Experimental study of high-temperature properties of zirconium carbide as a protective material for nuclear power and aerospace technologies (from 2000 to 5000 K)

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Abstract. The temperature dependences of the thermal and electro physical properties of the zirconium carbide ZrC + C and ZrC_{0.95} were studied in the temperature range 2000-5000 K. The Zr+C specimens were in the form of thin layers sputtered on quarts substrate and ZrC_{0.95} specimens were in the form of plates cut off from the sintered block. The properties are measured: temperature and heat of fusion, enthalpy, specific heat and resistivity, referred to the initial dimensions. A steep increase in the specific heat of these substances before melting and a sharp decrease after melting were observed at a heating rate of ~ 10^8 K/s, which is possibly due to the formation of Frenkel pair defects in the specimens.

1. Introduction
Zirconium carbide possesses a number of unique properties, which makes it a promising protective material for nuclear power and aerospace technologies [1-3]. Such properties include high melting point (~ 3500 K), low density (~ 6.6 g / cm3) as compared with refractory metals, high thermal and electrical conductivity and thermal diffusivity, nuclear physical properties. Its disadvantage as a protective material is a low resistance to oxidation (oxidized in air at a temperature above ~ 1200 K). Zirconium carbide is proposed to be used in the form of coatings of microspheres (TRISO fuel particle) in the matrices of fuels of high-temperature gas reactors (HTGR).

Despite a long period of study of the properties of zirconium carbide as a high-temperature material, a number of questions remain to be clarified: the region of the Zr-C phase diagram rich in carbon has been little studied; The region of melting of carbide and the properties of carbide in the liquid phase have not been sufficiently studied. In this paper, we investigated the temperature dependences of the enthalpy, specific heat and electrical resistivity of zirconium carbide in the temperature range 2000-5000 K. The studies were carried out by the method of rapid heating of a specimen by an electric current pulse (the method of electrical exploding wires), previously successfully used to study the thermophysical properties of metals and graphite [4-7]. For the study of conducting ceramics - zirconium carbide and tantalum carbide - this method was first used in [8],
however, temperature measurements in [8] were not carried out. Temperature measurement in the present work made it possible to obtain data on the specific heat of carbide in the solid phase before melting and in the liquid phase.

2. Method of investigation and measurement error
The method of research, including temperature measurements using a high-speed pyrometer, is described in [9-11]. The temperature measurements were performed at a wavelength of 856 nm. The uncertainties of the properties measurement for ZrC+C specimens were as follows: the Joule energy – 5 %; the resistivity – 5 %; the specific heat – 20-25 %; the temperature – from 50 to 140 K [12]. In the case of the properties measurement for ZrC0.95 specimens these uncertainties were as follows: the Joule energy – 10 %; the resistivity – 10 %; the specific heat – 26 %; the temperature – from 60 to 110 K [13].

3. Specimens
The ZrC + C (C/Zr ≈ 3.8) specimens were in the form of a mirror-like thin layer deposited on a quartz substrate by magnetron sputtering. The specimens of ZrC0.95 (designated as ZrC specimens) were cut off from the block sintered from carbide powder by the spark plasma sintering (SPS) method. The table shows the compositions of the specimens studied. Neglecting the impurities, we obtain the carbon content in the specimens in the first case - 86.4%, in the second case - 48.7%. Analysis showed that in both cases the specimens consist of zirconium carbide with cubic lattice. The thickness of the sputtered specimens was 4.9 μm, and of the sintered specimens 50-100 microns. The width and length of the first were 8×15 mm, density - 4.3 g/cm³, the second - 5×15 mm and density 6.57 g/cm³.

| Material | Zr | C | N | O | Al | As | Hf | Total |
|----------|----|---|---|---|----|----|----|-------|
| ZrC+C, at.% | 17,88 | 67,69 | 8,13 | 5,98 | 0,16 | 0,17 | - | 100,01 |
| ZrC, at.% | 47,4 | 45,0 | 3,4 | 3 | - | - | 0,4 | 99,2 |

3.1. Sputtered specimens
The experiments were carried out with three types of such specimens: (i) specimens with an exposed flat surface (experiments were carried out in water); (ii) specimens in the form of a wedge black body model (experiments in water); (iii) specimens sandwiched between the substrate and the top cover glass (experiments in the air).

