PHYSICS
OF NANOSTRUCTURES

Radiation Resistance of High-Entropy Nanostructured (Ti, Hf, Zr, V, Nb)N Coatings

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Abstract—The influence of high-fluence ion irradiation of nanostructured (Ti, Hf, Zr, V, Nb)N coatings is revealed for the first time. The energy of irradiating helium ions is equal to 500 keV, and their fluence falls into the interval 5×10^{16}–3×10^{17} ions/cm². The performance of the coatings in a nuclear reactor is simulated by conducting post-irradiation thermal annealing at 773 K for 15 min. The elemental composition, structure, morphology, and strength properties of the (Ti, Hf, Zr, V, Nb)N coatings are studied before and after irradiation. No considerable structural and phase modifications in the coatings are found after irradiation, except for the fact that crystallites in the coatings drastically reduce in size to less than 10 nm. Nor does the atomic composition of the coatings change. It is shown that the microhardness of the coatings depends on the fluence of irradiating ions nonlinearly. It can be argued that the (Ti, Hf, Zr, V, Nb)N coatings are radiation-resistant and hence promising for claddings of fuel elements in nuclear reactors.

INTRODUCTION

High-entropy nitride alloys, such as (Ti, Hf, Zr, V, Nb)N compounds, are of great interest owing to their unique properties. It was shown [1−7] that when the entropy extremely rises, relaxation has no time to proceed and the system remains nonequilibrium. This improves the operating performance of coatings, specifically, their properties such as strength, wear resistance, corrosion resistance, heat resistance, and high-temperature stability [1−5]. High entropy is achieved in a multicomponent single-phase disordered solid solution prepared by vacuum deposition. In this method, a coating is deposited on a substrate at a low temperature as a result of which the coating nucleation and growth rates are high. This feature adds to the entropy of the forming system and favors the formation of an ultra-fine-grained structure of the nanocrystalline film.

As is known [8], the state of the system is described in terms of the thermodynamic potential function

$$G = U + pV - TS, \qquad (1)$$

where G is the internal energy, p is the pressure, V is the volume, T is the temperature, and S is the entropy.

The stability of a thermodynamic system is characterized by a minimum of the Helmholtz free energy,

$$F = U - TS. \qquad (2)$$

With the internal energy and temperature fixed, the only adjustable parameter is energy. Consequently, a higher entropy state is thermodynamically more stable at a given temperature. It is not safe to say that this state is stable: it is rather metastable. However, it is known that a system can be disturbed from a metastable state by imparting some energy ΔE to it. At a fixed temperature, energy barrier ΔE can be represented as

$$\Delta E = F_1 - F_2 = (U - TS_1) - (U - TS_2)$$
$$= TS_2 - TS_1 = T(S_2 - S_1), \qquad (3)$$

where F_1 and F_2 are, respectively, the initial and final values of the system's free energy, and S_1 and S_2 are the initial and final values of the entropy. Thus, a change in the system's entropy, being directly proportional to a change in the free energy, is thermodynamically unfavorable in the metastable state.

Consequently, one can suppose that external actions, such as thermal heating, attack by corrosive media (acids, alkalies), and ionizing irradiation will slightly influence the structure and properties of high-entropy alloys if energy barrier ΔE is sufficiently high.

The behavior of such materials, which are promising for coating application, under the action of ionizing radiation, specifically, fast ions, has not been considered in the literature so far.

Elemental composition of (Ti, Hf, Zr, V, Nb)N coatings

No.	U_b, V	P, Pa	Concentration, at %						Lattice parameter, nm
			N	Ti	V	Zr	Nb	Hf	
505	−110	5×10^{-1}	49.15	16.63	5.91	8.17	8.88	11.26	0.4405
507	−50	5×10^{-1}	51.13	25.31	4.72	5.70	6.31	6.84	0.4362
512	−200	8×10^{-2}	46.65	17.03	2.79	12.01	12.54	8.99	0.4435
515	−200	3×10^{-2}	36.05	20.13	2.28	17.12	17.50	6.93	0.4433
523	−200	2.3×10^{-1}	43.44	17.80	1.45	16.39	16.99	3.92	0.4408

In this work, we study the radiation resistance of high-entropy (Ti, Hf, Zr, V, Nb)N coatings exposed to 500-keV He$^+$ ions.

