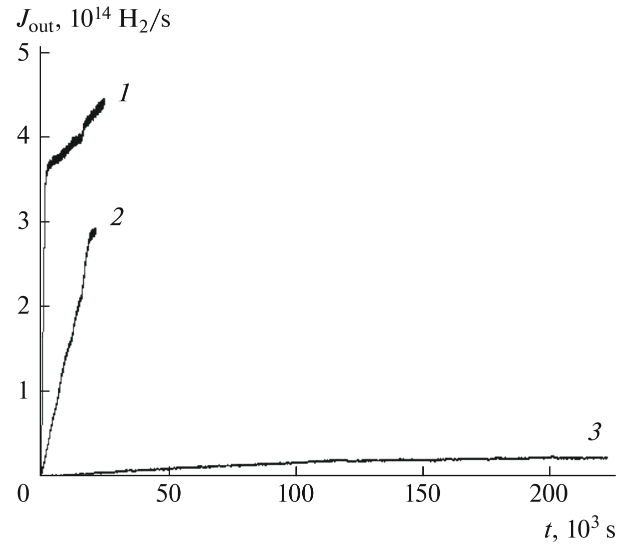

Fig. 2. Setting of a permeating flux through a hafnium membrane at 450°C for samples with input and output surfaces prepared in different ways: (*1*) ion etching with subsequent deposition of a 5-μm nickel coating by magnetron sputtering, (*2*) abrasive treatment with sandpaper, and (*3*) argon ion etching.

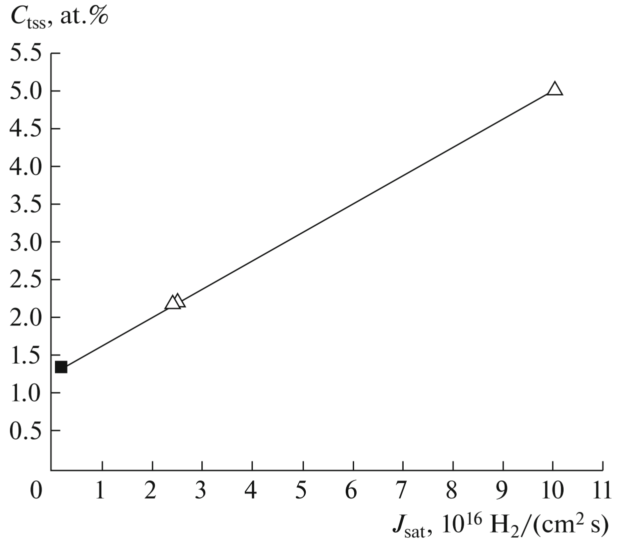

Fig. 3. Dependence of the terminal solid solubility, determined by the method in use, on the saturation flux at 450°C. Triangles are the values obtained in the experiments where pressure was maintained constant. Squares are the values for the case where the saturation flux was maintained constant at a level of ~2 × 10^{15} $H_2/(cm^2\ s)$ = 6.7 × 10^{-4} mol $H/(m^2\ s)$.

(i) the highest steady flux was observed for the samples having a nickel coating;

(ii) the flux for the samples subjected to abrasive cleaning was lower by a factor of ~1.3;

(iii) the flux through the samples subjected to only ion cleaning was an order of magnitude lower.

As a result, the treatment with only ion cleaning was considered as inappropriate. The use of nickel deposition complicated the object of study and its simulation due to the addition of two nickel layers to the membrane. Thus, the abrasive treatment performed directly before placing the sample in the vacuum system was considered to be the most appropriate for the planned experiments.

In addition, a qualitative XRD analysis of hafnium samples with a nickel coating, saturated with hydrogen to a concentration exceeding the terminal solid solubility, was performed at the Saint-Petersburg University Research Park (Resource Center “X-ray Diffraction Methods of Study”). As a result, formation of the phase of nonstoichiometric hafnium hydride $HfH_{1.628}$, belonging to the cubic system and sp. gr. $Fm\bar{3}m$ (225), at room temperature was revealed. The sample retained its integrity. This result indicates that the hydrogen content in the sample is fairly high and that, despite the small XRD depth in hafnium (510 μm), the hydride phase can be found in the near-surface membrane layers, both on the input and output sides.

DETERMINATION OF THE HYDROGEN TERMINAL SOLID SOLUBILITY IN HAFNIUM

The two key requirements to the protocol of method implementation are as follows:

(i) ensuring uniform distribution of hydrogen over the membrane thickness during its permeation;

(ii) achieving the values of average hydrogen concentration in the sample exceeding the hydrogen terminal solid solubility.

Concerning the hydrogen pressure at the input side, these requirements are contradictory. The first is fulfilled at low pressures, providing the surface-limited permeation regime. To fulfill the second requirement, the pressure must be sufficiently high to achieve the necessary hydrogen concentration.

