

<https://doi.org/10.15407/ufm.21.01.046>

**V.A. ZUYOK*, V.S. KRASNORUTSKYY,
T.P. CHERNYAYEVA, M.V. TRETYAKOV, and R.O. RUD**

National Science Centre 'Kharkiv Institute of Physics and Technology',
Science and Technology Establishment 'Nuclear Fuel Cycle',
1 Akademichna Str., UA-61108 Kharkiv, Ukraine

INFLUENCE OF STRUCTURE OF HAFNIUM RODS ON THEIR MECHANICAL PROPERTIES, CORROSION AND RADIATION RESISTANCES

The results of studying the dependence of mechanical properties, corrosion and radiation resistances of hafnium rods on their structure are presented and reviewed in this paper. As observed, the rods in a fully recrystallized state with a fine-grained structure possess optimal mechanical properties (high strength and ductility). Tensile strength of these rods at room temperature is of ≈ 575 MPa, percentage elongation is of 27–28%. Autoclave corrosion tests and anode polarization curves reveal that oxide films formed on hafnium samples in a fully recrystallized state are the most protective that is due to the low surface activity at the medium–metal interface. The corrosion rate of such hafnium rods at the initial period of oxidation (before the pre-transition period) is well described by the empirical power equation with the power coefficient of 0.242 ± 0.015 . After the transition point (≈ 6000 h), the corrosion kinetics is described by a linear dependence with the oxidation rate of $3.12 \cdot 10^{-4} \pm 2.07 \cdot 10^{-5}$ mg/(dm²·h). As shown, there is a correlation between the radiation growth of hafnium rods and their texture coefficient (Kearns's parameter) according to the results of radiation tests carried out at the JSC 'SSC RIAR' (RF) as well as structural-textural studies of the same samples of hafnium rods in various structural states performed in this work. The results presented in this paper reveal that the coefficient of radiation growth linearly decreases with an increase of the Kearns's parameter to a value of 0.33. This indicates that hafnium rod samples with a more isotropic texture are less susceptible to radiation growth. The radiation growths differ, depending on the rods' structure. For rods with the same texture and different grain sizes, the samples with a fine-grained structure are less disposed to radiation growth. While Kearns's parameters are similar, the hafnium rods with a coarse-grained structure show a higher rate of radiation growth. The deformation

* valeriyz@kipt.kharkov.ua

Citation: V.A. Zuyok, V.S. Krasnorutskyy, T.P. Chernyayeva, M.V. Tretyakov, and R.O. Rud, Influence of Structure of Hafnium Rods on Their Mechanical Properties, Corrosion and Radiation Resistances, *Progress in Physics of Metals*, **21**, No. 1: 46–71 (2020)

of the radiation growth of rods with a recrystallized structure, the Kearns's parameter of ≈ 0.1 , and an average grain size of less than $20\text{ }\mu\text{m}$ is almost equal to zero when the rods are irradiated at a temperature of $260\text{--}300\text{ }^{\circ}\text{C}$ up to a fast neutron fluence of $7.8 \cdot 10^{21}\text{ cm}^{-2}$.

Keywords: hafnium, structure, texture, mechanical properties, corrosion, radiation growth.

1. Introduction

Deformation is one of the main and most frequently used operations in the technological process chain of manufacturing products of the required shape. The optimal combination of temperature, degree and speed of deformation of the rods and the temperature of subsequent annealing allows obtaining a developed, homogeneous and stable microstructure. Deformation should be considered not only from the standpoint of form change, but also as a powerful way of affecting the structurally sensitive properties of metals and alloys that directly affect their performance. The combination of deformation with the processes occurring during annealing (tempering, polygonization, primary recrystallization, collective and secondary recrystallization) allows one to obtain hafnium products in various structural and textural states, and, accordingly, with different structurally sensitive properties.

The results of studying changes in the structure and texture of nuclear grade hafnium rods (HFE-1 brand) with a change in the deformation-temperature regimes of their manufacture are presented in Refs. [1–3]. In the works [4–7], authors presented the results of the studying the corrosion of hafnium rods in a fully recrystallized state under autoclave conditions at a temperature of $350\text{ }^{\circ}\text{C}$ and a pressure of 16.5 MPa in a model medium of VVER-1000 reactor primary coolant and in water vapour at temperature range of $350\text{--}1100\text{ }^{\circ}\text{C}$. Radiation tests of hafnium samples supplied by the Science and Technology Establishment (STE) 'Nuclear Fuel Cycle' (NFC) of the National Science Centre (NSC) 'Kharkiv Institute of Physics and Technology' (KIPT) were carried out at the JSC 'SSC RIAR' (RF). The obtained results were published in Refs. [8–11]. At the same time, the available set of test and research results allows determining a change in the geometric dimensions of the samples under study, but does not allow determining the optimal structural and textural state of hafnium products (rods), in which they possess high dimensional stability under irradiation, high strength and ductility along with high corrosion resistance. This paper presents the results and review analysis of a comprehensive study of the influence of deformation and heat treatment on the structurally sensitive properties of hafnium rods. As a goal, we aimed to establish a correlation between the structure and the main structurally sensitive properties of hafnium

rods, such as strength and ductility, corrosion resistance and dimensional stability under irradiation.

2. Materials and Research Methods

Nuclear grade metal hafnium (HFE-1 brand) was used as the base material for research. In accordance with the attached certificate, the chemical composition of the hafnium ingot corresponds to TY Y 14312708.183-95 (according to the DSTU grade). Samples for research were made from rods obtained from ingots by forging. The detailed manufacturing sketch is given in Refs. [1–3].

Microhardness was measured on a PMT-3 microhardness tester. A standard method for preparing hafnium samples for metallographic studies was used [11].

Corrosion tests of hafnium rods were carried out in laboratory autoclaves at a temperature of 350 °C and a pressure of 16.5 MPa in a model medium of the VVER-1000 primary coolant of the following composition: 7 g/dm³ of H₃BO₃, 0.025 g/dm³ of KOH, and 2.8 mg/dm³ of NH₄OH. The chemical grade and the analytical grade reagents were used without additional purification for the preparation of the model medium. The pH value of the medium measured at a room temperature using the pH-150MA pH-millivoltmeter was of 7.2 units. Chemically demineralized water with a conductivity of 0.25 µS was used to prepare a corrosion medium. The methodology for conducting such tests is described in ASTM standards [12–15].

Exposure time at each stage of tests in high temperature medium was of 500 h. After the unloading from autoclaves, the samples were examined at a magnification of up to 10 times and weighed on a VLR-20 microbalance with an accuracy of 0.01 mg.

The surface preparation of hafnium samples for corrosion autoclave tests was carried out according to the following scheme: grinding with abrasive paper with decreasing abrasive grain size, chemical polishing in a solution of 5% of HF + 45% of HNO₃ + 50% of H₂O, washing in a 15% Al(NO₃)₃ solution to remove traces of the etchant, rinsing and boiling in chemically type 1 reagent water [12].

Polarization measurements were carried out using the IPC-Pro potentiostat in a standard electrochemical three-electrode cell with a platinum auxiliary electrode and silver chloride reference electrode EVL-1M1, the potential sweep speed was of 1 mV/s [16].

Radiation tests of the hafnium samples manufactured in STE NFC NSC KIPT according to various technological schemes were previously carried out at the JSC 'SSC RIAR' (RF) [8–10]. The tests were carried out in the SM reactor for 300 effective days in an aqueous coolant at a temperature of 260–300 °C and a pressure of 15 MPa to a maximum fast

neutron fluence of $7.8 \cdot 10^{21} \text{ cm}^{-2}$ ($E > 0.1 \text{ MeV}$). In this work, we studied the texture of samples cut from rods of the same batches that were used in the JSC 'SSC RIAR' (RF) in radiation tests. Using x-ray diffraction patterns, reverse pole figures were plotted and the Kearns's parameter was calculated for the longitudinal direction of the rods. The above-mentioned x-ray diffraction patterns were obtained on a DRON-3M x-ray unit equipped with a counting and recording device from the cross-section of the rod in CuK_α radiation with a nickel filter. The main task was to determine the correlation between the Kearns's orientation parameter (sample production technology) and radiation growth. The tendency of materials to radiation growth is determined by the coefficient of radiation growth, calculated as the ratio of the change in the length of the rod, expressed as a percentage, to the neutron fluence corresponding to this change.