When a metal is irradiated by light ions (H$^+$, He$^+$) with an energy of several hundred kiloelectronvolts, there are two channels for energy losses: the energy is spent on the excitation of the electronic subsystem of the solid and on the formation of simple structural defects. Under these conditions, cascades of atomic displacements (fading out of which terminates by the formation of complex ensembles of defects) do not arise [9], so that theoretical interpretation of the mate-

rial's post-implantation properties in terms of free energy, entropy, and the influence of grain size simplifies considerably. Note also that the irradiation of metals and alloys by helium ion beams with an energy varying from several hundred kiloelectronvolts to several megaelectronvolts is used to simulate radiation damage of structural materials for nuclear reactors, most frequently for fuel claddings [10].

EXPERIMENTAL

(Ti, Hf, Zr, V, Nb)N coatings were produced by vacuum arc deposition with different bias voltage U_b and different partial nitrogen pressure P in a vacuum chamber (see the table). A Bulat-T vacuum arc device with an rf generator was used. A bias potential was applied to the substrate from the rf generator, which generated pulses of damped oscillations with a frequency of no higher than 1 MHz and a pulse width of 60 μs. The pulse repetition rate was about 10 kHz. The negative self-bias on the substrate was equal to 2−3 kV owing to the rf diode effect. Nitrides were deposited by introducing atomic nitrogen into the vacuum chamber with substrates. The pressure and substrate bias were varied.

The samples were irradiated by 500-keV helium ions with a fluence varying from 5×10^{16} to 3×10^{17} ions/cm^2 on an AN 2500 ion accelerator (High Voltage Engineering Europe B.V.). Then, the coatings were annealed at 773 K for 15 min. Both processes were aimed at simulating the influence of the environment in a nuclear reactor, where structural materials are subjected to ionizing radiation and also are irradiated by thermal and fast neutrons [9]. The elemental composition of test coatings was examined by the Rutherford backscattering (RBS) of 1.5-MeV helium ions. The resolution of the detector was 15 keV. The structure of the coatings was studied using optical microscopy and X-ray diffraction analysis on a DRON-3 diffractometer in the Bragg−Brentano configuration. Diffraction reflections were recorded pointwise in the scan mode. The scanning pitch was 0.1%; the count time per point, 15 s. X-ray diffraction analysis was carried out with monochromatized CoK$_\alpha$ radiation at an accelerating voltage of 30 kV and an anode current of 10 mA. As a
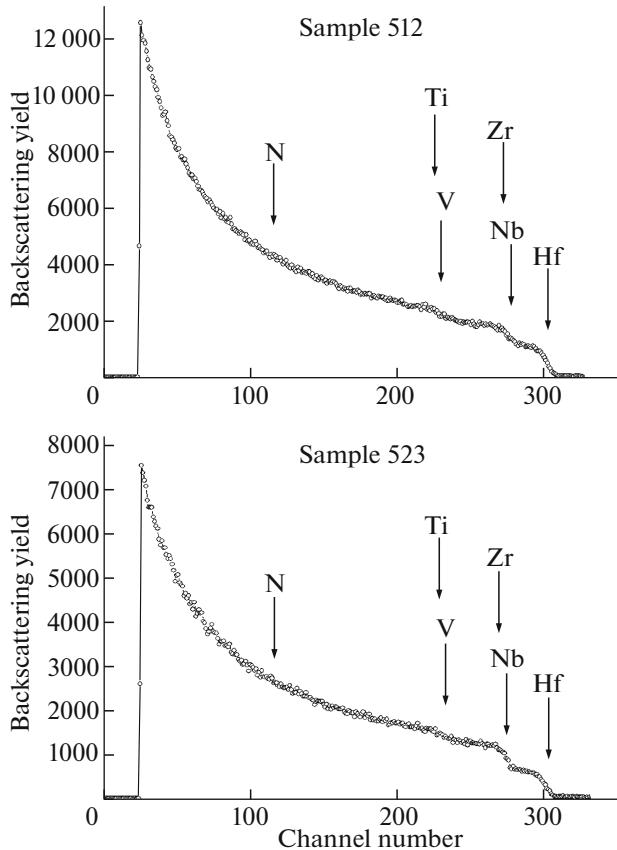

