Experimental investigation of thermophysical properties of eutectic Re–C at high temperatures

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Abstract. Using the previously described experimental setup for investigation of thermophysical properties of refractory materials under high pressures and temperatures a few experiments with samples of cast eutectic Re–C were carried out. The experimental technique was extended for millisecond electrical heating of the samples under the high static pressure of inert gas. First experimental data on the specific enthalpy, specific heat capacity and linear thermal expansion of ReC₀.₃ were obtained.

1. Introduction

Equations of state for refractory materials and mixtures of chemical elements are of considerable interest today. Numerous studies are devoted to the high-temperature equations of state of refractory metals [1] and the incongruent phase transitions in binary mixtures [2]. So using the method of electric heating to study the properties of nonstoichiometric mixtures of refractory metals and carbon appears promising. The purpose of this work was to demonstrate the possibility of using the millisecond electric heating method to study the thermophysical properties of eutectic mixtures, including those not forming carbides, and to obtain data on high-temperature thermophysical properties of Re–C eutectic composition.

This article presents new experimental results on the thermal properties of rhenium metal-carbon systems in the region of eutectic melting at high pressures and temperatures. The experimental technique is based on rapid volumetric heating of a conductive sample up to the melting temperature and above due to Joule heating [3]. The current pulse with magnitude of 2–10 kA and duration of 1–5 ms was used for sample heating. The samples are heated under isobaric conditions at a high static pressure of the inert gas of about 30–120 MPa.

It should be noted that usually metal carbides and metal-carbon binary systems have free carbon and microinhomogeneities in their structure due primarily to the production technology and composition stoichiometry. For this reason, in order to achieve uniform volumetric heating, it is necessary to increase the duration of heating in order to ensure the equalization of the temperature field due to thermal conductivity. Additionally free carbon because of its intensive sublimation at high temperatures can give rise to electric discharge on a sample surface at low gas pressures. Therefore, it becomes necessary to investigate such substances at high pressure of inert gas that surrounding a sample. Another important requirement is also increase of the
samples dimensions in order to reduce the influence of inhomogeneities on measured properties. Preliminary experiments showed that the heating time of well-prepared cast samples should be more than 1 ms for the Re–C eutectic compositions. The typical cross-sectional dimension for cast samples was 2–4 mm², which is much larger than the crystallite size (20–30 μm) and also other structural inhomogeneities.

Nowadays, data on the thermophysical properties of carbides at high temperatures, available in the handbooks [4–6], are usually obtained up to temperatures not exceeding 2500–3000 K and at higher temperatures are extrapolated. It should also be noted that data on the thermophysical properties of nonstoichiometric binary metal-carbon systems in the high-temperature region are practically absent, and the behavior of such substances in the temperature range close to or exceeding the melting point has not been studied at present.

2. Experimental technique and material under study
For experimental investigation of Re–C eutectic compositions the method of fast (1–5 ms) volumetrically homogeneous heating of conductors by current pulse at high pressures [3] was used. The experimental setup that implements this principle provides the following measurement errors: for specific enthalpy δ(ΔH) = ±2.5%, for specific heat capacity δ(Cₚ) = ±6%, for relative linear expansion δ(ΔL/L₀) = ±5%.

The ingots for ReC₀.₃ samples were made from 99.995% high purity graphite powders and 99.98% purity Re by melting in a graphite crucible in a high-temperature furnace in argon at a temperature of about 3000 K. Samples had the form of a rectangular parallelepiped with typical dimensions of about 1.5 × 2.0 × 17 mm³. X-ray diffraction analysis of the selected samples was carried out. The samples were analyzed on XPERT PRO x-ray diffractometer (PANalytical, The Netherlands) on CuKα radiation (λ = 1.5418 Å, Ni filter) in reflection geometry with Bragg–Brentano focusing. It was found that the sample consists of two main phases: metallic rhenium (Re, hexagonal system, P6₃/mmc) and graphite. The peaks of rhenium are noticeably broadened, which indicates a strong defectiveness. The x-ray diffraction pattern is shown in figure 1. The figure clearly shows the absence of interaction between these substances.

3. Experimental data
For investigation of the thermophysical properties of the ReC₀.₃ system nine experiments were carried out. These experiments demonstrate extended eutectic melting plateau at temperature of 2750 ± 30 K that is in good agreement with the congruent melting temperature of eutectic composition ReC₀.₃ (Tₑₘ = 2753 K) measured in steady state experiments [7].

The data for the dependences of the specific enthalpy and heat capacity of ReC₀.₃ in the high-temperature region are not presented in the reference literature today. For this reason, for comparison of the obtained data on enthalpy and heat capacity with reference data we used the Kopp–Neumann law (or the additivity principle) to calculate the enthalpy and heat capacity of the system under study.

It should be noted that the eutectic melting temperature of ReC₀.₃ is more than 700 K below the melting temperature of pure rhenium, which is equal to 3458 K [8]. In figure 2 the experimental data on the change of specific enthalpy in the temperature range from 2000 K to Tₑₘ and data calculated according to the Kopp–Neumann law are depicted. Data on the enthalpy of graphite from [9] and on the enthalpy of rhenium from [10] were taken for this calculation.

