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Investigation of the emissivity of zirconium and hafnium in a wide temperature range

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The temperature and wave dependences of the emissivity of metallic zirconium and hafnium were measured. The measurement method is radiation, in an argon atmosphere. The heating method is resistive. The temperature range covered the solid−liquid phase transition. The spectral emissivity was studied in the wavelength range $0.69-10.6\,\mu$m. Numerical values of the experimental results are presented. A comparative analysis with the literature data and calculation results in the Drude approximation is carried out.

Keywords: emissivity, solid and liquid phases, temperature and wave dependences, zirconium, hafnium.

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Introduction

Recently, the unique physico-chemical and thermophysical properties of zirconium and hafnium metals were widely used in the design, manufacture and operation of equipment elements of nuclear power plants of various capacities [1,2]. There is a need to know not only the heat capacity, density, and thermal conductivity of the materials used, but also the emissivity in a wide range of temperatures and waves. The conducted search showed the presence of few papers studying the emissivity of metallic zirconium and hafnium in solid and liquid phases. The works have a significant spread over the years of research with no mutually overlapping results. A discrepancy in the values of the emissivity of metals is observed when considering the comparison of the experimental values of the authors of the present paper with data from various sources. The authors attribute these discrepancies to differences in the methods and conditions of the experiments. Brief information about the methodological features of measurements of emissivity by other authors are presented below in the text in the form of tabular comparisons.

The authors present in this paper their own results of an experimental study of the integral emissivity ε_t and spectral emissivity ε_λ of metallic zirconium and hafnium in a wide temperature and wave ranges. The results obtained are an attempt to supplement and expand the research available at the present stage.

1. Conditions of the experiment

The experimental setup, the research methodology, and the design of the thermal radiation receiver used are described in detail by the authors in the papers in Ref. [3,4]. Radiation is the research method. This method is considered universal and applicable to almost all substances at all temperatures [5]. The essence of the method consists in alternating sighting by the receiver of the radiation of the heat flux from the surface of the sample under study and from the model of an ideal black body (IBB, Ideal Black Body) at the same temperatures. The measured thermal electromotive forces (TEMF) make it possible to calculate the emissivity of a metal sample using the expression of the form

$$\varepsilon_t = \varepsilon_{IBB}\,\frac{\alpha_2}{\alpha_1}, \qquad (1)$$

where ε_{IBB} — the emissivity of the IBB model (0.96 is accepted in accordance with Ref. [6]); α_1 — the TEMF developed by the thermal element of the radiation receiver when measuring the IBB model; α_2 —the TEMF, developed by the thermoelectric element of the radiation receiver when measuring a metal sample.

The zirconium and hafnium samples were mass-produced rods. The chemical composition of the samples according to the supplier is presented in Tables 1, 2.

A cylindrical glass made of tantalum was used as the IBB model. The temperature of the IBB model was measured along the cylinder at fixed three points on the outer surface, the fourth thermocouple was installed in the hole of the bottom of the model. Screens made of molybdenum foil were used to eliminate the end effects in the fasteners of the IBB model to the current leads. The radiation receiver was calibrated using the IBB model to a temperature of ~ 2800 K.

The experiments were carried out in a vacuum chamber with blackened walls. The samples were heated by direct transmission of a stabilized regulated current of industrial frequency through a tantalum plate (resistive heater). The samples were annealed in vacuum for 1 h at a temper-

Table 1. Composition of the studied zirconium

Element	Zr+Hf	Al	Be	B	Hf	Fe	Ca	Cd	Si	Mn
Composition, mass.%	99.8	0.005	0.001	0.00005	0.05	0.03	0.02	0.00005	0.008	0.001
	Cu	Ni	Pb	Ti	Cr	N	O	C	Li	Mo
	0.003	0.01	0.005	0.005	0.02	0.005	0.05	0.008	0.0002	0.005

