Specific heat of refractory carbides (ZrC$_{0.95}$, HfC$_{0.85}$ and Ta$_{0.8}$Hf$_{0.2}$C) in the temperature interval 2500-5000 K

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Abstract. A fast method for studying the physical properties of substances is considered, - heating by a single current pulse for 5-8 µs. Its advantages over the stationary methods is in obtaining bulk thermophysical properties of carbides at high temperatures (2500 – 5000 K). The temperature was measured by an optical method using high-speed photo-detectors PDA-10A (Thorlabs) and temperature lamp calibration. There is a sharp increase in the heat capacity of the solid phase for $\approx 300$ K before melting for all the studied carbides. It is assumed that the reason for the accelerated growth of heat capacity is associated with the formation of paired Frankel defects, in conditions of insufficient time for saturation of the volume with equilibrium vacancies.

1. Introduction
The main publications on the study of the physical properties of refractory carbides and nitrides in solid and liquid states by heating with a current pulse during 5-10 µs are given in [1-7]. As noted in [5], the method allows us to study the temperature dependences of the enthalpy, specific heat, and electrical resistance of a conducting substance in the solid phase, during melting, and in a wide range of the liquid state, as well as the temperature and enthalpy of phase transitions. In all these studies, the specific input (Joule) energy – Joule heat $E$, scattered in the sample, and the sample temperature were measured, which allowed us to calculate the specific heat $C_p = \Delta E/\Delta T$ at a fairly narrow temperature range $\Delta T$ (100-200 K) with an error of 10-15% for the solid phase and 15-25% for the liquid phase. During pulsed heating, a small pulsed pressure (less than 5-9 MPa) appeared in the samples, the influence of which can be ignored [5, 7] and considered the Joule heat equals to the enthalpy, and the measured specific heat equals to the heat capacity at constant pressure.

The temperature was measured by an optical method using a high-speed pyrometer based on PDA-10A type photodetectors (Thorlabs). In this case, we used literature data on the emissivity of the studied substances. In the absence of these, a wedge-shaped model of the blackbody was used, consisting of two glass plates with a thin layer of sputtered substance [1]. The fast method of microsecond current heating has a number of advantages over standard stationary methods [8, 9]:
- it is easy to reach the highest temperatures (the limit is the boiling point of the material);
- the short duration of the heating process leads to small thermal losses of all types, that constitutes a fraction of a percent of the Joule energy input, which makes it possible to measure thermal properties with acceptable accuracy;
- the volumetric heating of the sample takes place, which allows measuring its volumetric properties;
- the short duration of the heating process allows you to measure several thermophysical properties of solid and liquid states of a substance in a single experiment;
- the short duration of the heating process allows you to neglect the change in the composition of the sample during heating and neglect the interaction of the sample with the environment.

Note that with the exception of works [1-7], there are no experimental data in the literature on the specific heat of refractory carbides in the liquid phase, which is associated with very high melting temperatures of these substances. The behavior of the specific heat of all the carbides considered below has features that were previously found in metals [8, 9]. Immediately before melting (200-300 K before), the specific heat of these carbides increases abnormally, and after melting in approximately the same temperature interval, it quickly falls, approaching the estimates obtained for equilibrium conditions.

It can be assumed that an abnormal increase in the specific heat for the solid phase of carbides (as well as metals) in the melting region is associated with the rapid formation of non-equilibrium Frenkel defects and with a rapid increase in the energy of the crystal lattice just before melting. Immediately after the completion of melting, a sharp drop in specific heat is observed, due to the annihilation of excess defects. This leads to a decrease in the internal energy of the melt and to a drop in the specific heat to values close to equilibrium.

2. Zirconium carbide

The boiling point of ZrC at normal pressure is ~ 5370 K [10]. It was established [2] that the melting of zirconium carbide ZrCₓ (C/Zr = 0.95) occurs in a temperature range of 3420 – 3840 K. Figure 1 shows the temperature dependence of the specific heat of this carbide in the solid and liquid phases.

![Figure 1](image_url)

**Figure 1.** Temperature dependence of the specific heat of ZrC₀.95 carbide: 1-solid phase; 2- melting region; 3 – liquid phase.