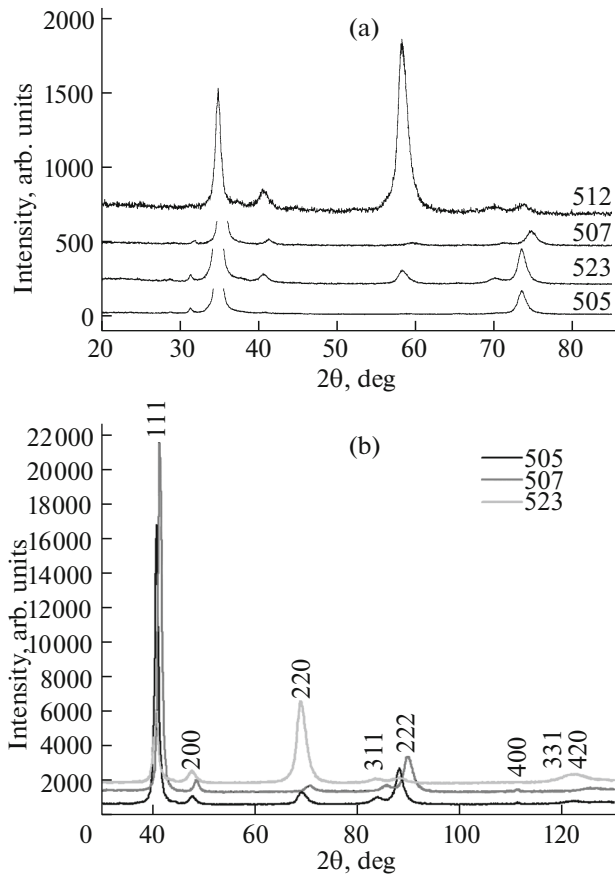**Fig. 1.** RBS spectra for helium ions backscattered from the (Ti, Hf, Zr, V, Nb)N coating.

Fig. 2. X-ray diffraction patterns taken of the (Ti, Hf, Zr, V, Nb)N coatings (a) before and (b) after irradiation by 500-keV helium ions with a fluence of 2×10^{17} ions/cm^2.
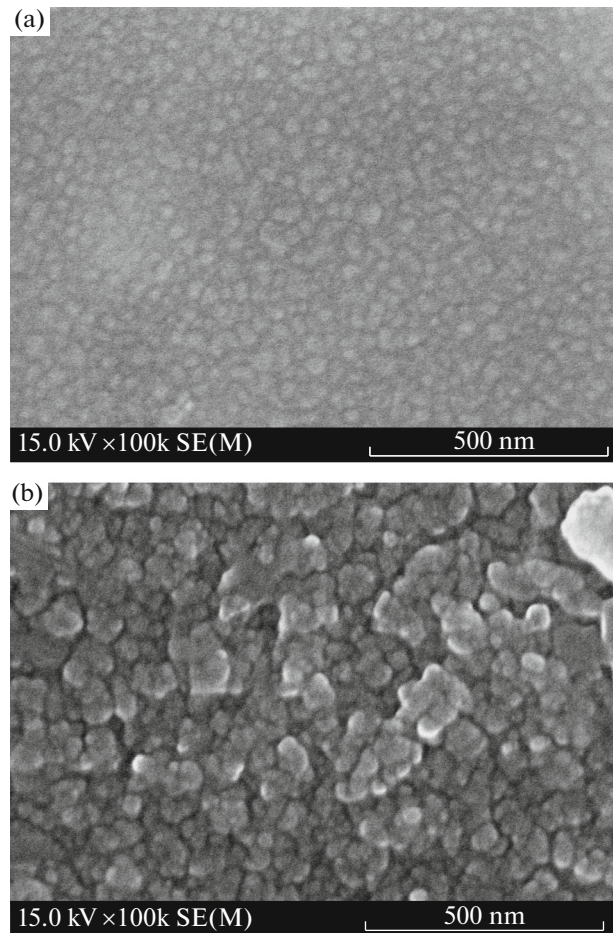

Fig. 3. Microstructure of the (Ti, Hf, Zr, V, Nb)N coatings under the scanning electron microscope: (a) as-deposited coating and (b) coating after irradiation by He$^+$ ions with a fluence of 3×10^{17} ions/cm^2 (the lower part of the coating is partly peeled off).

monochromator crystal, pyrolytic graphite was used, which was placed in the secondary (diffracted) beam. A diffraction pattern was recorded in the angular range $2\theta = 10°-130°$. Interplanar distances d/n were measured accurate to 0.0005 nm.

