Experimental investigation of refractory metals
in the premelting region during fast heating

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Abstract. This work demonstrates experimental possibility of investigation of high refractory materials around its melting point, particularly in premelting region with high accuracy. In this article authors describe the developed experimental setup based on rapid resistive self-heating of a sample by a large current pulse generated by a capacitor discharge circuit that allow fast pulse interruption by temperature feedback signal. The sample temperature was measured with a two-channel microsecond radiation pyrometer. Preliminary experiments were conducted on tantalum and molybdenum at heating speed of $10^8$ K/s. The method allows investigating thermophysical properties of refractory conductive materials such as melting temperature, melting heat, specific resistivity, specific enthalpy and specific heat capacity in solid and liquid phase, especially in premelting area.

1. Introduction
An experimental setup coupled with special technique allows one to study thermophysical properties of refractory conductive materials in the premelting area and in the liquid phase with high precision. The problem involved is of great importance for the investigation of the high-temperature properties of materials, which is especially significant for the creation of a new generation of nuclear reactors and aircraft engines operating at extremely high temperatures.

Nowadays interest in the numerical modeling of the thermodynamic properties of refractory metals by various methods is increasing dramatically. It is worth mentioning such kinds of simulation as first-principles calculation [1, 2], self-consistent thermodynamic model of a solid [3, 4], molecular dynamics method and others. These studies indicate a significant increase in the influence of the lattice anharmonicity and point defects on the thermodynamic and elastic properties of refractory metals in the premelting region $0.6T_m < T < T_m$, which is “difficult” for calculations and where there is an acute shortage of experimental data. For this reason, one has to use the experimental data of the seventies andeighties to verify the calculations; however, these data show considerable variation. Recent surveys [5,6] highlight the paucity of experimental studies of the kinetics of formation of equilibrium vacancies, considerable variation of available experimental data and the difficulties in high temperature experimental investigations.

2. Experimental setup
The experimental method consists in rapid electrical heating of the sample to $T_m$ and above during the time from 25 µs to 250 µs. The heating is carried out under isobaric conditions in
the pressure vessel at a static pressure of the inert gas. One can define energy input or enthalpy $H(t)$ by measuring the pulse current $I(t)$ and the voltage drop $e(t)$ between the potential probes at the central part of the sample:

$$H(t) = \frac{1}{m} \left\{ \int_0^t \left( I(t)e(t) - \varepsilon T S(T(t) - T_0) - q_\Sigma \right) dt + H_0 \right\},$$

where $\varepsilon_T$ is the total emissivity of the sample material, $\sigma$ is the Stefan–Boltzmann constant, $S$ is the sample surface area enclosed between the potential probes, $m$ is the mass of the sample contained between the potential probes, $H_0$ is the initial enthalpy of the sample, $T_0$ is the ambient medium temperature, $q_\Sigma$ is the power of heat loss through the sample mounts and heat transfer in a buffer gas. Thus, by measuring the surface temperature of the sample during the experiment $T(t)$, current $I(t)$ and the voltage $e(t)$, one can define the dependence $H_p(T)$ and $C_p(T)$ by differentiating the expression above.

Figure 1 shows a block diagram of the experimental setup, which consists of a high-pressure system, controlled high-voltage pulse power supply, high-speed pyrometer and data-acquisition system.

It is important that the experimental facility has pulse feedback control, which can turn off the heating current when the temperature reaches a predetermined value according to the pyrometer signal with the delay of about 3 $\mu$s.

For the sample temperature measurements a two-channel high-speed pyrometer was developed. Temperature measurements are carried out in a narrow spectral range of about 25 nm in a wavelength region $\lambda_1 = 650$ nm and $\lambda_2 = 900$ nm. The pyrometer has mirror field stop with diameter 0.4 mm, which provides a small area of view of about 0.3 mm. The temperature
of the photodiodes is kept constant by means of a positive thermostat with an accuracy of 0.1°C. Incoming monochromatic radiation generates a current proportional to the intensity of the radiation, then to convert current to voltage the pyrometer has high-speed logarithmic converters. Pyrometer has been calibrated in the range of 1773–3273 K by high-temperature blackbody model. Relative accuracy of calibration in the temperature range 1773–3273 K does not exceed 0.25%.

