# THERMAL, ELECTRICAL, AND RADIATIVE PROPERTIES OF TITANIUM, ZIRCONIUM, AND HAFNIUM IN THE TEMPERATURE REGION 1000-2100°K

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Using the ac induction heating method this paper studies the thermal, electrical, and radiative properties of titanium, zirconium, and hafnium over a wide temperature range and compares the data obtained with the literature. Special features in the properties of the metals studied are identified and discussed.

Titanium, zirconium, and hafnium belong to a group of metals which are finding increasingly wide use. However, until now the thermal, electrical, and radiative characteristics of these metals, particularly in the high-temperature range, have not received sufficient study.

The fact that group IV elements have received little study in the temperature range above 1000°K is associated with a specific feature of their properties, namely the enhanced capacity of metals of this group to adsorb oxygen and nitrogen, forming a solid intruded solution [1-3]. In addition, these metals undergo a phase transition, which may be accompanied under specific conditions by considerable deformations of the test specimen. All of this makes it very difficult to work with group IV metals.

One must consider these special features of the group IV elements in choosing a method for investigating their properties, offering an advantage over methods using large specimens, since the rate of diffusion of oxygen and nitrogen is small, and these are located in the surface layer. Therefore data obtained on specimens with a developed surface will be less reliable, in principle, than when large specimens are used, especially if one takes into account the possibility of the specimens deforming during phase transitions.

To study the properties of these elements it is desirable, for these reasons, to use complex methods which will evaluate a group of properties in a single experiment. It is also desirable that the experiment should be of short duration and should be conducted on a single specimen under identical conditions.

To investigate the thermal properties of group IV metals the authors have used a compound method of ac induction heating, offering a direct measurement of the thermal diffusivity $a$, the specific heat $C_p$, and the thermal conductivity $\lambda$ of the test specimen. The method is based on the use of radial temperature waves, created in a cylindrical specimen by modulated heating in a high-frequency oven [4, 5]. The specific electrical resistivity $\rho$ and the emissivity, the spectral value $\varepsilon_{\lambda,T}$ ($\lambda = 0.65\ \mu$m) and the integral value $\varepsilon_T$, were measured simultaneously with the thermal characteristics in the same facility [6] under identical conditions.

The zirconium specimen investigated, prepared by the iodide method, consisted of large grains elongated in the radial direction, with weak bonds between them. Since this can lead to some anisotropy in the properties of the specimen in mutually perpendicular directions, it should be stipulated that our data describe the thermal properties of zirconium in the radial direction, and the electrical properties in the axial direction. The zirconium specimen had a composition (weight %) of: 99.44 Zr; 0.3 Ti; 0.2 Al; 0.05 Mg; 0.02 (Si, Mn); < 0.01 Ni; 0.04 $SiO_2$.

The density and the specific electrical resistivity at 20°C were 6.26 g/cm$^3$ and 49.6 $\mu\Omega\cdot$cm, respectively, the specimen diameter was ~10 mm, and its length ~9 cm. The temperature was determined in a black body model, having a radial aperture of diameter ~1 mm and a depth of ~6 mm. Before the measurements the specimen was annealed for ~2 h in vacuum at a temperature of 1900°K. In reducing the experimental data for zirconium a correction was made for the thermal expansion of the specimen according to the data of [7].

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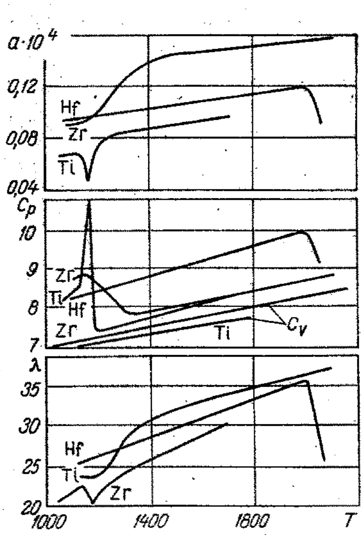