The structure and morphology of the coatings were also examined under a Hitachi SU3400 scanning electron microscope at an accelerating potential difference of 15 keV.

To see how irradiation influences the operating performance of the (Ti, Hf, Zr, V, Nb)N coatings, their microhardness was measured by the imprint method. In this method, the surface of the sample is indented by a diamond point for a certain time. Measurements were taken with a DuraScan 20 hardness meter. The indentation load was varied from 0.09 to 0.98 N.

RESULTS AND DISCUSSION

It is found by the RBS method that the elements are uniformly distributed over the depth (Fig. 1, the table).

Undesired impurities, such as oxygen, sulfur, and phosphorus, were not found. This indicates a high quality of the film coatings. The amount of nitrogen in the coatings is 50 at %. Consequently, stoichiometric titanium nitride TiN forms and the purely metallic phase is absent [11, 12]. Moreover, the absence of carbon, oxygen, boron, and other impurities that can produce interstitial phases in metals suggests that 90−95% of octahedral pores in the crustal lattice are occupied by nitrogen atoms.

Figure 2 shows X-ray diffraction patterns taken of the (Ti, Hf, Zr, V, Nb)N coatings. Before irradiation (Fig. 2a), the coatings contain only one fcc phase, namely, a substitutional solid solution based on IV and V nitrides having a NaCl lattice. Ti, Hf, Zr, V, and Nb metals substitute for each other in the metallic sublattice, and nitrogen penetrates into octahedral pores, producing a sublattice displaced relative to the metallic sublattice by a half period along the cube diagonal. That is, the lattice site [[000]] of the nitrogen sublat-
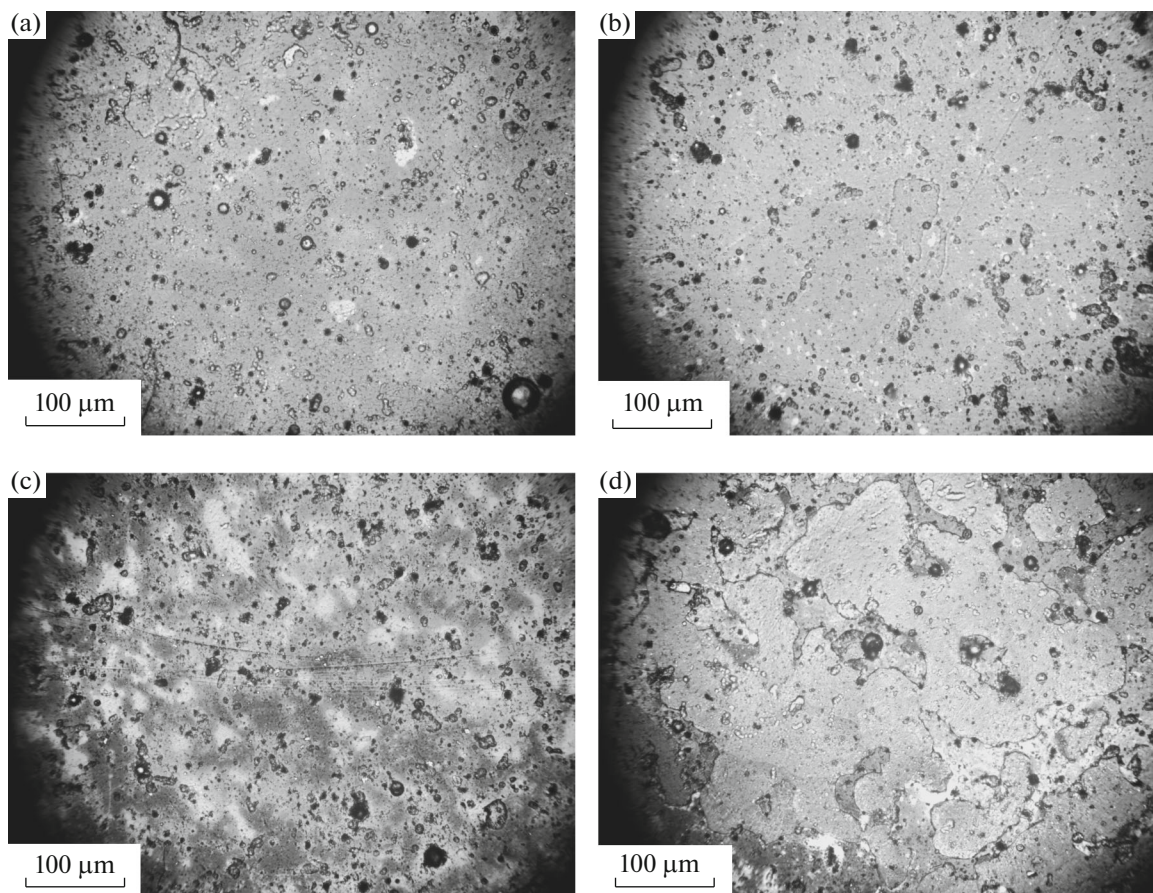
Fig. 4. Microstructure of the (Ti, Hf, Zr, V, Nb)N coatings irradiated by 500-keV He ions with a fluence of (a) 5×10^{16}, (b) 1×10^{17}, (c) 2×10^{17}, and (d) 3×10^{17} ions/cm^2.