Table 2. Composition of the studied hafnium

Element	Hf+Zr	Zr	N	Fe	Si	Ni	Ti	Al	Ca	Mg	Mn	C	Cr
Composition, mass.%	99.8	1	0.005	0.04	0.005	0.05	0.005	0.005	0.01	0.004	0.0005	0.01	0.003

ature of ~ 1500 K before the experiment. A series of measurements of the emissivity was carried out both with an increase and with a decrease of temperature with a mandatory isothermal exposure before each measurement. The temperature of the samples was measured by tungsten-rhenium thermocouples installed in pre-drilled holes in the near-surface layer. The emissivity of the solid phase samples was measured in a vacuum no higher than 10^{-3} Pa. The emissivity of samples in the liquid phase was measured in an atmosphere of prepared argon. The constant visual monitoring of the surface condition of the images was carried out in these experiments. After a series of experiments, the content of the main chemical element in the samples was evaluated by X-ray fluorescence analysis in order to identify possible diffusion of the substrate material into the sample. These studies showed that the chemical purity of the samples did not change.

The error of the experimental data obtained was estimated using the method described in Ref. [7]. The systematic errors in determining the emissivity of metals was calculated in accordance with the expression (1). Random errors were estimated based on the spread of the experimental data obtained. The total error of determination of the emissivity was $\pm(5-8)\%$ and depended on the temperature of the experiment.

2. Measurement results

The authors obtained a temperature dependence of ε_t in the temperature range of 410–2327 K in the study of zirconium ($T_{melt} = 2133$ K [8]) (Fig. 1). The data ε_t were compared with the literature values in solid and liquid phases [9,10].

The data from Ref. [9] were obtained by linear approximation of an array of experimental data with an expression of the form

$$\varepsilon_t = 0.1842027 + 7.142254 \cdot 10^{-5} T, \qquad (2)$$

where T is the sample temperature.

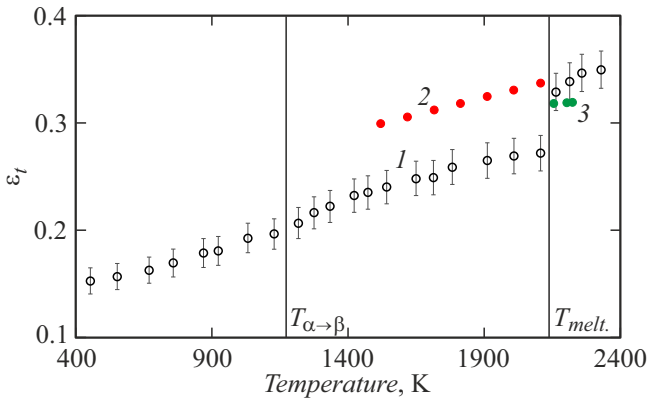

Figure 1. Temperature dependence ε_t of zirconium: *1* — results of the authors; *2* — [9]; *3* — [10].

The data from Ref. [10] were obtained by linear approximation of a number of experimental points with an expression of the form

$$\varepsilon_t = 0.317 + 1.77 \cdot 10^{-5}(T - T_{melt}), \qquad (3)$$

where the value of T_{melt} zirconium was assumed to be 2128 K; T is the sample temperature.

The polymorphic $\alpha \to \beta$-transition of zirconium at a temperature of 1147 K [11] was not recorded by the authors due to the limited technical capabilities of the experimental setup. An abrupt increase of ε_t of zirconium by $\sim 21\%$ was recorded during the solid–liquid phase transition. The numerical values of the experimental results are summarized in Table 3.