3. Effects of Strain and Annealing on the Change in Structure and Texture

3.1. Starting Points

Hafnium has two allotropic modifications: (1) a low-temperature modification of hafnium (α) with a h.c.p. structure stable up to a temperature of 1743°C ; (2) a high-temperature (β) phase with a b.c.c. lattice, stable from 1743°C , when the transformation occurs, up to a melting point of 2223°C [17].

The high temperature of $\alpha \leftrightarrow \beta$ -transformation makes it difficult to use polymorphic transformation to control the structure and texture of hafnium. Annealing at temperatures above the $\alpha \leftrightarrow \beta$ -transformation temperature leads to an increase in grain size up to several hundred microns, and, in some cases, up to several millimetres, that is unacceptable for the material used in the core of a nuclear reactor. Therefore, plastic deformation and subsequent recrystallization annealing are adopted as the basis for controlling structure and texture when manufacturing metallic hafnium products. This section describes the transformation of structure and texture during deformation-heat treatment of hafnium and the basic laws of their change.

3.2. Structural Change at a Strain

The effect of various methods (forging, rolling) and types (hot, warm, cold) of deformation on the change in the structure and texture of hafnium rods was studied earlier [1–3]. The values of the critical deformation degree were determined. The excess of these values is accompanied by the formation of macrocracks. Regardless of the method of deformation (forging, rolling, *etc.*), the degree of single reduction should not exceed 36% for hafnium, which has passed the stage of destruction of the cast

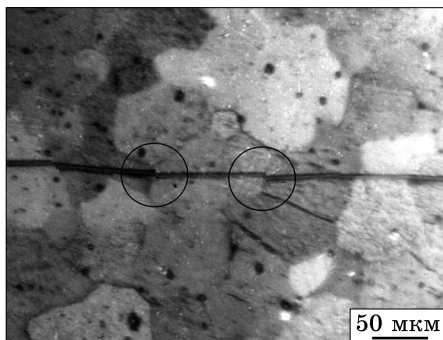


Fig. 1. Slippage along the grain boundaries and grain rotation in slightly deformed hafnium

structure of the ingot. Intermediate recrystallization anneals are necessary to achieve higher compression ratios.

Studies have shown that the deformation of hafnium occurs both by slippage (Fig. 1) and by twinning

(Fig. 2) [1]. For other grades of hafnium (Ukraine has the technology for producing calcium thermic nuclear grade hafnium GFE-1), the processes occurring during deformation of hafnium with indication of slip systems and twinning planes are described in detail in.

Slippage along the boundaries and grain rotation are observed at a negligible degree of deformation. Passing through the whole grain, the shift caused slippage of the grain boundaries, as well as their additional rotation (Fig. 1). Intensive plastic deformation often led to a change in shape, fragmentation, and dispersion of the grain structure (Fig. 3). The confirmation of each of the listed processes was obtained during the carrying out the cycle of tests.

Figure 2 shows the SEM image of a hafnium structure deformed by rolling at room temperature by 20%. According to available information, the main twinning system in Hf is $\{10\bar{1}2\} \langle 1011 \rangle$ [18–21].

At high degrees of deformation, a significant change in the shape of the grains is observed, they are elongated in the direction perpendicular to the applied load (compression direction), and a change in the texture of the rods occurs (Fig. 3) [2].

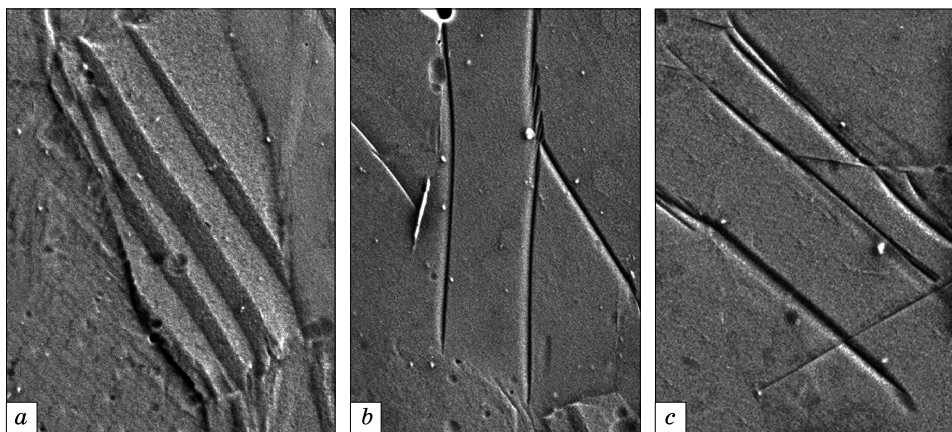


Fig. 2. SEM views of twins in hafnium. Degree of deformation is $\approx 20\%$

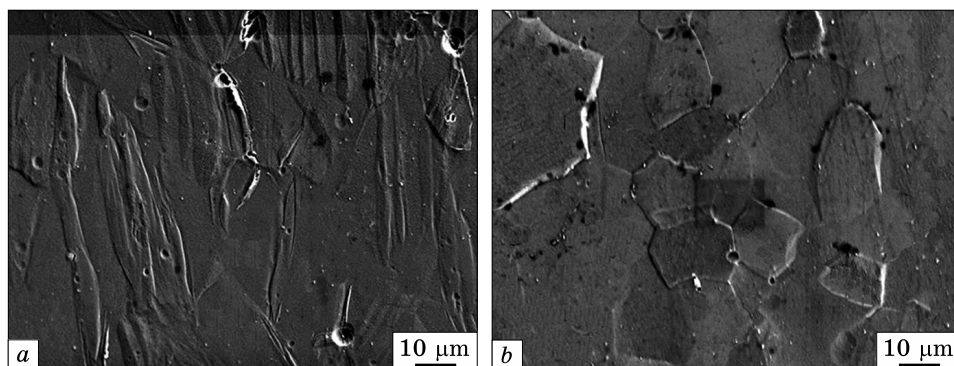


Fig. 3. SEM-images of hafnium structure in the initial (unstrained) state (a) and in deformed (36% strain degree) state (b)