Fig. 1

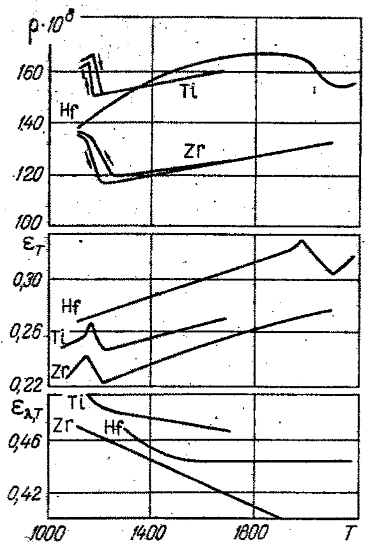

Fig. 2

Fig. 1. Thermal diffusivity $a$, the specific heats $C_p$ and $C_V$, and the thermal conductivity $\lambda$. Units are: for $a \cdot 10^4$, m²/sec; for $C_p$, cal/g-atom · deg; for $\lambda$, W/m · deg; and for T, °K.

Fig. 2. Specific electrical resistivity $\rho$, integral $\varepsilon_T$ and spectral $\varepsilon_{\lambda,T}$ emissivity; $\rho$ is in $10^8$ Ω · m; T in °K.

TABLE 1. The Thermal ($a$, $C_p$, $\lambda$), Electrical ($\rho$), and Radiative ($\varepsilon_T$ and $\varepsilon_{\lambda,T}$) Properties of Zirconium

| $T$, °K | $a \cdot 10^6$, m²/sec | $C_p$, cal/g-atom · deg | $\lambda$, W/m · deg | $\rho \cdot 10^8$, Ω · m | $\varepsilon_T$ | $\varepsilon_{\lambda,T}$ |
|---|---|---|---|---|---|---|
| 1100 | 9,6 | 8,6 | 24,1 | 135,7<br>136,3* | 0,233 | 0,470 |
| 1135 | 9,6 | 8,95 | 24,1 | 134,2<br>136,4* | 0,242 | 0,468 |
| 1200 | 10,8 | 8,6 | 24,1 | 116,2<br>126,1* | 0,220 | 0,461 |
| 1300 | 13,0 | 7,9 | 29,6 | 118,2<br>118,9* | 0,229 | 0,453 |
| 1500 | 14,6 | 8,0 | 32,4 | 122,3<br>122,8* | 0,247 | 0,435 |
| 1700 | 15,0 | 8,25 | 34,0 | 126,4<br>126,6* | 0,259 | 0,417 |
| 1900 | 15,4 | 8,55 | 35,5 | 130,4<br>130,6* | 0,269 | 0,399 |
| 2100 | 15,8 | 8,85 | 37,3 | 134,5<br>134,5* | 0,275 | 0,381 |

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* The resistivity values are for the reverse change in temperature.

Smoothed data from the study of six properties of transition metals of group IV are shown in Figs. 1 and 2, and for zirconium in Table 1 (the data for titanium and hafnium and a comparison with the literature values are given in [8, 9]).

The change in thermal diffusivity for zirconium in the $\alpha$–$\beta$ transition is appreciably greater than the same thing for titanium, and is more than 50%.

The difference between the specific heat values of the $\alpha$- and $\beta$ phases of zirconium is about 17%. Our data lie above the results of [10] by ~7% and of [11] by ~15%, and have practically the same temperature behavior.

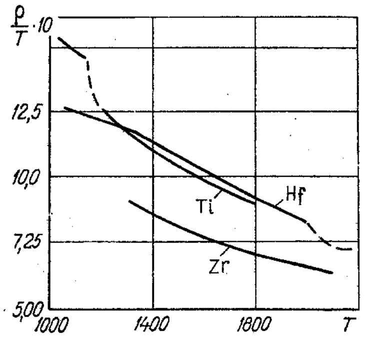

Fig. 3. Values of $\rho/T\cdot 10$, $\Omega\cdot$m/deg; T, K°.