3. Experiment

Experiments with the tantalum and molybdenum samples were carried out. The samples were made of Ta foil with a thickness of 0.05 mm and a sheet with a thickness of 0.3 mm of 99.95% high-purity tantalum. The molybdenum samples were made of foil with a thickness of 0.05 mm and a sheet with a thickness of 0.3 mm of high purity 99.97% molybdenum.

The aim of the first phase of the experiments was the test of the instrumentation of the experimental setup and the verification of an accuracy of current, voltage and temperature measurements. To do this, the calibration of measuring channels in conjunction with divisors and differential amplifiers was carried out. Particular attention was paid to pyrometer and temperature measurement technique. When calculating the true temperature of flat samples the published data on the spectral emissivity [7] was used. For tantalum samples, the melting temperature variation is not more than 50 K.

The second phase of the experiments was to study the behavior of the specific heat of metals in the premelting area. A number of experiments with fast electrical heating of Ta and Mo specimens at speeds up to $10^8$ K/s was carried out.

Figure 2 shows a typical heating thermogram of Ta sample, voltage drop and current through the sample measured in experiment with temperature controlled current breaking. Kink in the voltage dependence agrees well with the geometric intersection of the lines in the thermogram in the end of melting, which gives additional grounds for the use of appropriate mathematical processing of the data. It is of great important when choosing a temperature range for the calculation of the heat capacity in the premelting area. Thus, the calculation of the heat

![Figure 2](image-url)
capacity of the solid phase was carried out up to the temperature of 3200 K. Figure 3 shows the dependence of the specific heat of Ta, measured at our experiments in comparison with data from other sources. The error in the heat capacity determining does not exceed 5% in the temperature range 2400–3200 K. The figure confirms that our experimental data show good agreement with the data from [3] up to the temperature of 3150 K. The data from [3] were obtained by calculation and take into account the influence of the nonlinear contribution of the anharmonicity of the lattice, the electronic component of the heat capacity and the contribution of equilibrium vacancies. At higher temperatures in the range of \( T_m - 100 \) K, our data show an increase in specific heat. Abnormal growth of the specific heat was observed [8] during fast heating at a rate of about \( 10^8 - 10^9 \) K/s on samples which were cylindrical blackbody models made of thin foil with \( \delta = 0.013 \) mm. The very rapid growth of tantalum heat capacity in premelting area at heating rates of \( 10^9 \) K/s authors [8, 10] explained of a formation of non-equilibrium defects of Frenkel’s pairs type. However, a substantiation of such guess requires additional experimental researches.

Thus, our experiments showed in contrast to stationary and subsecond heating more rapid growth of the heat capacity in the premelting region, which makes the investigations of the kinetics of formation of non-equilibrium vacancies possible.

At the first stage, experiments with the flat samples were performed. The calculation of the true temperature was based on the published data of the spectral emissivity [7], which have been extrapolated up to the melting point. This approach does not take into account sudden changes in emissivity in the premelting area, that observed for Ta and other refractory metals [11, 12], and leads to significant errors in the heat capacity measurement.

In order to reduce the methodological error in determining of the true temperature, the specimens were made of foil with the emitting cavity. Radiation of the cavity in this case was

Figure 3. Temperature dependence of the specific heat of tantalum: 1 — present work, 2 — [3], 3 — [8], 4 — [9].
close to the gray-body radiation. In figure 2, the true temperature of the tantalum sample measured by two-channel pyrometer during the experiment with temperature controlled current breaking is shown.

4. Conclusion
Finally, one should notice that the origination of the true temperature from the measured brightness temperature involving steady-state data on the spectral emissivity produces higher systematic error and can lead to significant errors in determining of the specific heat in the premelting area. It should be emphasized that the contribution to the heat capacity of the lattice anharmonicity, the electronic component of the heat capacity of equilibrium vacancies represents a deep scientific interest.

Using the new microsecond polychromatic pyrometer on the existing experimental setup for fast electrical heating of refractory materials will improve the accuracy of the true temperature measurement in the premelting area and liquid phase.

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