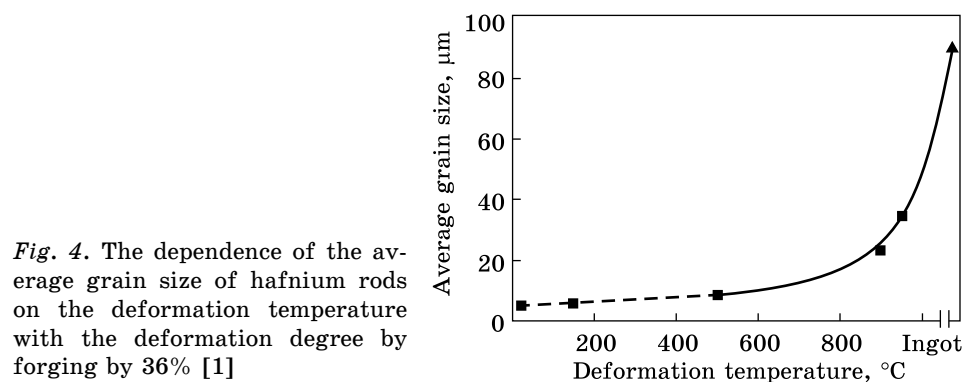
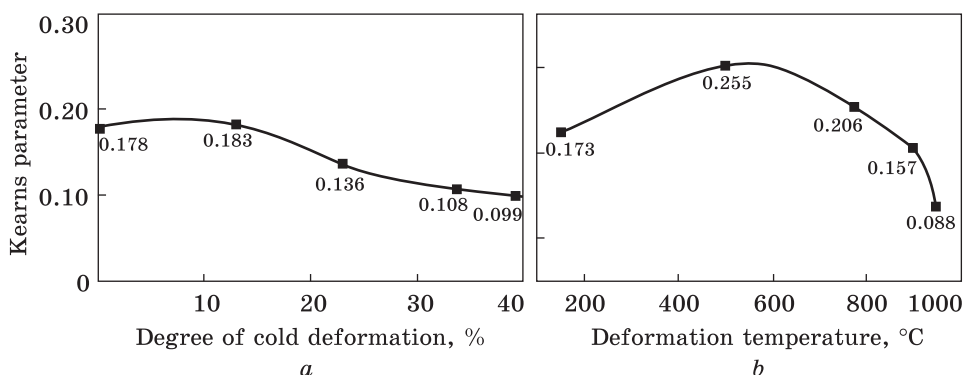
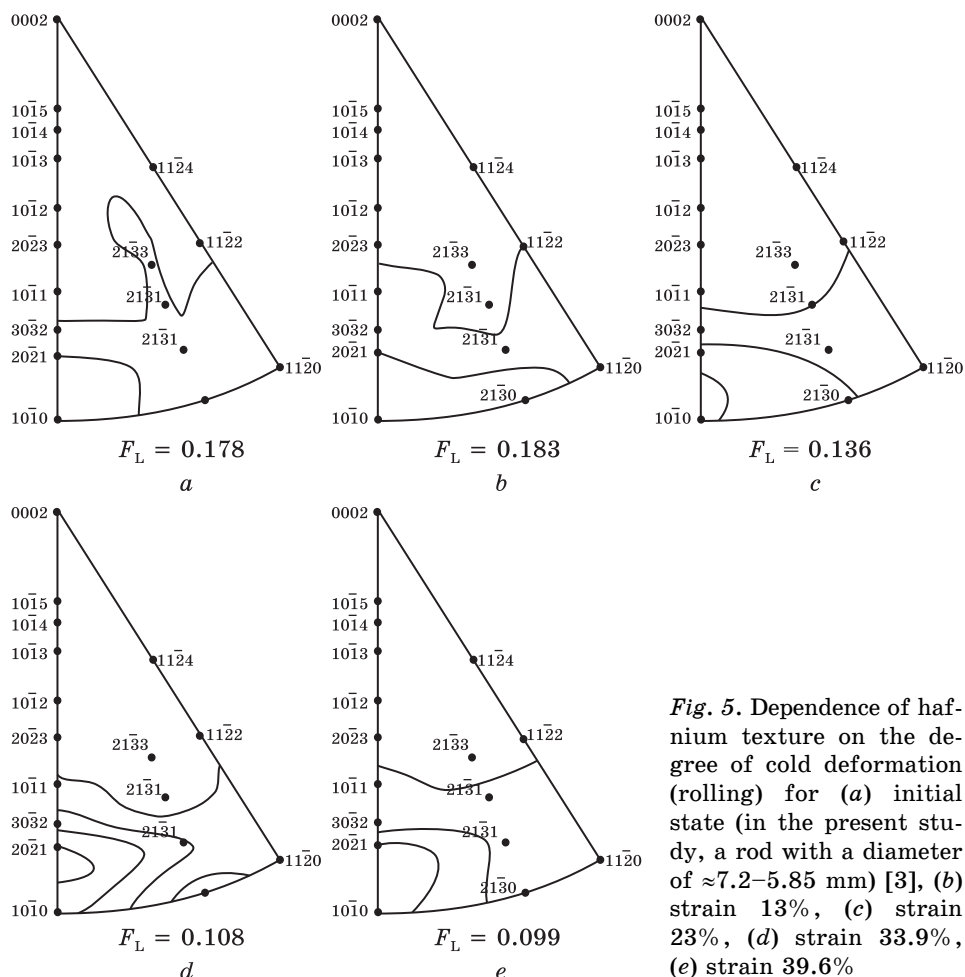


Fig. 4. The dependence of the average grain size of hafnium rods on the deformation temperature with the deformation degree by forging by 36% [1]

Regardless of the method of deformation, an increase in the degree of deformation usually leads to a refinement of the hafnium grain structure. At the same time, this is not applicable to high-temperature deformation, during which recrystallization annealing occurs, accompanied by an increase in the (average) size of the grain [2]. Figure 4 shows the dependence of the average grain size (taking fragments into account) on the deformation temperature of the rod by forging. To carry out this study, hafnium rods with an initial grain size of $\approx 45 \mu\text{m}$ were used, and the deformation degree during forging was of $\approx 36\%$.

3.3. Textural Change during Deformation

Deformation causes not only the shape change of the sample, but also the shape change and rotation of the grains [3]. The influence of the deformation degree on the change in crystallographic orientation was studied on the same samples on which the change in the grain structure was studied during the deformation of hafnium rods by rolling (Fig. 5). An increase in the deformation degree leads to crystallographic reorientation of the grains, which, in turn, leads to an increase in the axial



texture $\langle 10\bar{1}0 \rangle$ and a decrease in the density of the basal planes (0002) along the axis of the rod, which leads to a decrease of the Kearns's parameter in the longitudinal direction.

Figure 6, a shows the dependence of the Kearns's parameter of hafnium rods on the degree of cold deformation (rolling). Warm and hot deformations are accompanied by a similar change in the orientation parameter, while recrystallization significantly affects the nature of the texture. Figure 6, b shows the dependence of the Kearns's parameter in the longitudinal direction on the deformation temperature at the deformation degree of 36% [1].

3.4. Structural Changes during Annealing

A series of studies was carried out on the effect of annealing temperature on the structure of hafnium rods. Figure 7 shows the dependence of the average grain size of cold-deformed hafnium rods on the annealing temperature, and Fig. 8 — on the annealing exposure for different temperatures. The results of these studies are published in detail in Refs. [1–3]. When carrying out this set of studies, the following parameters were determined: the critical degree of deformation, the temperature of the beginning and end of primary recrystallization and its dependence on the time of isothermal annealing for hafnium with different hardening values. Collective recrystallization was studied, the energy characteristics of primary recrystallization and grain growth were determined, and the evolution of texture during annealing was studied.

In studying the effect of annealing on the structure of hafnium rods deformed to various degrees of deformation (rolling), a critical degree of deformation is determined. This is of great practical importance, since annealing at a critical degree of deformation leads to the formation of a coarse-grained structure with an average grain size of $\approx 240 \mu\text{m}$ (enlargement ratio 9.6) (Fig. 9). The critical degree of deformation is of 2.5–3% in the manufacture of hafnium rods at the most probable temperature of recrystallization annealing, selected on the basis of studies carried out in this work (850 °C).

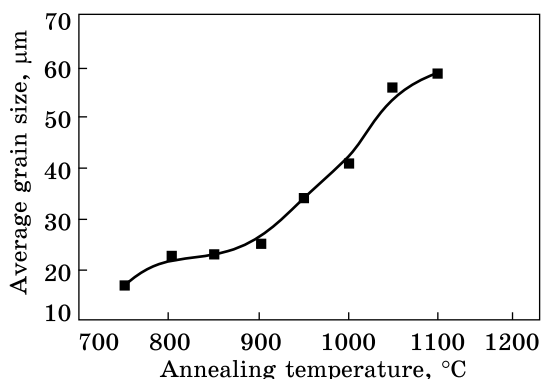


Fig. 7. Average grain size vs. the annealing temperature for hafnium, previously strained via rolling by 36%. Duration of annealing: 1 h

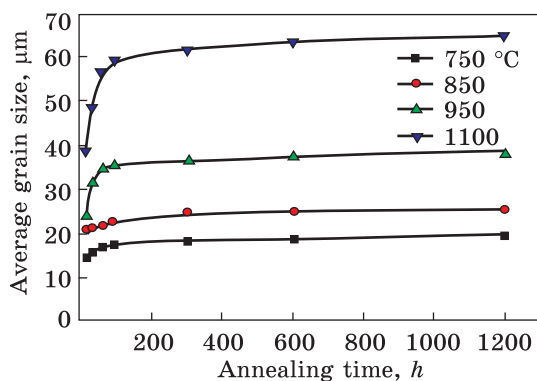


Fig. 8. The dependence of the average grain size in hafnium rods deformed through rolling by 36% on the time of isothermal annealing at various temperatures

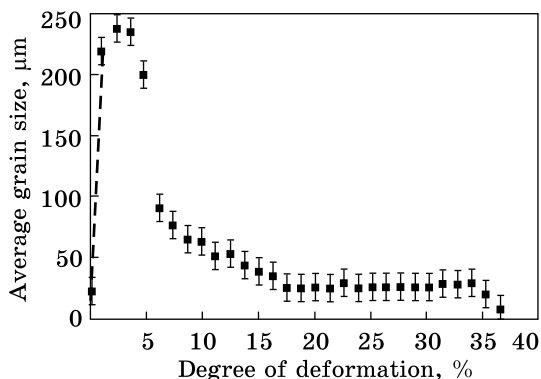


Fig. 9. The dependence of the average grain size of hafnium annealed at 850 °C for 1 h on the degree of preliminary deformation by rolling at room temperature

of the average grain size on the temperature and annealing time for rods deformed by rolling at a temperature of 150 °C; this figure also shows the temperature–time intervals of primary and collective recrystallization.

3.5. Textural Changes in the Cold-Formed Hf Rods at Annealing

Along with the study of the effect of annealing on the structure of hafnium rods, much attention was paid to the study of texture. The studies were performed on deformed samples annealed at temperatures in the range including the temperature of primary and collective recrystallization, as well as partially the temperature of secondary recrystallization.