A temperature dependence ε_t in the temperature range of 420–2648 K was obtained in the study of hafnium ($T_{melt} = 2506$ K [8]) (Fig. 2). There is satisfactory agreement with the data in Ref. [12]. ε_t smoothly increases with the temperature increase starting from 420 K. The polymorphic $\alpha \to \beta$-transition of hafnium at a temperature of 2023 K [13] was also not recorded by the authors for the reason indicated above. An abrupt increase of ε_t of hafnium by $\sim 20\%$ relative to the solid phase during the transition to

Table 3. Values ε_t of zirconium

T, K	ε_t	T, K	ε_t	T, K	ε_t	T, K	ε_t	T, K	ε_t	T, K	ε_t
410	0.151	835	0.177	1190	0.205	1451	0.234	1769	0.258	2158	0.328
510	0.155	890	0.179	1250	0.215	1522	0.239	1900	0.264	2210	0.338
630	0.161	1000	0.191	1310	0.221	1633	0.247	2000	0.268	2256	0.346
720	0.168	1100	0.195	1399	0.231	1698	0.248	2100	0.271	2327	0.349

Table 4. Values ε_t of hafnium

T, K	ε_t	T, K	ε_t	T, K	ε_t	T, K	ε_t	T, K	ε_t	T, K	ε_t
420	0.195	790	0.227	1210	0.261	1702	0.291	1990	0.31	2475	0.332
500	0.205	870	0.235	1305	0.263	1800	0.298	2100	0.315	2542	0.401
570	0.211	1044	0.244	1472	0.273	1870	0.301	2250	0.321	2575	0.411
720	0.221	1130	0.251	1603	0.281	1920	0.308	2400	0.331	2648	0.416

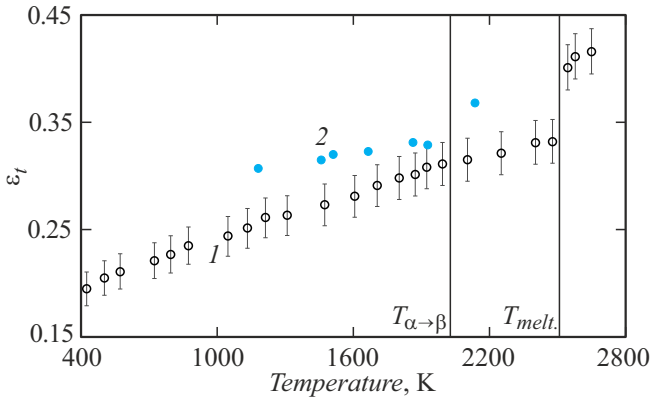

Figure 2. Temperature dependence of ε_t of hafnium: *1* — results of the authors; *2* — [12].

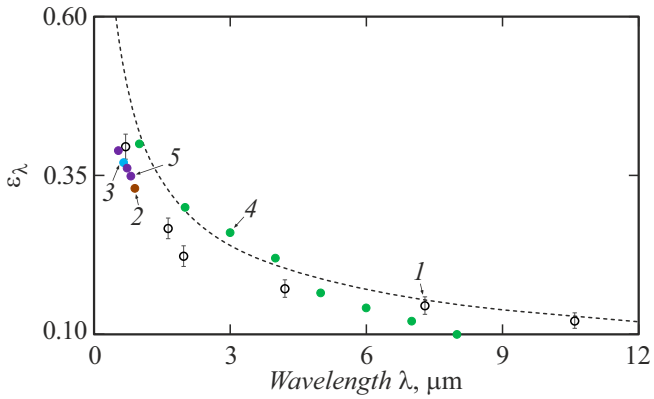

Figure 3. Wave dependence of ε_λ of zirconium (solid phase): *1* — results of the authors; *2* — [9]; *3* — [11]; *4* — [15]; *5* — [16]; dashed line — Drude approximation

the liquid state was obtained. The numerical values of the experimental results are summarized in Table. 4.

The abrupt change of ε_t in the region of the phase transition of the first kind is explained by the destruction of the crystal lattice during melting and the transition of the long-range order of the metal to the near-range order [14].