The use of the black body model allowed to measure the true temperature of the specimens and also to measure the spectral emissivity of carbide at a wavelength of 856 nm in the solid phase at temperatures 2000-3100 K and in the liquid phase at 3150-3400 K. The black body model shown in figure 1 was composed of two substrates with sputtered layers to form a mirror-like inner surface of the wedge-shaped cavity.

3.2. Sintered specimens
The quartz cell with the specimen is shown in figure 2. In this case, specimens were studied in the form of plates clamped between the quartz substrate and the upper quartz glass. Between the quartz glasses and the specimen there were layers of adhesive with a thickness of ~ 10 μm. Literature data on the emissivity of zirconium carbide were used to determine the temperature of the specimens. The data on emissivity obtained for the ZrC+C carbide were used also.
Figure 1. Wedge-shaped black body model made up of two substrates coated with a mirror-like layers of ZrC+C (wedge cavity).

Figure 2. A cell made of quartz glass with a specimen of sintered ZrC (dark strip) inside the cell.

4. Results of experiments

The results of the experiments are the temperatures of the beginning and the end of melting, the heat of melting, and the temperature dependences of the specific energy of the energy dissipated in the specimen (enthalpy), specific heat and electrical resistance, referred to the initial dimensions of the specimen. A comparison of the results with the literature data is presented in [12, 13].

4.1. Melting temperature

Estimates show that, despite the short heating time, the specimen during melting is in local thermodynamic equilibrium [12]. This makes it possible to use the equilibrium phase diagram of the Zr-C system to analyze the rapid process of heating and melting of the specimens.

Figure 3. The phase diagram of Zr-C [14]. The carbon content in the specimens (in atomic fractions, excluding impurities) was: the ZrC + C specimens - 0.86; the ZrC_{0.95} specimens - 0.49.
In figure 3 shows one of the variants of such calculated phase diagram [14], from which it follows that the solidus and liquidus temperatures of the ZrC+C alloy should be 3200 K (eutectic temperature) and ~ 4300 K, and the solidus and liquidus temperatures for ZrC\(_{0.95}\) should be ~ 3500 K and 3700 K.

Figure 4. The dependence of temperature on Joule heating energy for ZrC + C specimens: 1 - black body model (emissivity 0.95); 2 - clamped specimen (measured emissivity was 0.6). The solidus temperature was determined with the line 1 but the liquidus temperature was determined with the line 2 (see below).

On the thermograms \(T(t)\), the melting region has the form of a plateau, the initial section of which corresponds to the beginning of the melting with the solidus temperature \(T_{\text{sol}}\) and the end of plateau corresponds to the finish of melting with the liquidus temperature \(T_{\text{liq}}\).

The same form (the presence of a plateau) has the dependences of temperature on the Joule heating energy \(T(E)\) shown in figure 4. Curve 1 in this figure corresponds to the heating of the specimen in the form of black body model (emissivity of the model 0.95), curve 2 - heating of the clamped specimen (the spectral emissivity measured in this work is 0.6±0.1). It can be seen that these two curves agree well up to the energy of ~ 5 kJ/g. This indicates the correctness of the determination of the emissivity for a flat clamped specimen. At the energy of more than 5 kJ/g delamination of the not clamped sputtered specimens occurred [12] that not allowed conducting the measurements with black body model. The clamped specimen is stored up to energy of ~ 7 kJ/g. Therefore, the temperature \(T_{\text{sol}} = (3150\pm50)\) K was determined from the dependence of 1, and the end of melting \(T_{\text{liq}} = 3640\) K on the curve 2, as shown in Figure 4. For ZrC + C specimens, the solidus temperature practically coincide with that indicated on the phase diagram (figure 3) and with the literature data and the liquidus temperature is below the expected value. The reason for this decrease may be a rather large amount of impurities in the specimens.