The value of the temperature of the onset of recrystallization ($T_{o.r.}$) in deformed hafnium is in a certain ratio with the melting temperature: $T_{o.r.} = \delta T_{melt}$, where the value of δ belongs the range 0.35–0.39. The value of δ depends (to some extent) on the deformation and annealing modes, varying slightly with their change within the indicated limits.

Based on metallographic studies, the temperature of the onset of secondary recrystallization was determined, the hallmark of which is the appearance of grains with the size much larger than in the matrix surrounding them. During secondary recrystallization, the average size of the bulk of the matrix grains does not change and there is a significant change in grain size distribution (Fig. 10).

Based on the obtained experimental data, three-dimensional recrystallization diagrams were constructed. Figure 11 shows the dependence

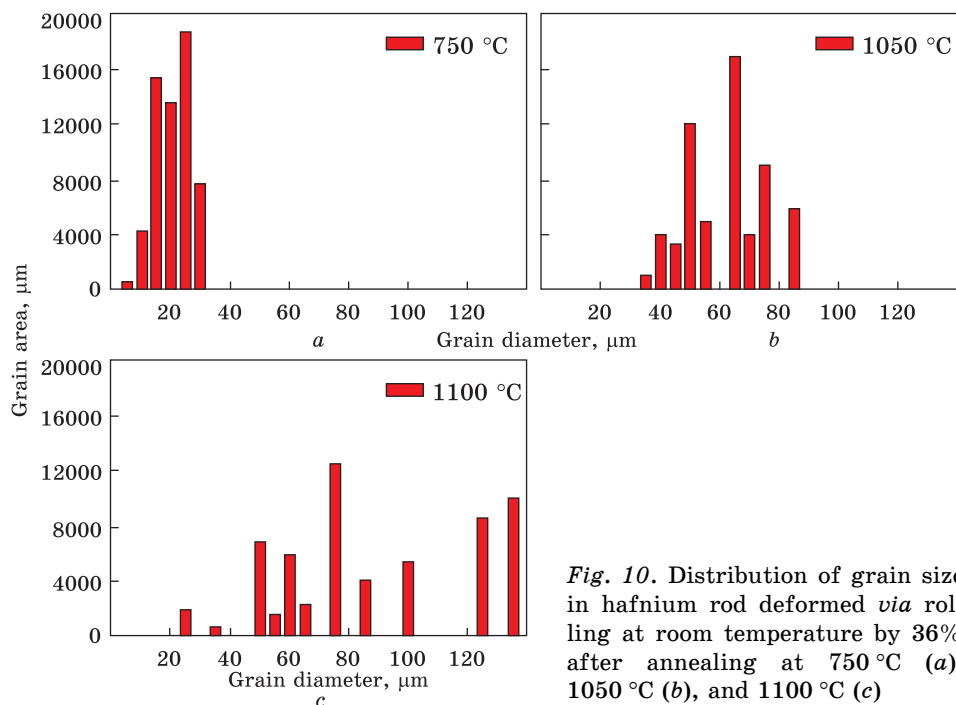
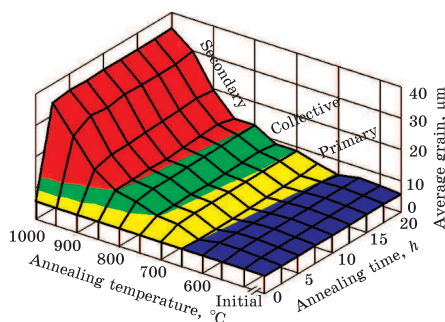


Fig. 10. Distribution of grain size in hafnium rod deformed *via* rolling at room temperature by 36% after annealing at 750 °C (a), 1050 °C (b), and 1100 °C (c)

Fig. 11. Average grain size *vs.* temperature and annealing time for hafnium rods strained at 150 °C [1]. The temperature-time intervals of primary, collective, and secondary recrystallization are also shown



stallization. Figure 12 shows the dependence of the texture (pole density for a number of planes along the longitudinal direction) of hafnium rods on the annealing temperature of rods deformed by rolling by 36%.

As follows from the results of the studies, the annealing of deformed hafnium rods results to the grain reorientation, a decrease in the density of the poles of planes (10 $\bar{1}$ 0) and (20 $\bar{2}$ 1), and an increase in the density of poles (11 $\bar{2}$ 0) and (21 $\bar{3}$ 2) along the axis of the rod, which is accompanied by a slight increase in the Kearns's orientation parameter, but does not completely destroy the deformation texture.

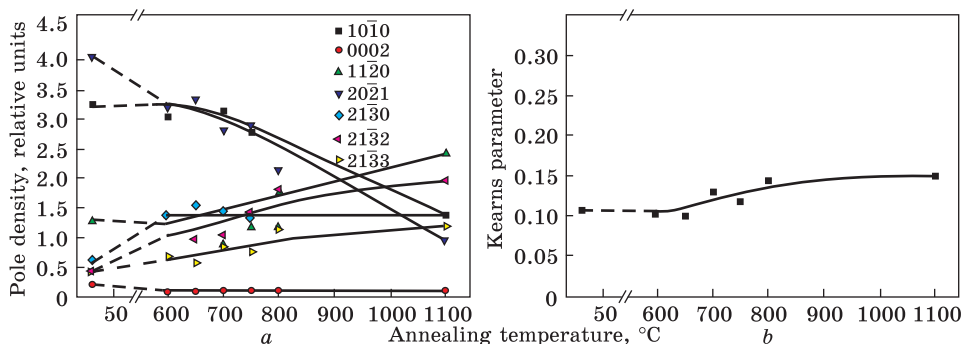


Fig. 12. Dependence of texture characteristics of hafnium rods (cold-deformed by 36%) on the annealing temperature: *a* — pole density; *b* — Kearns orientation parameter [3]

4. Structural and Textural Impacts on the Mechanical Properties, Corrosion Kinetics, and Radiation Stability

Hafnium is a typical representative of metals with an h.c.p. lattice [17]. The low symmetry of the h.c.p. lattice largely determines the dependence of the mechanical and thermophysical properties of hafnium products on their texture and microstructure, and hence, on the technological operations used in their manufacture.

This section discusses the influence of the texture and structure of hafnium rods on their mechanical properties (hardness, strength, and ductility), corrosion resistance, and radiation growth.

4.1. Mechanical Properties

Hardening is a change in the structure and, accordingly, properties of metals and alloys caused by plastic deformation at a temperature below the recrystallization temperature. The hardening phenomenon is explained by the accumulation of part of the deformation energy in the metal, which is spent on distorting the crystal lattice, reorientation of crystals, and changing the dislocation structure. Hardening can be the result of the action of external deforming forces, as in the case of these experiments with hafnium or under certain conditions of phase transformations. Hardening can lead to a significant change in the structurally sensitive properties of the material: an increase in hardness and strength, as well as a decrease in ductility.

Short-term mechanical tests were carried out on ‘Gagarin’ samples cut from hafnium rods at a temperature of 20 °C, manufactured according to the deformation–thermal conditions used in the work. Some results of single tests of HFE-1 nuclear grade hafnium rod samples were already presented in Ref. [22].

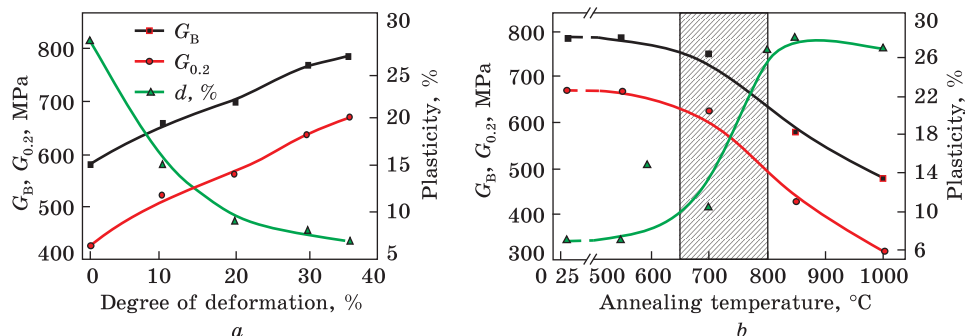


Fig. 13. The yield strength, tensile strength, and elongation of hafnium samples vs. the degree of finish deformation (forging) of the rods from which they are cut (a) and vs. the annealing temperature of the deformed hafnium rods (b)

Figure 13 shows the dependence of the tensile strength, yield strength, and elongation of hafnium samples with a fine-grained structure on the degree of deformation of the rods from which these samples were cut. The relative elongation of samples made from hafnium rods in the initial state was of $\approx 28\%$. The main trend is an increase in strength (tensile strength and yield strength), as well as a decrease in the ductility of hafnium samples with an increase in the degree of rod deformation. Deformation of the initial rod by 36% led to an increase in the tensile strength and yield strength to 775 and 675 MPa, respectively. After preliminary deformation of hafnium samples by forging to 10–15%, the relative elongation sharply decreased to $\approx 7\%$ at maximum rod deformation (36%).