The above illustrative material shows the presence of qualitative coincidences with the data of literary sources on the pattern of behavior of ε_t in certain temperature ranges. However, the quantitative values of ε_t in intensity have a significant variation (up to $\sim 24\%$ in the solid phase for zirconium), which is explained by differences in technical and methodological approaches in studies (Table 5).

Removable narrow-band infrared dispersion filters were used in spectral studies of emissivity of metals. Each filter has an effective wavelength [4]. The spectral characteristics of the filters after a series of experiments were confirmed by checking on appropriate spectrophotometers.

A monotonously decreasing curve of ε_t was obtained depending on the wavelength in the study of zirconium in the solid phase (Fig. 3). The comparison of the obtained values ε_λ correlates satisfactorily in the confidence probability corridor with the results of other studies [9,11,15,16].

Fig. 3 also shows the result of the theoretical calculation of ε_λ according to the classical electromagnetic theory — Drude approximation [17]:

$$\varepsilon(\lambda, T) = 0.365\left(\frac{\rho_0}{\lambda}\right)^{1/2}, \qquad (4)$$

where ρ_0 — the specific electrical resistance of the metal at a given temperature of the experiment; λ — the wavelength.

Experimental data on ρ_0 of zirconium from [18] were used in calculations.

Studies of the liquid phase of zirconium in the melting region, presented in Fig. 4, clearly illustrate the classical change of ε_λ from wavelength. The values of ε_λ are compared with the results of calculations of zirconium properties in the melting region based on the quantum

Table 5. Experimental varieties of studies of ε_t of zirconium and hafnium

Authors	Method	Temperature, K	Chemical purity,%	Medium	Error, %
[9]	Pulse	1400–2000	99.9	Vacuum	2.5–3
[10]	Levitation	1850–2220	99.9		3.6–7.2
[12]	Pulse	1177–2174	99.3		2.4–5.6

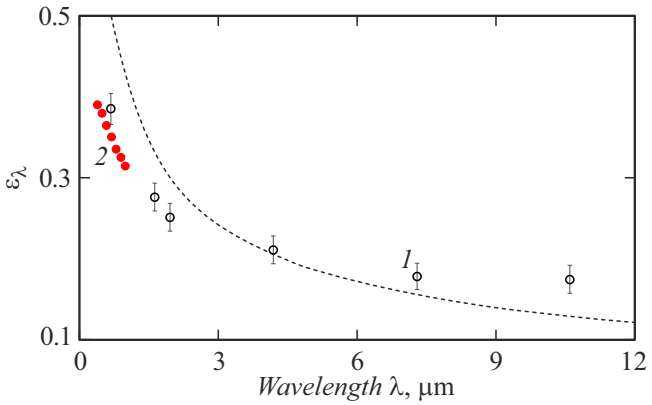

Figure 4. Wave dependence of ε_λ of zirconium (liquid phase): *1* — results of the authors; *2* — [19]; dashed line — Drude approximation

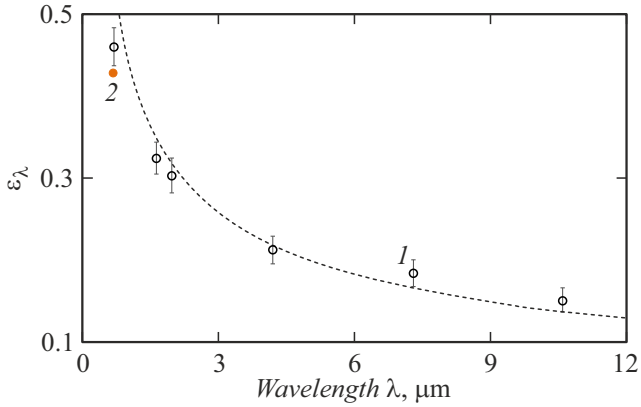

Figure 6. Wave dependence of ε_λ of hafnium (liquid phase): *1* — results of the authors; *2* — [23]; dashed line — Drude approximation