The dependence of \(T(E)\) for ZrC specimens (figure 5) gives \(T_{\text{sol}} = (3450\pm60)\) K that agrees with the phase diagram and \(T_{\text{liq}} = (3850\pm110)\) K that exceeds the value in the presented phase diagram, but coincides with the maximum liquidus temperature in the other phase diagrams [13].
Figure 5. Dependence of temperature on the energy of Joule heating for ZrC specimens. $T_{\text{sol}} = (3450 \pm 60) \text{ K}, E_1 = 2.2 \text{ kJ/g (at } T_{\text{sol}}); T_{\text{liq}} = (3850 \pm 110) \text{ K}, E_2 = 3.3 \text{ kJ/g (at } T_{\text{liq}})$. Heat of fusion $\approx 1.1 \text{ kJ/g}$.

4.2. Enthalpy

The specific energy of the Joule heating of the specimen is calculated by the formula:

$$E(t) = \frac{1}{m} \int_0^t I(t) U(t) dt,$$

where $m$ is the mass of the specimen; $I(t)$ is the current through the specimen; $U(t)$ is the voltage drop across the active resistance of the specimen. Most of the Joule energy $E$ is scattered in the specimen and goes to its heating. In the case of constant pressure (experiments in water), this energy is equal to the enthalpy. As the estimates show, the effect of pressure growth in experiments with clamped specimens can be neglected and considered that this energy is also equal to the enthalpy. The dependences of $T(E)$ presented in figures 4 and 5 can be easily converted to the dependences of the enthalpy on the temperature with accounting for heat losses.

In the case of sputtered specimens, the Joule energy is spent to heat the specimen, to heat the substrate, to radiate and to heat the water layer (in experiments in water), or to heat the upper glass for a clamped specimen. The sputtered layer of ZrC+C had a good thermal contact with the substrate, which led to the need to take into account the thermal losses on the heating of the substrate. As estimates have shown, these losses at a temperature of about 3000 K are $\approx 10\%$ ($\approx 0.3 \text{ kJ/g}$). The remaining components of heat loss can be neglected taking into account the short heating time. This is confirmed by the coincidence of curves 1 and 2 in figure 4, obtained for different heating conditions and different losses.

In the case of sintered specimens, the losses of Joule energy, in particular, losses on substrate heating can be neglected. In fact, in this case the ZrC plate is separated from the substrate by a layer of glue that evaporates upon heating. At high temperatures, the substrate material - SiO$_2$ (boiling point 3130 K) also evaporates, thus the specimen is separated from the substrate by a layer of vapor having a low thermal conductivity. The remaining types of losses, as in the case of clamped sputtered specimens, are small. So the enthalpy $H(T)$ is approximately equal to $E(T)$. 
4.3. Heat of fusion

The heat of fusion $\Delta E$ was determined as the difference in the energies of the end and the beginning of melting. In the case of sputtered specimens the difference of Joule energy was taken accounting for the fact that the heat losses on substrate heating are approximately the same for the beginning and the end of melting (this is the main type of loss). We have obtained $\Delta E = 3.2$ kJ/g (figure 4). In the case of sintered specimens, the difference of the Joule energy was taken also, and we obtained $\Delta E = 1.1$ kJ/g. This value is consistent with literature data. The heat of fusion in the first case is higher due to the presence of free carbon, the dissolution of which in the melt requires additional energy. As is known, the heat of fusion of pure carbon is $\approx 10$ kJ/g [7].

4.4. Specific heat

The specific heat was determined from the $E (T)$ dependences as $C_p (T) = \Delta E / \Delta T$, ($\Delta T \approx 150$-250 K). The temperature dependences of the specific heat are shown in figure 6 and figure 7.