The variation in the thermal conductivity of zirconium during a phase transition is ~20%. Our results practically coincide with those in [12, 13], and exceed the data of [14] for a specimen of closely similar chemical composition. The data of [15] lie above ours by ~30% at a temperature of ~1500°K.

The specific electrical resistance of zirconium varies by ~12% in a phase transition both for the forward and the reverse variation in temperature. In the transition region hysteresis occurs, but its nature is different: for titanium the values of $\rho$ during the $\alpha$-$\beta$ transition lie above the same values for the $\beta-\alpha$ transition, and for zirconium the reverse is observed. The question of whether the anomalous nature of the hysteresis branch for zirconium relative to titanium, can be related with the fact that the specimen of zirconium we studied may not have been sufficiently pure, or with the number of phase transitions experienced by this specimen before and during the experiment (in the experiments with zirconium this was considerably larger than with titanium) can be explained only with additional experiments. One can reliably assert that the increase in the number of phase transitions leads to both an increase in the temperature range in which transition begins and ends, and also to a smoother variation in all the properties of the metal within the range. In particular, in [15] the temperature range of transition is more than 100 degrees, which is evidence of a large number of $\alpha-\beta$ transitions experienced by the specimen, and therefore the smooth dependence of $\rho$ obtained in this work in the transition region cannot be considered typical of zirconium. A small difference in the temperature below 1800°K (Fig. 2) is observed in the $\beta$ phase in the values of $\rho$ for zirconium in the forward and reverse temperature change. The results of measurement of $\rho$ for zirconium agree well with the data of [13] and are 2-5% above the data of [15, 16].

The values of integral emissivity $\varepsilon_T$ of the metals studied show discontinuities of ~8% in the region of phase transition temperatures. Within the limits of measurement error of $\varepsilon_T$ our data agree with the data of [13, 16] for $\beta$ of zirconium.

The results for the spectral emissivity of zirconium agree with the data of [16]. We note that none of the group IV metals studied showed sharp variations in $\varepsilon_{\lambda,T}$ during phase transition, like those shown with titanium in [17]. In [18] for $\varepsilon_{\lambda,T}$ of titanium a discontinuity comparable in magnitude with that for $\varepsilon_T$ was observed.

From this study of titanium, zirconium, and hafnium one can single out certain characteristics in the thermophysical properties of these metals.

First one should note the increase in thermal diffusivity with temperature (Fig. 1) which distinguishes this group from all of the transition metals, which, according to [19], have a negative temperature coefficient of thermal diffusivity.

Because we studied the properties of group IV elements in the range $(0.4-0.99)T/T_f$, the matter of the heat capacity of these elements warrants particular discussion. As can be seen from Fig. 1, the variation in heat capacity is linear with temperature even in the region far from the melting temperature. A similar relation is observed for other transition metals [19], and from this one can conclude that there is a similarity in the temperature dependence of the heat capacity of refractory metals and that there is no significant rise in the heat capacity near fusion temperatures, as was associated in [20, 21] with the role of thermal vacancies. In particular, in [21] the heat capacity of titanium at 1900°K reaches 10.06 cal/g-atom • deg. However, the concentration of vacancies found from these values is an order of magnitude smaller than from the other data. Since the experiment in [21] was conducted with large rates of temperature variation, the role of the kinetics of vacancy formation and the influence on heat capacity remain unclear. Finally, it should be noted that the experiments in [20, 21] are not conclusive, that the data on the temperature dependence of the specific electrical resistivity of the materials studied were not measured directly, but taken from the literature data, which is particularly undesirable for group IV elements because of the noted specific behavior of their properties.

Figure 1 shows isochors of specific heat of titanium and zirconium (for the $\beta$-phase), calculated from known formulas, using the experimental data for constant-pressure specific heats. It can be seen that $C_V$ also increases monotonically (and linearly) with temperature, which does not conform with the Dulong–Petit law. If one assumes that the anharmonic contribution is small, one should evidently seek an explanation for this in the increase with temperature of the electronic heat capacity, which leads to an increase in the contribution of electronic specific heat to the specific heat of the metal. For a more detailed study of this question one must conduct systematic investigations, using the methods of ultraacoustic engineering, of the longitudinal and transverse sound speeds in metals in the high-temperature region.