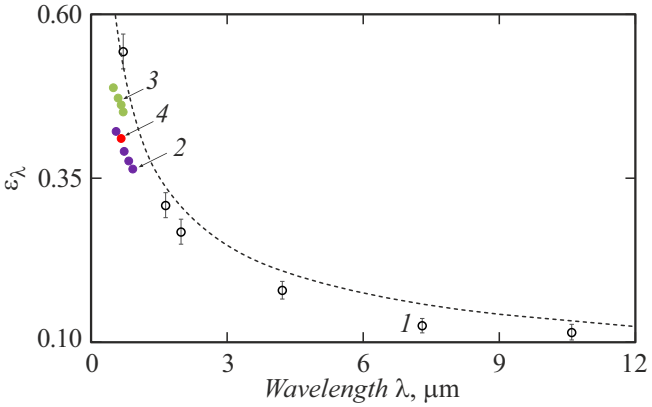

Figure 5. Wave dependence of ε_λ of hafnium (solid phase): ○ — results of the authors; *1* — [16]; *2* — [21]; *3* — [22]; dashed line — Drude approximation

molecular theory [19]. The results of the theoretical calculation based on the Drude approximation show a satisfactory agreement with the authors' experiment. ρ_0 data are taken from the recommendations [20].

The values of the spectral emissivity of hafnium in the solid phase decrease smoothly with the increase of the wavelength (Fig. 5).

The authors of [13] note that the main body of available experimental data on ε_λ of hafnium in the solid phase was studied mainly in a narrow spectral range. The calculation performed in the Drude approximation showed good agreement with the experimental values. ρ_0 data for the calculation are taken from [18].

The authors obtained a smoothly decreasing curve of ε_λ of dependence of liquid hafnium on the wavelength in the range of $0.69-10.2\,\mu$m (Fig. 6). The conducted search showed the presence of a single measurement [23] at $\lambda = 0.69\,\mu$m. ρ_0 data from [18] were used for calculating ε_λ in the Drude approximation. The theoretical calculation shows a good coincidence of the dependence of ε_λ on wavelength with experimental results.

The numerical values of ε_λ of zirconium and hafnium in the melting region are summarized in Table 6.

All discrepancies in the results ε_λ of the authors with the currently available values of other works can be explained both by the variety of the applied experimental techniques and the chemical purity of the samples (Table 7).

Conclusion

A comprehensive study of emissivity of metallic zirconium and hafnium in a wide temperature range was performed. The obtained temperature dependences of ε_t of metals monotonously grow and change abruptly in the melting point region. The behavior of ε_λ of metals in the range of $0.69-10.6\,\mu$m demonstrates a decrease of the intensity with an increase of the wavelength. A need for

Table 6. Values of ε_λ of zirconium and hafnium in the melting region

λ, μm	0.69	1.63	1.97	4.2	7.3	10.6
Zirconium ($T_{exper.} = 2090$ K)						
ε_λ	0.395	0.267	0.223	0.172	0.145	0.121
Zirconium ($T_{exper.} = 2150$ K)						
ε_λ	0.385	0.276	0.251	0.211	0.178	0.174
Hafnium ($T_{exper.} = 2480$ K)						
ε_λ	0.542	0.308	0.268	0.179	0.125	0.1154
Hafnium ($T_{exper.} = 2530$ K)						
ε_λ	0.462	0.325	0.304	0.213	0.184	0.151

Table 7. Experimental varieties of study of ε_λ of zirconium and hafnium

Authors	Method	Temperature, K	Chemical purity, %	Medium	Error, %
[11]	Pulsed	2100	99.8	Argon	±3.5
[15]	Induction	1678	99.99	Vacuum	±4
[16]	Pulsed	1856–1981 2134–2292	Zr–99.8 Hf–96.9	Argon	±2
[22]	Levitation	2471	99.7	Helium	±5
[23]	Pulsed	2510	99.95	Argon	1.5–3

further detailed study of the properties of zirconium and hafnium is traced.

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