**Figure 6** [12]. Specific heat for ZrC+C specimens. Left curve is obtained with the blackbody model and right curve is obtained with the clamped specimen. Arrows show the start (3150 K) and the end (3640 K) of the phase transition according to figure 4.

**Figure 7** [13]. Specific heat for ZrC specimens. Arrows indicate the start (3450 K) and the finish (3850 K) of melting (according to result of figure 5). The uncertainties are shown by horizontal and vertical bars.

The specific heat of ZrC + C specimens is $\approx 0.8$ kJ/g in the temperature range 2200-2800 K, which is in agreement with the estimated calculation ($\approx 1$ kJ/g [12]), which takes into account a large amount of free carbon. The specific heat of ZrC specimens is $\approx 1.0$ kJ / g in the temperature range 2500-3000 K, which is 25-30% higher than the literature data. The values of the specific heat of these two types of specimens in the liquid phase approximately coincide and coincide with the literature data.

A characteristic feature of the $C_p (T)$ dependences is a steep increase in the specific heat before melting (300-400 K before the beginning of melting) and a steep decrease after melting. The same change in the specific heat during rapid heating is also observed when melting refractory metals [4, 5]. A possible explanation for this behavior of $C_p (T)$ is the assumption that Frenkel's nonequilibrium pair defects are formed just before melting and then quickly disappeared during and after melting.
4.5. Electrical resistivity, referred to the initial dimensions

Figures 8 and 9 show the dependences of the electrical resistivity of the specimens on the Joule energy $\rho(E)$ in the solid and liquid phases. A large content of free carbon (and possibly the influence of impurities and the structure of the specimens) gives a regular increase in the resistivity of the sputtered specimens as compared with the sintered specimens. The resistivity of sputtered specimens grows from 700 $\mu\Omega\cdot$cm to 1100 $\mu\Omega\cdot$cm with an increase in temperature from 2500 to 4000 K. Recall that the resistance of liquid carbon at the melting point is 1200 $\mu\Omega\cdot$cm [6, 7].

![Figure 8](image1.png)  
**Figure 8.** The resistivity for ZrC+C specimens (referred to initial dimensions). The result is obtained with clamped specimen. Arrows show the phase transition (solid–liquid) according to figure 4.

![Figure 9](image2.png)  
**Figure 9.** The resistivity for ZrC specimens (referred to initial dimensions). Arrows show the start and the finish of specimen melting, just the same as it was obtained in figure 5.

The resistivity of sintered specimens in the same temperature range varies from 200 to 300 $\mu\Omega\cdot$cm, which is consistent with the literature data. The drop in resistivity of sintered specimens with an increase in the energy of Joule heating from 2 to 4 kJ/g is possibly due to the increase in pressure in tightly clamped specimens [13]. For ZrC + C specimens, the pressure increase was smaller due to the gaps in the quartz cell [12]. The resistivity of these specimens has a growing character throughout the temperature range of the investigation, with the exception of the local peak (near the left arrow) possibly associated with the structural changes in the specimen near the melting.

The authors do not know the literature data on the electrical resistivity of zirconium carbide in the liquid phase.

5. Conclusion

The temperature dependences of the thermal and electro physical properties of the zirconium carbide ZrC + C and ZrC$_{0.95}$ were studied in the temperature range 2000-5000 K. The Zr+C specimens were in the form of thin layers sputtered on quartz substrate and ZrC$_{0.95}$ specimens were in the form of plates cut off from the sintered block. The obtained solidus temperatures for these two materials are consistent with the phase diagram of Zr-C. The liquidus temperature for sputtered specimens is reduced compared to the phase diagram by ~ 300-400 K, which is possibly associated with large impurities content. The liquidus temperature of ZrC$_{0.95}$ is consistent with the phase diagrams. The properties are measured: heat of fusion, enthalpy, specific heat and resistivity, referred to the initial dimensions. A steep increase in the specific heat of the investigated materials before melting was
observed and a sharp decrease after melting at a heating rate of ~ $10^8$ K/s, which is possibly due to the formation and disappearance of Frenkel defects in the specimens.

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