Annealing of the strained hafnium rods led to a decrease in their strength and an increase in ductility. Maximum ductility was observed for deformed hafnium rods after annealing at a temperature of 800–850°C that corresponds to the temperature of the end of primary recrystallization. As shown in Fig. 13, b, the area of the primary recrystallization course is shaded (650°C — the beginning, 800°C — the end of the primary recrystallization). A further increase in the annealing temperature of deformed hafnium rods led to a slight decrease in ductility, which is probably due to an increase in the average grain size.

It was possible to evaluate the contribution to the changes in the strength and ductility of those processes that occur during annealing: recovery (polygonization) and the beginning of primary recrystallization, basing on the obtained experimental data of changes in the tensile strength, yield strength, and elongation of deformed hafnium samples with annealing temperature. It requires carrying out a set of tests with annealing at temperatures in the range of 550–800°C with step not exceeding 50°C. The same applies to the influence of the deformation degree of the rods (rolling) on the change in their strength. The rod

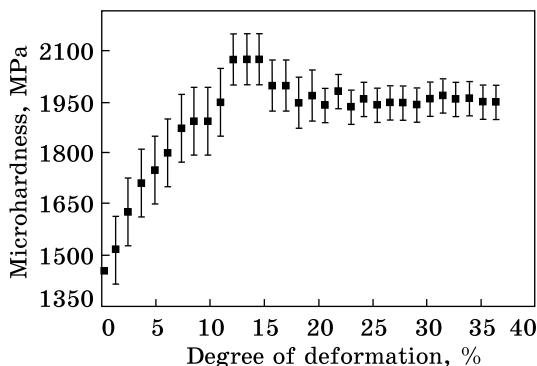


Fig. 14. The dependence of the microhardness of hafnium rods on the degree of deformation by rolling at room temperature

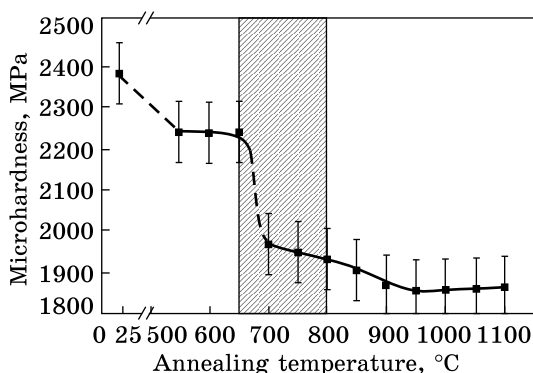


Fig. 15. The dependence of microhardness on the annealing temperature for hafnium previously deformed through rolling by 36% at room temperature. Annealing time: 1 h

noticeable in the region of small deformations. Thus, rolling deformation by $\approx 10\%$ caused an increase in microhardness to 1900 MPa, which, presumably, is associated with an increase in material hardening and fragmentation of the grain structure.

A further increase in the degree of deformation by rolling to 15% leads to a slight increase in microhardness (up to 1950 MPa) due to the high degree of strain hardening. Next, the stage of reduction in microhardness begins, associated with the beginning of crystallographic reorientation and a change in the shape of the grains. After that, the microhardness of hafnium rods with an increase in the degree of deformation by rolling practically does not change.

A significant scatter of the results when measuring microhardness is caused not by the error of the measuring device, but by the tex-

deformation from 0 to 36% covers the entire necessary area, while the rod deformation step (10%) is not enough to assess the contribution of small deformations to the change in strength. In this regard, a set of studies was carried out to determine the dependence of the microhardness of a hafnium bar on the degree of deformation (up to 36%, rolling) with a step in deformation of 1.2–1.4% and a step in annealing temperature of 50 °C (Fig. 13). Microhardness measurements were performed on the longitudinal (diametric) section of the rod (rod samples were cut along the axis into four segments).

According to the obtained results, the microhardness of the hafnium rod in the initial state (fully recrystallized), measured in the longitudinal section of the rod, is of ≈ 1453 MPa. With an increase in the degree of deformation, the microhardness of hafnium rods increases, which is especially

turing and anisotropy of the mechanical properties of the studied hafnium rods.

According to the obtained results, the main structural changes that lead to an increase in the microhardness of hafnium occur when the degree of rods deformation is of under 10–15%. Figure 14 shows the dependence of the microhardness of a hafnium rod deformed by rolling at room temperature by 36% on the annealing temperature. The annealing time was of 1 h. For this set of tests, the microhardness was measured on the lateral surface of the sample in the radial direction.

The annealing-temperature dependence of microhardness can be divided into several sections (Fig. 15), each corresponding to certain stages of restoration of the structure of deformed hafnium. Proceeding at temperatures below 650 °C, the first stage includes processes that do not lead to a significant decrease in microhardness (recovery stage, including polygonization).

The second stage, which is responsible for a sharp decrease in microhardness, begins at a temperature of ≈ 700 °C and corresponds to the transition to intensive recrystallization. The microhardness of previously deformed and annealed at a temperature of 750 °C hafnium is of ≈ 1950 MPa that corresponds to the completion of primary recrystallization.

Apparently, the stage of grain enlargement, which is typical for this temperature range, is responsible for a further slight decrease in microhardness with increasing annealing temperature up to 900 °C. After annealing at 900 °C, the average grain size is comparable to the pyramid indentation of the microhardness tester. Hence, the hit probability of the pyramid indentation at the grain boundary significantly reduces. This effect can lead to some decrease in the microhardness value.

Mechanical properties of nuclear grade HFE-1 hafnium rods obtained in this work are comparable with data presented in Ref. [22]. Comparison of the results with the data for HFI-1 grade hafnium given in Ref. [23] revealed that in the recrystallized state the ductility of HFI-1 hafnium (30–36%) is higher than that of HFE-1 hafnium ($\approx 28\%$), and the tensile strength is lower (440–480 MPa and 575 MPa, respectively).

Based on the results obtained for the interrelation of the mechanical properties of hafnium rods with its structure, we can argue that the rod in a fully recrystallized state will have the most acceptable set of mechanical properties.

4.2. Corrosion Kinetics in the High-Temperature Water of VVER-1000 Primary Coolant

Hafnium possesses high chemical reactivity due to its nature. A standard reduction potential of hafnium is 1.72 V *vs.* the normal hydrogen electrode at 24 °C and hafnium is more reactive than either titanium

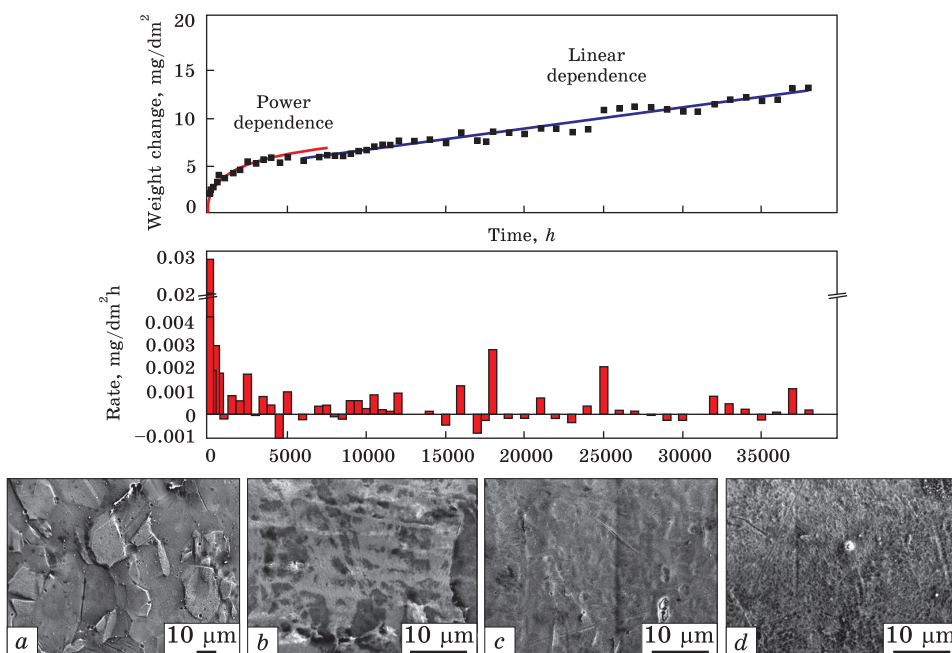


Fig. 16. Weight change of a hafnium and its corrosion rate depending on the exposure time at autoclave tests at 350 °C and 16.5 MPa in a model medium of the VVER-1000 primary coolant. Surface morphology of the samples: *a* — before testing, *b* — 2000 h, *c* — 5000 h, and *d* — 10000 h [5]