tice coincides with the lattice site [[1/2, 1/2, 1/2]] of the metallic sublattice. The lattice parameter varies between 0.4362 and 0.4435 nm depending on the elemental composition of the coatings. The difference in the positions of peaks in the diffraction patterns is explained by different periods of crystal lattices with differing elemental compositions: Hf, Nb, and Zr atoms increase the lattice parameter, whereas Ti and V atoms diminish. Broadening of the diffraction peaks indicates a nanostructure of the coatings. The grain size calculated by the Selyakov–Sherrer formula [13] was found to lie in the interval 240–250 nm.

As follows from Fig. 2b, the diffraction pattern after irradiation by 500-keV helium ions with a fluence of 2×10^{17} ions/cm^2 in general changes insignificantly. As before, the coating is single-phase, that is, represents a solid solution of nitrogen in the metallic NaCl-type fcc lattice. It was found that irradiation by helium ions with the fluence varying in the interval $(1-2) \times 10^{17}$ ions/cm^2 makes grains (crystallites) finer. For example, in the (Ti, Hf, Zr, V, Nb)N coatings exposed to helium ions with a fluence of 2×10^{17} ions/cm^2, the grain size calculated by the Selyakov–Sherrer formula [13] was 5–10 nm; in other

words, it decreased by more than an order of magnitude.

Figure 3 shows the micrographs of the coatings obtained by scanning electron microscopy (SEM) in which grains are distinctly seen. The micrograph in Fig. 3b was taken of an area from which the coating partially peeled off after irradiation by helium ions with a fluence of 3×10^{17} ions/cm^2. Here, a more structured surface relief is seen. The grain size is in the interval 240–250 nm before irradiation (Fig. 3a) and 50–60 nm after irradiation by 500-keV helium ions with a fluence of 3×10^{17} ions/cm^2. These micrographs support the data of X-ray diffraction analysis, which gives the same values of the grain size before and after irradiation. Hence, high-fluence (3×10^{17} ions/cm^2) ion irradiation disintegrates grains of high-entropy coatings. SEM examination did not reveal large blisters. This suggests that helium does not produce large bubbles, at least up to 40–50 nm in size. It is likely that helium forms nanoclusters in the coatings upon irradiation (see [14]).

Figure 4 shows optical micrographs of the irradiated (Ti, Hf, Zr, V, Nb)N coatings.

It is seen from Fig. 4 that the morphology of the coatings remains virtually unchanged up to a fluence
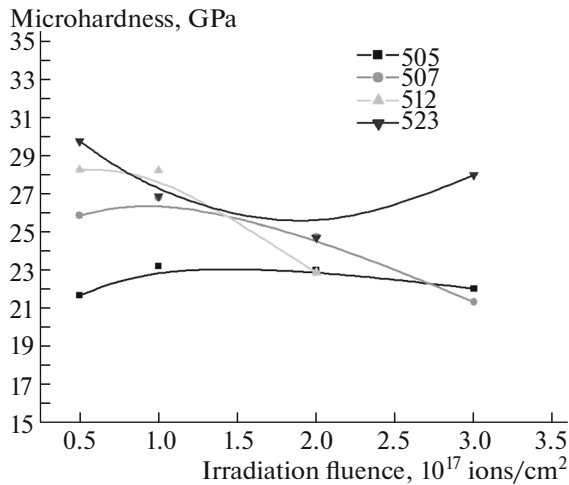
Microhardness, GPa