The first experiments, performed on hafnium samples at high input pressures (~10–40 Torr), obviously sufficient to produce the hydride phase, showed that the obtained values of terminal solid solubility depend on the input pressure and, as a consequence, the rate of sample saturation with hydrogen (saturation flux) (Fig. 3, triangles). This is explained by the fact that, at a high membrane saturation rate, the concentration distribution deviates significantly from uniform, and the hydride phase production rate is insufficient to ensure equilibrium between the hydride and hydrogen solution.

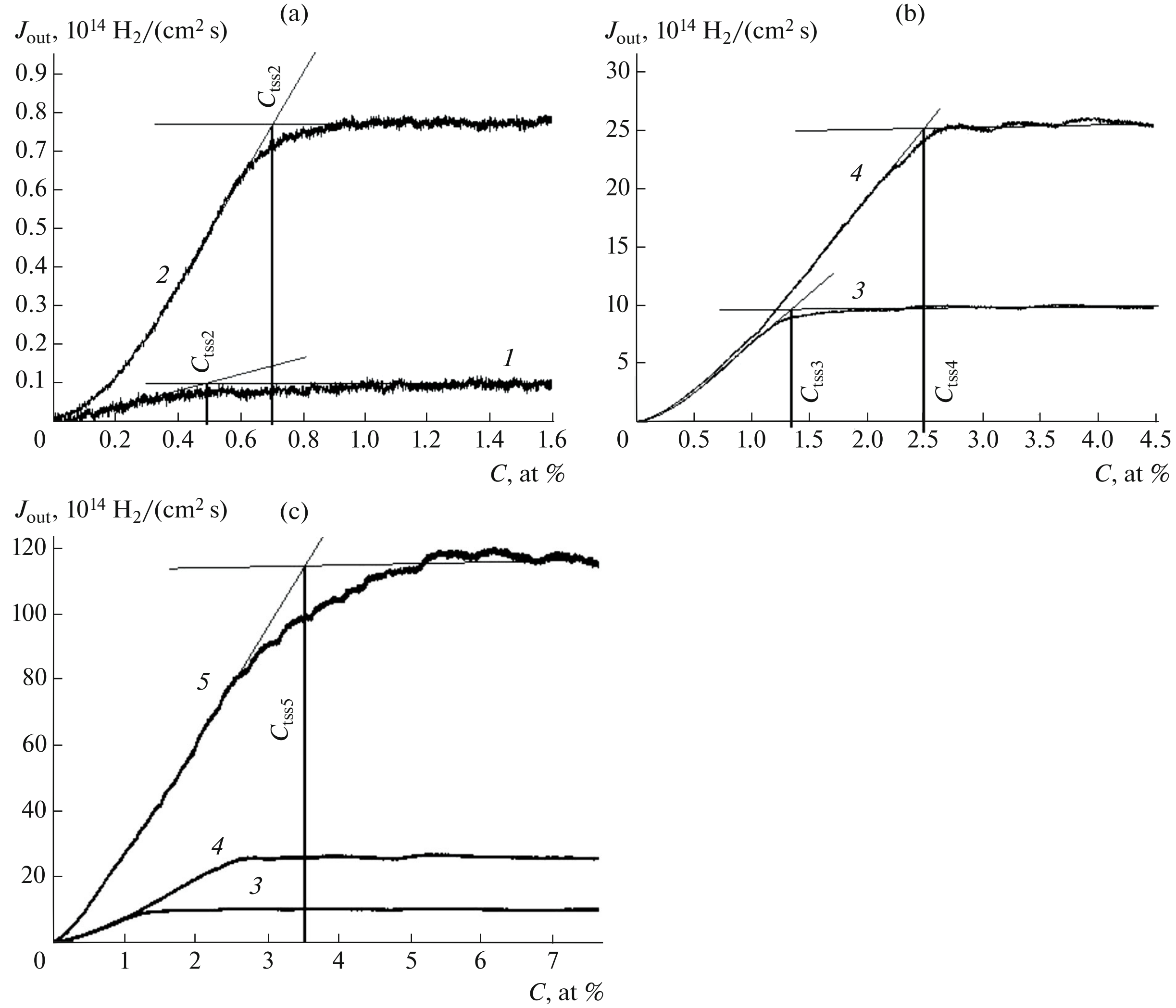

Fig. 4. Dependences of the permeating hydrogen flux on the hydrogen concentration in a hafnium plate for different temperatures: (*1*) 350, (*2*) 400, (*3*) 450, (*4*) 500, and (*5*) 550°C.

This result led us to abandon the experiments at a constant input pressure in favor of the regime in which a low membrane saturation flux (i.e., the difference between the input and output fluxes) is implemented, providing a slow membrane saturation, a state close to equilibrium between the hydride and solution, and a close-to-uniform distribution of hydrogen concentration in the sample. To this end, initially low pressure (<1 Torr) is supplied to the input membrane side, which thereafter increases with increasing the output permeating flux. The saturation flux was chosen to be at a level of ~2×10^{15} $H_2/(cm^2 s)$ = 6.7×10^{-4} mol $H/(m^2 s)$. The C_{tssp} value, obtained at this flux at 450°C, is shown by a filled square in Fig. 3. It can be seen that the values of terminal solid solubility, determined by the method in use, are described well by a linear dependence on the saturation rate. One can also state that the saturation flux of 2×10^{15} $H_2/(cm^2 s)$ is sufficiently low to make the determined terminal solid solubility deviate from the value corresponding to infinitely slow (equilibrium) saturation by no more than 5–10%.