(−1.63 V) or zirconium (−1.53 V). At the same time, extremely high corrosion resistance of hafnium is determined by formation of a thin, tenacious oxide layer when exposed to most chemical environments. Oxide layers can also be formed by anodizing and by treatment in steam autoclaves and in air at elevated temperatures. The most commonly formed oxide is hafnium dioxide (HfO_2) [24–27]. To study the mechanisms of corrosion occurring on the surface of structural materials in water-cooled reactors, thermodynamic calculations often use. Potential-pH diagrams (Pourbaix diagrams) for iron, nickel and chromium in water at different temperatures are given in Ref. [28]. Their analysis gives a clear idea at what temperatures stable compounds or complexes will form, and which will not form. This significantly reduces the complexity of the experiments and simplifies interpretation of the results.

Theoretical methods are currently have reached such level that they can be practically used even if they do not provide sufficient accuracy of quantitative characteristics, but in combination with experimental data, a powerful analytical and experimental base is created for forecasting the trouble-free operation of NPP equipment. However, now and in the near future, experimental study is the only source giving the most reliable data.

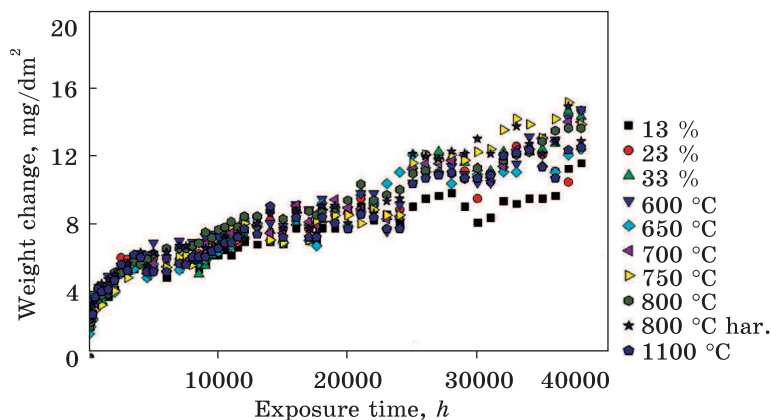


Fig. 17. The dependence of the weight change of hafnium samples on the exposure time at autoclave tests at 350 °C and 16.5 MPa in the model medium of the VVER-1000 primary coolant [5]

Tests carried out in high-temperature water under pressure, depending on the conditions, are divided into the groups.

Autoclave tests with an exposure time of more than 35 000 h revealed that the corrosion of hafnium in the model medium of the VVER-1000 primary coolant at a temperature of 350 °C is a combination of two processes. They are the oxidation of hafnium, accompanied by an increase in its weight, and a parallel process of spalling of the thin outer oxide layers leading to a slight decrease in its weight (Fig. 16).

In the initial period of oxidation (before the transition point), the kinetic curves of hafnium oxidation are well described by the empirical power equation with an exponent of 0.242 ± 0.015 (Fig. 17). After the transition point (≈ 6000 h), the corrosion kinetics is described by a linear dependence with the rate of $3.12 \cdot 10^{-4} \pm 0.207 \cdot 10^{-4}$ mg/(dm²·h).

Hafnium rod samples with a recrystallized structure were cold rolled at 20 °C until a degree of deformation was reached 13, 23, and 33% to study the effect of the structural state of hafnium on its corrosion resistance. The average grain size of samples deformed by 13% was of 15–20 μm, for 23%, 10–15 μm, and for 33%, 7–10 μm. A batch of the rods deformed by 33% was subjected to recrystallization annealing at a pressure of $5 \cdot 10^{-3}$ Pa for 1 hour at temperatures of 600, 650, 700, 750, 800, 1100 °C. A hafnium sample annealed at a temperature of 800 °C was subjected to rapid cooling (hardening) in water (in Figs. 17–19, hardening is denoted as ‘har.’). The average grain size of such a sample was of 20 μm. The characteristics of the rods that underwent such types of processing are described in the previous paragraphs of this paper.

The dependence of the weight change of hafnium samples in a different structural state (manufactured by different technological

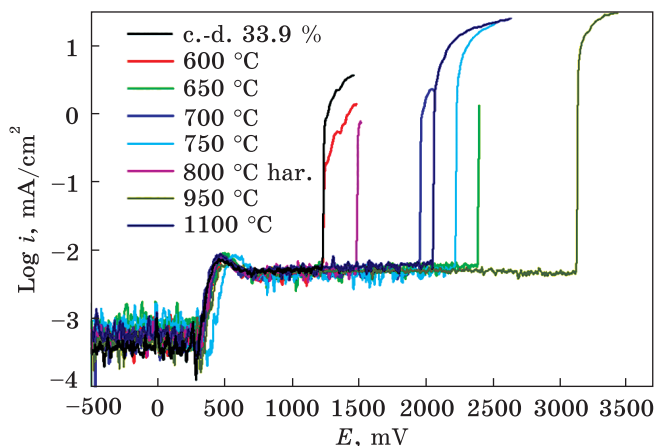


Fig. 18. Anodic polarization curves of unoxidized hafnium samples, cold-deformed (c.-d.) by 33.9%, as well as deformed by 33.9% and annealed at 600, 650, 700, 750, 800, 950, and 1100 °C [5]

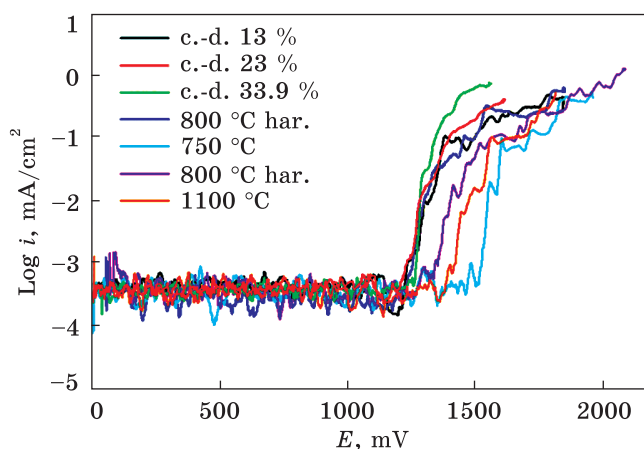


Fig. 19. Anodic polarization curves of hafnium samples cold-deformed (c.-d.) by 13, 23, and 33%, as well as deformed by 33% and annealed at 750, 800, and 1100 °C after oxidation in the medium with the composition and parameters of the VVER-1000 primary coolant for 2000 h [5]

schemes) on the exposure time is given in Fig. 17. Samples cold deformed by 13, 23 and 33% are characterized by fine grain, a large extent of grain boundaries and a significant number of crystal lattice defects. The results of microhardness measurements showed that the largest number of defects is typical for samples compressed by 33%. Samples subjected to annealing at temperatures of 600 and 650 °C had a polygonization structure, while annealed samples in the temperature range 700–1100 °C were recrystallized and differed only in grain size. This is because, at

the same isothermal exposure time, an increase in the annealing temperature leads to enlargement of the grain structure.

The obtained experimental data (Fig. 17) do not allow revealing the laws of the influence of the hafnium structure on its corrosion resistance. For example, a decrease in the corrosion activity of hafnium, deformed by cold rolling by 13%, can be due to both a decrease in the diffusion permeability of oxygen to the metal in this structural state, and a large amount of hafnium oxide that has transferred (spalled from the surface of the sample) to the corrosion medium.

