Experimental investigation of thermophysical properties of eutectic Mo–C, graphite and tantalum at high temperatures

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Abstract. An experimental technique based on fast electrical heating for investigation of thermophysical properties of refractory materials under high pressures and at high temperatures is considered. A set of thermophysical properties of refractory materials such as specific enthalpy, specific heat capacity, specific resistivity, melting heat of eutectic Mo–C and thermal expansion of graphite and tantalum were determined. The obtained temperature of eutectic melting of MoC₀.₈₂ shows close agreement with equilibrium Mo–C phase diagram.

1. Introduction
Using the experimental setup for investigation of the thermophysical properties of materials under high pressure and temperature a few experiments with the refractory materials were carried out. This article represents the experimental data on the specific enthalpy, heat capacity, electrical resistance of Mo–C eutectic composition and thermal expansion of graphite at high temperatures. Thermophysical properties of eutectic molybdenum carbide are of significant interest especially in respect of the development of high-temperature fixed points [1].

The experimental method allows studying a number of thermophysical properties of refractory materials, phase diagrams of metal–carbon systems and verifying multiphase equations of state of these materials in a wide range of temperatures [2].

2. Experimental technique and experimental setup
The experimental setup with its main elements (high pressure system, high-voltage pulsed current source, multi-channel high-speed pyrometer, data acquisition and control system) was described in detail previously [3].

The method involved consists in the fast (from 100 to 1500 µs) electrical heating of the conductive sample up to the melting temperature due to a uniform volumetric heat generation. The heating of the sample is carried out in a pressure chamber under high static pressure of inert gas.

By measuring the surface temperature of the sample \( T(t) \), current \( I(t) \) and voltage \( U(t) \), one can determine the dependence of the enthalpy \( H(T) \), specific heat \( C_P(T) \) and resistivity...
Figure 1. Typical experimental data for MoC$_{0.82}$ sample: brightness temperature, current and voltage.

$\rho(T)$ in the solid and liquid phases. Considering the moments of beginning and end of melting one can determine the enthalpy of melting $\Delta H_m$ or other structural transitions. Performing additional measurements of the sample cross-sectional size change $\Delta L(T)/L$ one can determine the expansion coefficient of the sample material.

For temperature measurements a high-speed 2-channels optical pyrometer with automatic switch-off system was developed. This system makes possible to stop the heating when the necessary temperature is reached, so far one can obtain a considerable amount of temperature measurements at the required point, e.g. at the melting temperature. Thus the accuracy of temperature measurement can be significantly improved.

3. Experiments and sample preparation

For the experiments on volumetric electrical heating specimens that may be uniformly heated or temperature field of which is straightened by conduction were used.

Samples of Mo–C eutectic composition were prepared by melting molybdenum powder with subsequent dissolution of carbon powder in molten molybdenum inside the graphite capsule in a high-temperature furnace at 3000 K. High-purity fine graphite with purity of 0.9995 and metal powder with purity 0.9998 for Mo were used. The process was carried out in an argon atmosphere without oxygen. Density of the samples was 8.39 g/cm$^3$. The specimen consisted mainly of hexagonal carbide $\alpha$-Mo$_2$C and free carbon (3.5%).

Figure 1 shows a typical thermogram of MoC$_{0.82}$ specimen heating, as well as voltage and current dependences. Current and voltage are almost parallel indicating a nearly constant resistance of material. The heating pulse in this experiment ends at 380 $\mu$s, virtually at the melting point. From about 300 $\mu$s and practically until the end of the heating the curve clearly
shows the melting plateau. There were no kinks typical for the metals on the voltage slope at the beginning and at the end of melting. The reason probably consists in the special electronic structure of this material, in the lattice of which characteristic equilibrium between the acceptor capacity of the molybdenum atoms and donor capacity of the carbon atoms is established [4].

As far as temperature curve is concerned, it has a prominent plateau. It should be noted that the melting plateau at the thermogram of carbides current pulse heating has not been registered previously, which probably can be explained by the inhomogeneity of the samples used [5].

For the measurement of the actual temperature the assumption of a linear dependence of the spectral emissivity of MoC₀.₈₂ from the wavelength was used, which is typical for many metals and carbides [6]. Due to the small (about 5 K) noise of the pyrometer and using the averaging of a great number of measurements (about 800 points of the plateau) one can determine the emissivity from the system of equations for the brightness temperatures [7].

A peculiarity of emissivity behavior should be noted: it varies slightly at temperatures above 2300 K in the solid phase, which is typical for liquid metal, where conductivity is weakly dependent on temperature. The behavior of electrical resistivity correlate with the emissivity of MoC₀.₈₂ at temperatures above 2300 K, where both of them change slightly. On the figure 2 one can see a dependence of the resistivity of MoC₀.₈₂ on the sample temperature.

Figure 2 shows the temperature dependence of the effective specific electrical resistivity of MoC₀.₈₂. Dependence of the electrical resistivity ρel of MoC₀.₈₂ in the temperature range 300–2000 K can be approximated by the following formula, the accuracy is equal to 3% (where ρel is in μΩ cm, T is in K):

$$\rho_{el} = 8.59137 + 24.508T - 2.12252 \times 10^{-4}T^2 + 1.0157 \times 10^{-7}T^3 - 1.91606 \times 10^{-11}T^4.$$  \hspace{0.5cm} (1)

In the temperature range from 2000 K to Tm, electrical resistivity of MoC₀.₈₂ changes slightly and roughly equals to 157 μΩ cm. An approximation of the dependence of specific enthalpy on temperature in the temperature range 300–1600 K was used to calculate the temperature dependence of electrical resistivity at these temperatures.