At the aforementioned saturation flux, we performed measurements by the hydrogen permeation method in the temperature range of 350–550°C. The obtained kinetic curves of permeating flux setting were used to plot the dependences of the permeating (output) flux on the average hydrogen concentration in the sample (Fig. 4).

These dependences were used to determine the values of terminal solid solubility, which are presented in Fig. 5. The temperature dependence of the terminal solid solubility can be described by a linear

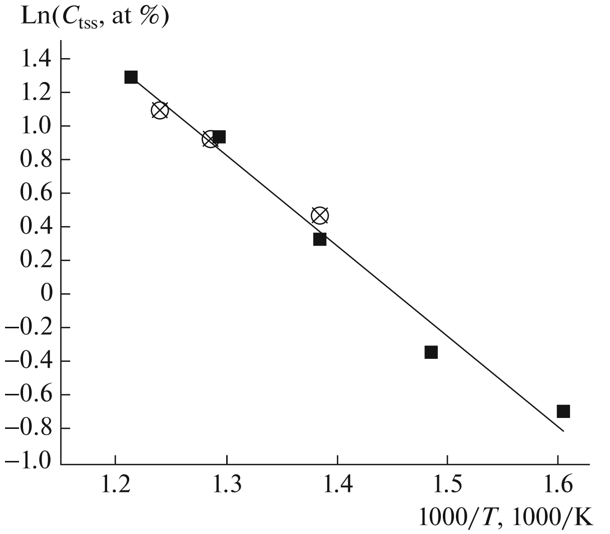

Fig. 5. Temperature dependence of the hydrogen concentration corresponding to terminal solid solubility in hafnium in Arrhenius coordinates: (■) experimental data obtained in this study, (⊗) data of [13], and (black line) linear approximation of the data of our study.

dependence in Arrhenius coordinates and the expression

$$C_{tssp}\,[\text{at }\%] = 2300\,[\text{at }\%] \times \exp\left(-\frac{44.5[\text{kJ/mol}]}{R\,[\text{kJ/(K mol)}]T\,[\text{K}]}\right). \quad (1)$$

A comparison of the obtained C_{tssp} values with the results obtained in [13, 14] at temperatures of 450°C and higher shows them to be in good agreement (Figs. 5, 6). At the same time, the results of our study expand significantly the experimentally investigated temperature range to lower values (down to 350°C).

CONCLUSIONS

Based on the results of the performed studies, we can conclude the following:

(i) an increase in the rate of hafnium saturation with hydrogen leads to an increase in the observed terminal solid solubility;

(ii) to obtain close-to-equilibrium values of hydrogen terminal solid solubility in hafnium, one should provide a low constant saturation flux (~2×10^{15} H_2/(cm^2 s));

(iii) values of terminal solid solubility for isothermal hydride production (C_{tssp}) were obtained in the temperature range of 350–550°C, which significantly expands the area for which data in the literature were available to date (above 450°C);

(iv) the temperature dependence of the terminal solid solubility has an Arrhenius form (1);

(v) the obtained values of hydrogen terminal solid solubility in hafnium are in good correspondence with the existing data in the literature on the equilibrium of the solution phase and hafnium hydride.

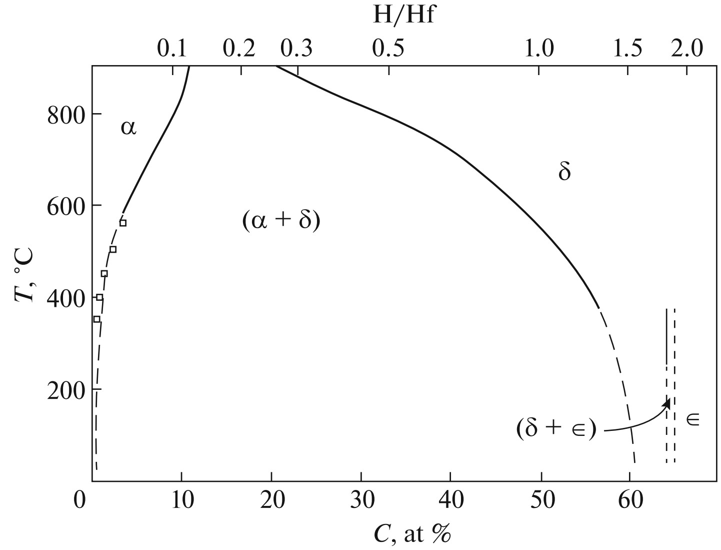

Fig. 6. Values of the terminal solid solubility obtained in this study (squares), plotted in the phase diagram of the hafnium–hydrogen system from [14].

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CONFLICT OF INTEREST

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

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