In this paper, we approximate the temperature dependence of the experimental values of the specific heat ZrC₀.95 in the liquid phase obtained in [2]. Figure 2 shows the Cₛ(T) curve of liquid ZrC₀.95 in the range 3840-5000 K. Abnormal increase in specific heat begins about 300 K before the start of melting (3420 K) [2]. For the studied zirconium carbide in the solid phase, this effect is
associated with the appearance of paired Frenkel defects, under conditions of insufficient time for the diffusion of equilibrium vacancies. After completion of melting (3840 K), the specific heat decreases rapidly (within ~1-2 µs) to equilibrium values at temperatures of 4200-5000 K.

The approximation of the specific heat curve of liquid ZrC\textsubscript{0.95} in the temperature range 3840-5000 K is presented by the equation:

\[ C_p(T) = -4293.6 + 1.0269 T - 6.6273 \times 10^{-5} T^2 + 2.1757 \times 10^{10} T^{-2} \text{ (J\cdot mol}^{-1}\text{ K}^{-1}). \]

This relationship is shown in Figure 2.

**Figure 2.** Dependence of the specific heat for liquid zirconium carbide ZrC\textsubscript{0.95} on temperature: 1-experimental values [2]; 2-approximating values.

3. Hafnium carbide

The boiling point of HfC at normal pressure is \sim 5670 K [10].

Hafnium carbide HfC\textsubscript{x} (C/Hf\sim 0.85) was studied under rapid heating by a current pulse, for a time of 5-8 microseconds. The carbide plate was clamped between two glass plates to prevent evaporation of the carbide and prevent surface discharge at high voltage along the sample.

The normal spectral emissivity of HfC was assumed to be 0.6 [11]. Figure 3 represents the specific heat of the solid and liquid phases of hafnium carbide.

Even before the start of melting, there is an accelerated increase in heat capacity (above 3500 K), which, in our opinion, is associated with the formation of Frenkel defects. Moreover, in the entire range from 2500 to 3500 K, the specific heat is slightly higher than that obtained under stationary heating conditions. This may be due to the presence of various types of initial defects in the carbide volume (including impurities), which remain in the volume during rapid heating. In contrast to stationary heating, in which these defects and impurities can migrate and leave the sample, in a fast process they remain in the sample until melting. Immediately after melting, the Frenkel defects
annihilate, and the original defects disappear, in particular, due to increased diffusion. At $T$ more than 4800 K, we observe a drop in the specific heat to the equilibrium value for the liquid phase, which is lower than the specific heat of the solid phase in the temperature range from 2500 to 3500 K.

**Figure 3.** The dependence of the specific heat of the solid and liquid states of one of the HfC$_{0.85}$ samples on the temperature: 1-solid phase; 2-melting region; 3-liquid phase. Dotted lines show the boundaries of the temperature intervals in which the specific heat was calculated.

4. **Mixed carbide Ta$_{0.8}$Hf$_{0.2}$C [6]**

The boiling point of TaC at normal pressure is ~ 5770 K [10]. The study was performed with the film samples of 1 µm thick deposited on glass substrates. The result of the experiment for a sample sandwiched between two substrates is shown in Figure 4. The radiation curve (3) clearly shows the moment of the beginning of melting (vertical arrow) and its end (horizontal arrow).
Figure 4a) [6]. Waveforms of one of the experiments with pulsed heating of a micron film Ta_{0.8}Hf_{0.2}C: 1 – current flowing through the sample; 2 – voltage along the sample; 3 – radiation at a wavelength of 856 nm (high sensitivity); 4 – radiation (low sensitivity). The entire sweep is 10 microseconds.

b) [6]. Specific heat of carbide Ta_{0.8}Hf_{0.2}C versus temperature: 1 – solid phase; 2 – melting; 3 – liquid phase. The melting point of the carbide is 4300 K. An arrow marks the beginning of accelerated growth of the heat capacity at 3800 K. The dotted lines show the boundaries of the temperature intervals in which the heat capacity was calculated.

The reduction of radiation at the moment of melting (vertical arrow in Figure 4a) is due to the fact that the molten surface of the film becomes "mirror-like" (grain boundaries and pores disappear) than it was before, the emissivity of the surface decreases and the melting plateau has appeared.

The dependence of the heat capacity on temperature is shown in Figure 4b. The behavior of the specific heat observed the same pattern, as in the case of the other two of the considered carbides: from 3900 K and prior to melting at 4300 K, there is a rapid increase in specific heat, and then after melting a rapid drop in the temperature range from 4300 K up to 4600 K. Above 4700 K, the specific heat of liquid carbide is almost constant and is higher than the specific heat of the solid phase.

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