According to the data presented in this paper, hafnium possesses an ultimate corrosion resistance in water and steam. The corrosion rate of HFE-1 grade hafnium is significantly lower than the corrosion rate of zirconium alloy Zr-1% Nb both in steam and in a medium simulating the composition and parameters of the VVER-1000 primary coolant [4]. The obtained experimental results of the corrosion resistance of HFE-1 grade hafnium and the published data on the corrosion resistance of iodide hafnium cannot be correctly compared, since the literature [29, 30] gives test results carried out under conditions that different from those given in this paper. However, when comparing the available results, one can conclude that the corrosion resistance of the HFE-1 recrystallized hafnium samples is significantly higher than the corrosion resistance of iodide recrystallized hafnium samples, both in steam and in the model medium of the VVER-1000 primary coolant.

4.3. Electrochemical Behaviour of Hafnium

Polarization measurements hafnium samples were carried out in order to evaluate the kinetic peculiarities of electrochemical reactions and to determine the dependence of hafnium corrosion resistance on structural condition of the metal. For this purpose, polarization dependences of hafnium were obtained in 3% NaCl solution at room temperature. Electrochemical measurements were carried out using the direct current voltammetry method, both on unoxidised samples and on samples after their exposure to high-temperature water. This method makes it possible to study the processes occurring at the metal/corrosion medium interface; because its research in high-temperature water under pressure is complicated by more stringent experimental conditions, and in some cases, its study is impossible [16]. Testing in 3% NaCl solution results from the fact that in the absence of corrosion activation ions, the corrosion kinetics of hafnium is completely controlled by the diffusion of particles through the oxide film [31]. The external polarization of the samples, up to several volts, did not cause the occurrence of electrode processes on the surface of the oxide film, as evidenced by the complete absence of any response current. Therefore, to obtain the necessary polarization

dependences, corrosion activation ions in the form of chloride ions were introduced into the working solution.

The passive region on the polarization curves indicates the tendency of hafnium to passivation. It should be noted that under standard conditions, the peak of active dissolution is clearly manifested on the polarization dependence, which indicates that hafnium is not in a passive state under these conditions (Fig. 18). According to published data, at higher temperatures, up to 300 °C, the peak of active dissolution can virtually disappear in metals susceptible to passivation [32].

The trend of the anode polarization curves of unoxidised hafnium samples in different structural states (Fig. 18) revealed that the smallest potential for the onset of dissolution (the highest electrochemical activity) is inherent in samples in cold-deformed (33% c.-d.) and polygonised (tempering stage) states. Hardened samples (from 800 °C) showed high anodic activity, which may be due to a significant number of crystal lattice defects.

The most positive value of the dissolution onset potential is observed for hafnium in a fully recrystallized state (more than 3000 mV). This state is achieved by annealing samples deformed by 33% at temperatures of 700, 750, 950, and 1100 °C. In this structural state, hafnium possesses a low density of defects in the crystal lattice, grain size from 10 to 20 µm and a characteristic grain size distribution in the samples that underwent primary (700 and 750 °C), collective (950 °C) and partially secondary recrystallization (1100 °C).

Oxidation of hafnium samples in an autoclave at a temperature of 350 °C for 2000 h leads to a shift in the oxidation onset potential (Fig. 19). Hafnium samples with increased structural imperfection (c.-d. 13%, 23, 33%, and 800 °C quench.) possess a less positive potential of the dissolution onset compared to samples in the recrystallized state.

4.4. In-Pile Tests

The main criterion for the radiation resistance of core internals is the ability to maintain integrity, shape and geometric dimensions under core irradiation [23].

Earlier, radiation tests of hafnium samples supplied by the NFC STE NSC 'KIPT', manufactured according to different technological schemes, were carried out at the JSC 'SSC RIAR' RF [33]. The effect of irradiation on the structural change and radiation growth of hafnium rods was studied. The dependences of the influence of the neutron fluence on the length and diameter change of the samples were plotted for the rods manufactured according to various technological schemes [8–10].

Tests were carried out in the SM reactor during 300 effective days in an aqueous coolant at a temperature of 260–300 °C and a pressure of

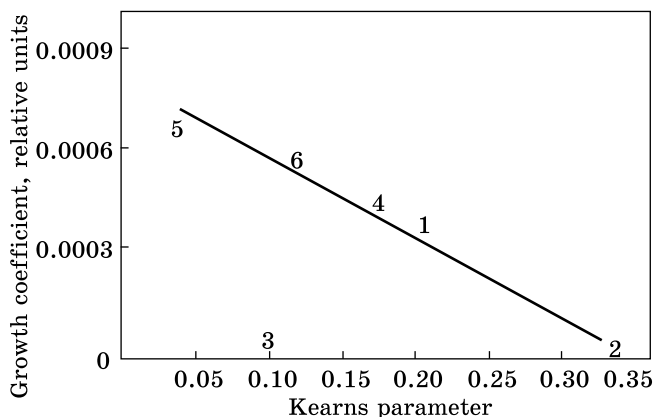


Fig. 20. The dependence of the growth coefficient on the Kearns orientation parameter

15 MPa up to a maximum fast neutron fluence of $7.8 \cdot 10^{21} \text{ cm}^{-2}$ ($E > 0.1 \text{ MeV}$). Hafnium samples retained their shape and integrity after irradiation. There were no traces of oxidation and other defects on the surface of the samples.

An increase in neutron fluence led to a decrease in density in all samples. The maximum decrease in density was $\approx 1\%$ [8–10].

The change in length did not exceed 0.35% for all samples after irradiation to a fast neutron fluence of $7 \cdot 10^{21} \text{ cm}^{-2}$. Moreover, the minimum size change was $\approx 0.04\%$ for samples with a Kearns's parameter in the longitudinal direction (F_L) of 0.33 and 0.19 .

It was revealed that samples with a fine-grained structure and texture that is close to isotropic possess the lowest tendency to radiation growth (increase in length under irradiation). The change in diameter was not observed on any of the samples.

When performing this work, the results of post-reactor studies of samples manufactured in the NFC STE NSC 'KIPT' were compared with the results of studies of the same batches of samples tested in-pile. The main task was to determine the correlation between the Kearns's orientation parameter (sample manufacturing technology), the structure of the rods (grain size), and radiation growth.

The tendency of materials to radiation growth is determined by the coefficient of radiation growth. The coefficient of radiation growth is calculated by the following expression: the ratio of the change in the rod length, expressed as a percentage, to the neutron fluence corresponding to this change. Growth coefficients were calculated for rods manufactured according to different technological schemes, basing on the results of post-reactor studies carried out at the JSC 'SSC RIAR' (RF) and the results of rod studies obtained when performing this work. The final data on the neutron fluence and the corresponding rod elongation were used when calculating the growth coefficient in each case.

The values of the radiation growth coefficient G are shown in Fig. 20. Points nos. 1, 2, 4, 5, and 6 correspond to hafnium samples with the same structure (average grain size of $\approx 25\text{--}30\text{ }\mu\text{m}$) and different textures (Kearns's parameter) for this group of samples. Point no. 3 corresponds to a hafnium sample with a fine-grained structure (up to $20\text{ }\mu\text{m}$); radiation growth is practically absent on this sample.

From the obtained results, it follows that there is a correlation between the radiation growth of the bars and the Kearns's orientation parameter for samples with the same structure (Fig. 20). The radiation growth linearly decreases with an increase in the Kearns's parameter for the group of samples marked by points nos. 1, 2, 4, 5, and 6. The averaged line has an angular slope of 0.0024 and a starting point of 0.00081, which shows that samples with a more isotropic texture are less susceptible to radiation growth. A higher rate of radiation growth is typical for hafnium rods samples with a coarse-grained structure, when Kearns's parameters are similar.

The radiation growth observed upon irradiation of the samples varied significantly depending on their structure. With a similar rod structure, rod samples with a fine-grained structure are less susceptible to radiation growth than samples with a coarse-grained structure. The deformation of radiation growth was almost absent after irradiation of rods with fine-grained structure to a fast neutron fluence of $7.8 \cdot 10^{21}\text{ cm}^{-2}$.

The obtained relationships render possible to make a prediction that hafnium rods with an anisotropic texture and large grain will have the maximum radiation growth rate.

5. Conclusions

It was shown that the mechanical properties of hafnium are structurally sensitive. According to studies, it was found that hafnium rods in a fully recrystallized state with a fine-grained structure have optimal mechanical properties (high strength and high ductility). At room temperature, their tensile strength was $\approx 575\text{ MPa}$, elongation of 27–28%. Collective and secondary recrystallization leads to a decrease in strength and a decrease in ductility. At the same time, even slight cold deformation of the rod leads to an increase in tensile strength and a decrease in elongation.