We now consider the question of the behavior of the specific heat of the metals studied (Fig. 1). It is noteworthy that the heat capacity of titanium does not fall off with increase of temperature and tend to asymptotic values, as would follow from elementary kinetic theory, but increases, and the temperature coefficient is large in comparison with its value for the other transition metals [19].

Analysis of the question of factors governing the behavior of the specific heat leads to the conclusion that the temperature dependence of specific heat is determined primarily by the nature of the temperature dependence of the electrical conductivity, and by the deviation from linearity of $\rho(T)$, since in both cases the main portion of the resistance is determined by the electrons. A summary of the variation in specific electrical resistance with temperature for the metals studied is given in Fig. 3 as a graph of $\rho(T)/T$ as a function of temperature. It can be seen that the function $f(T) = \rho/T$ decreases noticeably with increase of temperature. The faster $\rho/T$ falls off with temperature, the sharper is the temperature dependence $\lambda(T)$, and the latter is positive. By comparing the relations obtained with similar relations for tungsten [22], molybdenum [23] and a tantalum–tungsten–carbon alloy [24] (for these metals and the alloy $\rho/T$ increases, but $\lambda(T)$ falls off with temperature), one can evidently assert that the dependence of $\lambda(T)$ is determined by the nonlinear dependence of resistance on temperature. Analysis of the experimental curves of $\rho/T$, shown in Fig. 3, reveals a single law, and the larger the value of $\rho$, the sharper is the fall off of the function $\rho/T$ with temperature. From this one can calculate that high values of $\rho$ and the nonlinear nature of $\rho/T$ evidently stem from the same cause. The cause may be the interaction of the S–d electrons in the transition metals – the larger the role of this interaction in absolute values of $\rho$, the larger is its influence on the temperature coefficient.

Amongst the typical features of group IV elements one should note the sharply pronounced nonlinear nature of the variation of $\rho$ with temperature in the $\alpha$-phase (for rhenium, which also a hexagonal lattice, a similar picture is observed [25]), and a linear variation in the $\beta$-phase, as well as a very large absolute value of $\rho$, larger by a factor of 2-5 than $\rho$ for the other refractory metals.

To explain the role of the lattice component of thermal conductivity one must consider the behavior of the Lorentz number. The Lorentz number for all the metals we studied exceeds the theoretical value and depends on the temperature (L drops off with increase of the latter), asymptotically approaching the theoretical value $L_0$. This behavior of L is the same for all the transition metals [19], including group IV metals. At the same time in [15] the Lorentz numbers for zirconium increase with temperature, and this is at variance with experimental data for transition metals and with the conventional theoretical ideas. In fact, computation of the lattice component of thermal conduction $\lambda_p$ on the basis of the data of [15] for $\lambda$ and L gives an increase with temperature, i.e., a decrease in the thermal resistance of the lattice with increase in temperature, which is scarcely understandable physically. The results obtained in [15] for zirconium once again confirm the above-mentioned viewpoint, namely that it is inappropriate to study the properties of group IV elements in small specimens (wire or foil), where the inability to calculate properties with sufficient accuracy can strongly distort the true picture.

Identification of the lattice component of the thermal conductivity of titanium, zirconium, and hafnium on the basis of our data shows that $\lambda_p$ for the metals studied at T ~ 1000°K is approximately 20% of the total thermal conductivity, and falls off with increase of temperature, while the relation $\lambda_p(T)$ does not follow the Aitken law, even allowing for the error in the method of determining $\lambda_p$, which may be large.