Measurements of MoC₀.₈₂ specific enthalpy and specific heat capacity at the temperature range 1600–2800 K were performed. Temperature dependences of these calorimetric properties are depicted at figures 3 and 4, approximation equations are shown below:

$$\Delta H_{298} = -105.03175 + 0.38668T + 3.47902 \times 10^{-5}T^2 + 8.47686 \times 10^6 \exp(-34251.2/T),$$  \hspace{0.5cm} (2)

$$C_P = 386.68 + 6.695804 \times 10^{-2}T + 2.90058 \times 10^{-11}T^{-2} \exp(-34251.2/T),$$  \hspace{0.5cm} (3)

where $\Delta H_{298}$ is in J/g, $C_P$ is in J/(kg K)

For calculation of the heat capacity, the following equation was taken [8]:

$$C_P = a + bT + \Delta C_P,$$  \hspace{0.5cm} (4)

where the first two terms represent the linear dependence of the heat capacity for the temperature range up to 0.6Tm obtained from experimental measurements and extrapolated up to $T_m$. The averaged heat capacity increment due to the vacancy contribution equals $\Delta C_P = \Delta H/(T - 298 \text{ K})$ and follows the exponential law.

Experimental value of the heat of fusion of MoC₀.₈₂ equals to 298 ± 18 kJ/kg (figure 5).

Estimated uncertainties of the experimental data are: for the specific enthalpy $\delta H_{\text{spec}} = 2.5\%$, for specific heat $\delta C_P = 6\%$, for specific resistivity $\delta \rho_{el} = 3\%$, for relative thermal linear expansion $\delta L/L_0 = 10\%$, for the heat of fusion $\delta H_m = 6\%$.

Measurements of expansion of the sample were carried out directly via shadowgraphy images and by snapshots of thermal radiation images. The analysis of the shadowgraphy images shows that the linear thermal expansion of eutectic Mo–C sample at the melting point is less then 8%.
Figure 2. Dependence of the resistivity (without expansion) of MoC$_{0.82}$ upon temperature.

Figure 3. Experimental temperature dependence of specific enthalpy of MoC$_{0.82}$ in comparison with data from [9].
Figure 4. Experimental temperature dependence of specific isobaric heat capacity of MoC$_{0.82}$.

Figure 5. Experimental dependence of temperature versus specific Joule energy for MoC$_{0.82}$ specimen.
Table 1. Experimental data on relative linear thermal expansion of tantalum.

| T, K | ΔL/L, %  | Method                |
|------|----------|-----------------------|
| 1770 | 1.4      | shadowgraphy          |
| 2105 | 1.68     | shadowgraphy          |
| 2425 | 1.96     | shadowgraphy          |
| 2760 | 2.8      | thermal radiation images |
| 3120 | 3.9      | thermal radiation images |
| 3300 | 5        | thermal radiation images |

Table 2. Experimental values for isobar linear thermal expansion of graphite quasi-single-crystal UPV-1T.

| T, K | ΔL/L, % |
|------|---------|
| 2690 | 13.1    |
| 3391 | 22.3    |
| 3417 | 19.0    |
| 3922 | 25.8    |
| 4354 | 38.5    |

Experiments showed that for high pressures of inert gas refraction of shadowgraphy laser beam in the region of heated gas in the vicinity of the specimen might lead to errors in measurements of linear expansion comparable to the measured value. For this reason in case of a high pressure (1 kbar) for a correct expansion measurement one should use snapshots of thermal radiation images of the heated sample.

This experimental method was tested on tantalum specimens, because its thermal expansion is well-known up to the high temperatures. Experimental measurements of linear thermal expansion of tantalum show close agreement with the literature data (figure 6, table 1).

Experimental measurements of isobar thermal expansion of graphite quasi-single-crystal UPV-1T at the temperature range 2700–4300 K were performed. Static pressure of the inert gas during the experiment was equal to 1 kbar. Dependence of the relative linear thermal expansion of this material in the perpendicular to the basal plane direction from table 2 are shown at figure 7.

4. Discussion

For the temperature of melting point of eutectic Mo–C the values obtained coincide with the stationary measurements (2856 K [1], 2859 K [10]) with the error of ±28 K.

The aim of the experiments with MoC₀₈₂ is investigation of the behavior of solid upon its heating with its crystalline structure changing congruently during melting when reaching the eutectic temperature.

The few published data [4] for stoichiometric molybdenum carbide α-Mo₂C+C show the character of dependence of the resistivity on the temperature similar to that obtained in our experiment and uncharacteristic for other refractory carbides. A dramatic increase of resistance at the initial stage of heating turns into a weak and insignificant growth after reaching a certain temperature.
**Figure 6.** Temperature dependence of the linear expansion of tantalum in comparison with data from [11, 12].

**Figure 7.** Experimental isobar linear thermal expansion of graphite quasi-single-crystal UPV-1T in the perpendicular to the basal plane direction in comparison with data from [13, 14].
The reason of the discrepancy between the measured quasi-single-crystal graphite expansion and literature data [13] is probably the difference of the pressure during the experiment (in our case, the pressure was static and equal to 1 kbar; in [13], it was changing during the experiment up to 10 kbar).

5. Conclusion
The authors have obtained first experimental data on the heat of melting, electrical resistivity, specific enthalpy, heat capacity of MoC$_{0.82}$ at high temperatures. Measurements were carried out at heating rates $10^6–10^7$ K s$^{-1}$. For the first time in such experiments with eutectic Mo–C, thermograms demonstrated a horizontal melting plateau and the heating of the liquid phase.

Performed experiments with MoC$_{0.82}$, graphite and tantalum have shown that the setup and the method involved are appropriate for the investigation of the thermophysical properties of refractory materials at high temperatures up to the melting point.

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