Fig. 5. Microhardness of the (Ti, Hf, Zr, V, Nb)N coatings with a different concentration of the components (see the table) vs. the fluence of 500-keV helium ions.

of 2×10^{17} ions/cm^2. Surface defects seen in Figs. 4a and 4b are radiation-induced ones. At a fluence of 2×10^{17} ions/cm^2 (Fig. 4c), local damage is observed throughout the surface presumably due to selective sputtering of the coating's constituents (primarily nitrogen) and accumulation of tiny (nanometer) helium blisters in the coating (for details, see [14, 15]). At a fluence of 3×10^{17} ions/cm^2 (Fig. 4d), sites of exfoliation-induced damage of the coating are observed. In these sites, the hardness of the coating is 50−60% of the initial value. This means that damage does not reach the substrate: it penetrates to a depth where the concentration of radiation-induced defects and impurity helium is maximal. This inference is supported by the data of X-ray elemental microanalysis carried out using a dedicated attachment to a SU3400 Hitachi scanning electron microscope: the elemental composition determined by this analysis in the lower (intact) part of the coating after its partial damage is the same as in the initial (nonirradiated) coating. Micro- and macroclusters of blisters in the coatings were absent at any fluences.

The stability of the mechanical properties against radiation was studied by conducting hardness tests (Fig. 5).

It was found that the microhardness of the high-entropy coatings nonlinearly depends on the fluence. For samples 505, 507, and 512, the hardness grows by 4−10% up to a fluence of 1×10^{17} ions/cm^2. At a fluence of 3×10^{17} ions/cm^2, the microhardness drops by 9−15%. For samples with the lowest concentration of the heaviest metal (Hf), the trend in the fluence dependence of the microhardness is opposite: when fluence D grows to 2×10^{17} ions/cm^2, the microhardness decreases and then, at $D = 3 \times 10^{17}$ ions/cm^2, noticeably drops. At this fluence, hardness measure-

ments were taken of the intact (flaking-free) part of the coating surface.

The reason for such an intriguing nonlinear dependence of the microhardness of the high-entropy (Ti, Hf, Zr, V, Nb)N coatings exposed to helium ions is modifications in the crystal structure of the material. High-fluence ion irradiation induces effects described earlier in [9]. In our case, upon irradiation precipitation of a new phase was not observed, the lattice parameter changes considerably (as follows from the X-ray diffraction analysis data), but the microhardness remains the same. At moderate fluences of He$^+$ ions, the aforementioned disintegration of grains adds to the microhardness. The further decrease in the microhardness with rising fluence is due to radiation-induced relaxation processes in the high-entropy coating and, as a consequence, to an increase in the grain size. The accumulation of structural defects with rising fluence can reduce the microhardness as well.

CONCLUSIONS

Thus, we can conclude that a high entropy of (Ti, Hf, Zr, V, Nb)N alloys stabilizes the formation of a single-phase system in the form of a disordered solid solution and prevents the formation of intermetallics during crystallization. The coatings consist of grains 240−250 nm across. It was found that irradiation of (Ti, Hf, Zr, V, Nb)N coatings by 500-keV helium ions does not cause noticeable changes in the phase and structure of the coatings up to a fluence of 2×10^{17} ions/cm^2, except for the severe disintegration of grains. In addition, no blistering in the coatings was observed at any ion fluences. For a fluence of 3×10^{17} ions/cm^2, the film coating exfoliates to a depth where the concentration of radiation-induced defects and helium is maximal. It is also found that the microhardness of the (Ti, Hf, Zr, V, Nb)N coatings nonlinearly depends on the helium ion fluence. Finally, it is established that ion irradiation has a slight influence on the strength properties of the coatings. Specifically, the microhardness changes by 9−17% in the case of 500-keV helium ions with a fluence varying between 5×10^{16} and 3×10^{17} ions/cm^2.

The high radiation resistance of high-entropy nanostructured (Ti, Hf, Zr, V, Nb)N coatings is explained by the effective recombination of radiation-induced point defects in them, primarily, at grain boundaries. These coatings seem to be promising for radiation-resistant claddings of fuel elements in nuclear reactors.

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