The electronic component $\lambda_e$ of the thermal conductivity, according to our data, increases with increase of temperature and explains the positive nature of the temperature coefficient of the total thermal conductivity of group IV metals. We note that similar relations for the thermal conductivity and its components as a function of temperature were obtained also in [13, 25], in which measurements of the electrical and thermal conductivity were conducted, not along mutually perpendicular planes, as we did, but along a single axial direction.

## NOTATION

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|---|---|
| $a$ | is the thermal diffusivity; |
| $C_p$, $C_V$ | are the constant pressure and constant volume specific heats; |
| $\lambda$ | is the thermal conductivity; |
| $\rho$ | is the specific electrical resistance; |
| $\varepsilon_T$ | is the integral emissivity; |
| $\varepsilon_{\lambda,T}$ | is the spectral emissivity; |
| $T$ | is the temperature; |
| $L$ | is the Lorentz number. |

## LITERATURE CITED

1. V. I. Eremenko, Titanium and Its Alloys [in Russian], Izd. Akad. Nauk SSSR, Kiev (1960).
2. L. S. Moroz et al., Titanium and Its Alloys [in Russian], Sudpromgiz, Leningrad (1960).
3. A. MacWillen, Titanium [Russian translation], Inostr. Lit., Moscow (1968).
4. L. P. Filippov, Measurement of Thermal Properties of Solid and Liquid Metals at High Temperatures [in Russian], Moscow State Univ. (1967).
5. L. P. Filippov and I. N. Makarenko, Teplofiz. Vys. Temp., 6, No. 1 (1968).
6. I. N. Makarenko, A. V. Arutyunov, and L. P. Filippov, Zavod. Lab., No. 9 (1969).
7. V. M. Amonenko, P. N. V'yugov, and V. S. Gumenyuk, Teplofiz. Vys. Temp., 2, No. 1 (1964).
8. A. V. Arutyunov, S. N. Banchila, and L. P. Filippov, Teplofiz. Vys. Temp., 9, No. 3 (1971).
9. A. V. Arutyunov, S. N. Banchila, and L. P. Filippov, Teplofiz. Vys. Temp., 10, No. 2 (1972).
10. R. Hultgrem, R. L. Orr, R. D. Anderson, and K. K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys, N. V., London (1963).
11. O. Velmer, R. Broun, and R. Kohlhaas, Naturforsch Z., 22a, No. 5 (1967).
12. Thermophysical Properties of High-Temperature Solid Materials, 1, No. 4 (1967).
13. V. É. Peletskii, V. P. Druzhinin, and Ya. G. Sobol', Teplofiz. Vys. Temp., 8, No. 4 (1970).
14. D. L. Timrot and V. É. Peletskii, Teplofiz. Vys. Temp., 3, No. 2 (1965).
15. S. C. Jain, V. Sinha, and B. K. Reddy, J. Appl. Phys., 3, 1959 (1970).
16. G. A. Zhorov, Teplofiz. Vys. Temp., 8, No. 4 (1970).
17. F. J. Bradschow, Proc. Soc. Am., 63, 573 (1950).
18. G. A. Zhorov, Teplofiz. Vys. Temp., 5, No. 6 (1967).
19. L. D. Filippow, Int. J. Heat Mass Transfer, 16, 865 (1973).
20. G. G. Zaitseva and A. V. Kraftmakher, Zh. Prikl. Mekh. Tekh. Fiz., No. 3 (1965).
21. V. O. Shestopal, Fiz. Tverd. Tela, 7, No. 11 (1965).
22. A. V. Arutyunov and L. P. Filippov, Thermophysical Properties of Substances and Materials [in Russian], No. 5, Standartov, Moscow (1972).
23. I. N. Makarenko, L. N. Trukhanova, and L. P. Filippov, Teplofiz. Vys. Temp., 8, No 2 (1970).
24. A. V. Arutyunov and S. N. Banchila, Teplofiz. Vys. Temp., 10, No. 1 (1972).
25. A. V. Arutyunov and L. P. Filippov, Teplofiz. Vys. Temp., 8, No. 5 (1970).