The study into hafnium corrosion in the model medium of the VVER-1000 primary coolant revealed that the corrosion mechanism is a combination of two processes: the hafnium weight gain due to its oxidation and the parallel process of spalling of the thin outer layers of the oxide film, when the hafnium weight decreases. At the initial period of time (before the onset of the 'breakaway'), the kinetic curves of hafnium oxidation are well described by the empirical power equation with an

exponent of 0.242 ± 0.015 . Upon reaching the boundary thickness of oxide film, a sharp change in corrosion resistance ('breakaway') is observed. After that, the corrosion kinetics is described by a linear dependence; the corrosion rate in this case is of $3.12 \cdot 10^{-4} \pm 2.07 \cdot 10^{-5}$ mg/(dm²·h). The time to the change of the hafnium corrosion resistance ('breakaway') is of ≈ 6000 hours. An analysis of the anodic polarization curves of oxidized hafnium samples in different structural states (obtained according to different technological methods) showed that oxide films formed on hafnium samples in a fully recrystallized state possess the highest protective properties. This is due to a decrease in the degree of surface structure irregularity, a decrease in the diffusion permeability of the metal, and the formation on its surface of the barrier layer of corrosion films with high protective properties.

It follows from the results of radiation tests, structural and textural studies of hafnium rods in a different structural state, that there is a correlation between the radiation growth of the samples and the Kearns's orientation parameter. A line with an angular slope coefficient of 0.0024 and a starting point of 0.00081 represents this correlation, which shows that samples with a more isotropic texture are less susceptible to radiation growth. Radiation growth varied depending on the structure of the rods. Samples with a fine-grained structure are less susceptible to radiation growth than samples with a coarse-grained structure, when the texture of the rods is identical. The deformation of the radiation growth is almost absent at a fast neutron fluence of $7.8 \cdot 10^{21}$ cm⁻² for rods with a recrystallized structure and an average grain size of less than 20 μ m.

The combination of deformation with the processes occurring during annealing allows one to manufacture hafnium products in a different structural and textural states, and, accordingly, with different structurally sensitive properties. It follows from the generalized results presented in this paper that the non-textured ($F_L \cong 0.33$) samples of hafnium rods with a fine-grained (up to 20 μ m) recrystallized structure possess the most optimal combination of mechanical and corrosion characteristics during out-of-pile testing, and are also characterized by a high dimensional stability under irradiation.

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Received 26.06.2019;
in final version, 02.03.2020

В.А. Зуйок, В.С. Красноруцький,
Т.П. Черняєва, М.В. Трет'яков, Р.О. Рудь
ННЦ «Харківський фізико-технічний інститут»,
Науково-технічний комплекс «Ядерний паливний цикл»,
вул. Академічна 1, 61108 Харків, Україна

ВПЛИВ СТРУКТУРИ СТРИЖНІВ ГАФНІЮ НА ЇХНІ МЕХАНІЧНІ ВЛАСТИВОСТІ, КОРОЗІЙНУ ТА РАДІАЦІЙНУ СТІЙКОСТІ

У роботі подано й оглядаються результати дослідження залежності механічних властивостей, корозійної та радіаційної стійкостей стрижнів гафнію від їхньої структури. Встановлено, що оптимальні механічні властивості (високу міцність і пластичність) мають стрижні в повністю рекристалізованому стані з дрібнозернистою структурою. Межа міцності цих стрижнів за кімнатної температури складає ≈ 575 МПа, а відносне подовження — 27–28%. За результатами автоклавних корозійних випробувань і анодними поляризаційними кривими найбільш захисними є оксидні плівки, які утворюються на зразках гафнію в повністю рекристалізованому стані, що зумовлено низькою поверхневою активністю на межі поділу середовище–метал. Швидкість корозії таких стрижнів гафнію в початковий період окиснення (до настання «перелому») добре описується емпіричним рівнянням з показником степеня у $0,242 \pm 0,015$. Після настання «перелому» (через ≈ 6000 год) кінетика корозії описується лінійною залежністю зі швидкістю у $3,12 \cdot 10^{-4} \pm 2,07 \cdot 10^{-5}$ мг/(дм²·год). За результатами радіаційних випробувань,

яких було проведено в ДНЦ РФ НДІАР, і структурно-текстурних досліджень тих самих зразків стрижнів гафнію в різних структурних станах, проведених у даній роботі, показано, що є кореляція між радіаційним зростанням стрижнів гафнію та їхнім текстурним коефіцієнтом (Кернсовим параметром). Наведені в даній роботі результати свідчать про те, що коефіцієнт радіаційного зростання лінійно зменшується зі збільшенням Кернсового параметра до 0,33. Це вказує на те, що зразки стрижнів гафнію з більш ізотропною текстурою менш схильні до радіаційного зростання. Радіаційне зростання розрізнялося, залежно від структури стрижнів. Для стрижнів з однаковою текстурою та різним розміром зерна менш схильними до радіаційного росту виявилися зразки з дрібнозернистою структурою. Більш високу швидкість радіаційного зростання, при схожих Кернсових параметрах, показали стрижні гафнію з грубозернистою структурою. При опроміненні за температури у 260–300 °С до флюенсу швидких нейтронів у $7,8 \cdot 10^{21} \text{ см}^{-2}$ деформація радіаційного зростання стрижнів з рекристалізованою структурою, Кернсовим параметром у $\approx 0,1$ і середнім розміром зерен, меншим за 20 мкм, практично дорівнює нулю.

Ключові слова: гафній, структура, текстура, механічні характеристики, корозія, радіаційне зростання.

*В.А. Зуёк, В.С. Красноруцкий,
Т.П. Черняева, М.В. Третьяков, Р.А. Рудь*
ННЦ «Харьковский физико-технический институт»,
Научно-технический комплекс «Ядерный топливный цикл»,
ул. Академическая 1, 61108 Харьков, Украина

ВЛИЯНИЕ СТРУКТУРЫ СТЕРЖНЕЙ ГАФНИЯ НА ИХ МЕХАНИЧЕСКИЕ СВОЙСТВА, КОРРОЗИОННУЮ И РАДИАЦИОННУЮ СТОЙКОСТИ

В работе представлены и обобщаются результаты исследования зависимости механических свойств, коррозионной и радиационной стойкостей прутков гафния от их структуры. Установлено, что оптимальными механическими свойствами (высокой прочностью и пластичностью) обладают прутки в полностью рекристаллизованном состоянии с мелкозернистой структурой. Предел прочности этих прутков при комнатной температуре составляет $\approx 575 \text{ МПа}$, относительное удлинение — 27–28%. Из результатов автоклавных коррозионных испытаний и анодных поляризационных кривых следует, что наиболее защитными являются оксидные плёнки, образующиеся на образцах гафния в полностью рекристаллизованном состоянии, что обусловлено низкой поверхностной активностью на границе раздела среда–металл. Скорость коррозии таких прутков гафния в начальный период окисления (до наступления «перелома») хорошо описывается эмпирическим степенным уравнением с показателем степени $0,242 \pm 0,015$. После наступления «перелома» (через $\approx 6000 \text{ ч}$) кинетика коррозии описывается линейной зависимостью со скоростью $3,12 \cdot 10^{-4} \pm 2,07 \cdot 10^{-5} \text{ мг/(дм}^2 \cdot \text{ч)}$. Из результатов радиационных испытаний, проведённых в ГНЦ РФ НИИАР, и структурно-текстурных исследований этих же образцов прутков гафния в различных структурных состояниях, выполненных в данной работе, показано, что существует корреляция между радиационным ростом прутков гафния и их текстурным коэффициентом (параметром Кернса). Из результатов, приведённых в данной работе, следует, что коэффициент радиационного роста линейно уменьшается с увеличением параметра Кернса до значения 0,33. Это указывает на то, что образцы

прутков гафния с более изотропной текстурой менее склонны к радиационному росту. Радиационный рост различается в зависимости и от структуры прутков. Для прутков с одинаковой текстурой и разным размером зерна менее склонными к радиационному росту оказались образцы с мелкозернистой структурой. Более высокую скорость радиационного роста, при схожих параметрах Кернса, показали прутки гафния с крупнозернистой структурой. При облучении при температуре 260–300 °С вплоть до флюенса быстрых нейтронов $7,8 \cdot 10^{21} \text{ см}^{-2}$ деформация радиационного роста прутков с рекристаллизованной структурой, параметром Кернса $\approx 0,1$ и средним размером зёрен менее 20 мкм практически равна нулю.

Ключевые слова: гафний, структура, текстура, механические характеристики, коррозия, радиационный рост.