The figure shows that for a solid solution of rhenium with graphite, which do not form carbide, the Kopp–Neumann law is fulfilled in the temperature region below 2300 K. In the temperature range close to the temperature of eutectic melting, this law is inapplicable due to the interaction of rhenium with graphite. Obviously that at the eutectic temperature a eutectic reaction with the formation of a liquid phase occurs and the law is not valid. It should be noted that data [9, 10] show a calculated dependence of the specific enthalpy for the ReC₀.₃ system
Figure 1. X-ray diffraction pattern of Re–C eutectic composition. The digit 1 indicates peaks of Re, Gr are peaks of graphite.

to be close to linear in the temperature range up to 2800 K (but not exactly linear), since the temperature dependences of the heat capacity for graphite [9] and rhenium [11] for the same temperature range also show dependence close to linear. Probably, the reason for such behavior of the enthalpy according to these authors is the processing of experimental data on the enthalpy in a wider temperature region in order to obtain the corresponding calculated values for the heat capacity.

4. Analysis of experimental data
For the analysis of the experimental data on the specific enthalpy and heat capacity of ReC$_{0.3}$, a technique that takes into account the vacancy contribution in the form of an exponential term, described, for example, in [12] was used. Commonly such technique for describing the behavior of heat capacity is used for crystalline mono-substances that do not change their crystal structure during heating (for example, for pure metals). Besides, the required defect formation energy from the subexponential term reflects the sum of all types of point defects: monovacancies, divacancies, Frenkel defects, etc. Certainly the concentration of each type of defects depends on the temperature, thus their contribution to the enthalpy will also accordingly depend on the temperature. However, the practice of using a single value for the defect formation energy and a constant entropy factor for describing the enthalpy and heat capacity provides a good accuracy of the description of the experimental data and is sufficiently substantiated for crystalline mono-substances.

Therefore, for a solid solution of rhenium with graphite, which do not form carbide, as well as in the case of crystalline mono-substances it is possible to describe the accelerated growth of enthalpy and heat capacity in the form of an exponential term with some effective vacancy
Figure 2. Temperature dependence of the specific enthalpy of ReC$_{0.3}$.

Formation energies. Fast growth of enthalpy in premelting region can be expressed in terms of the average heat capacity $\Delta C_p$:

$$\Delta H_{vac} = \Delta C_p (T - T_{298}) = AE \exp\left( -\frac{E}{RT} \right),$$

where $T_{298} = 298$ K, $A$ is the entropy factor, $E$ is the effective vacancy formation energy, $R = 8.314$ J/(mol K) is the gas constant. To describe the average isobaric heat capacity, the following equation was used:

$$\bar{C}_p = a + bT + \Delta C_p = \Delta H_{298} / (T - T_{298}),$$

where $\Delta H_{298} = H(T) - H(T_{298})$. The first two terms $(a + bT)$ represent a linear dependence of the heat capacity in the temperature region below 2350 K obtained from experimental data on the specific enthalpy. The coefficients in the exponential term were chosen throughout the temperature range 2000–2740 K. While determining the coefficients the fitting range maximum temperature was taken less than the measured melting point by twice the amplitude of the pyrometer noise ($\sim 10$ K) in order to exclude from the calculation the points belonging to the two-phase region. Thus, the averaged coefficients $E = (304156 \pm 10400)$ J/mol = 3.14 eV, $AE = (8.4396 \pm 3.4994) \times 10^6$ J/mol were found from the experimental data, whereas the vacancy concentration at the melting temperature will be $c \sim 7.0\%$. It should be noted that the effective vacancy formation energy 3.14 eV is found to be close to the vacancy formation energy in graphite 3.0 eV from [13].

Experimental data on the change in specific enthalpy in the temperature range 2000–2740 K presented in figure 2 can be approximated by the following equation:

$$\Delta H_{298} = A_0 + A_1 T + A_2 T^2 + A_3 \exp\left( \frac{A_4}{T} \right),$$

(3)
Figure 3. Temperature dependence of specific heat capacity of ReC$_{0.3}$ in comparison with the specific heat capacity calculated by the Kopp–Neumann law.

\[ C_p = B_0 + B_1T + \frac{B_2}{T^2} \exp\left( \frac{B_3}{T} \right). \]  

As can be seen from the figure 3 the Kopp–Neumann law gives good agreement for a nonreacting solid rhenium–graphite solution up to the temperature of 2000–2200 K, but at higher temperatures a nonlinear growth of the specific heat occurs, which can only be explained by the interaction of these substances. It is known that rhenium carbides are not formed under normal conditions, therefore, the exponential growth can be explained by the mutual interaction between rhenium and graphite lattices with the formation of a greater number of defects in the eutectic melting region.

During the experiments a measurement of the linear expansion of the ReC$_{0.3}$ system was performed. To measure the linear dimensions of the samples under study by photoregistration of the luminescence of the heated samples a special technique was used. At the heating rate of about $\sim 10^6$ K/s a linear thermal expansion of the Re–C eutectic composition was measured in the melting region. The study of linear expansion was carried out in the high-temperature range from 2000 K to the temperature of eutectic melting, and also in the two-phase region. Figure 4 shows a photograph of the intrinsic luminescence of the heated sample made at the moment...
of a current pulse with a duration of 3.0 ms ending at $T_m = 2753$ K. One can clearly see the homogeneity of the glow of the sample, which indicates the uniformity of its temperature field.

The average coefficient of linear thermal expansion measured in the experiments with the ReC$_{0.3}$ eutectic composition at the melting point (2753 K) was $\bar{\alpha} = 2 \times 10^{-5}$ K$^{-1}$.

5. Conclusion
For the first time, data on the specific enthalpy, heat capacity and thermal expansion of Re–C eutectic composition at high temperatures and in the melting range were obtained experimentally.

A technique for thermal expansion measurement by photoregistration of the luminescence of the heated specimens has been developed. An important advantage of the technique is the possibility of direct measurement of the linear thermal expansion of the sample under study. It allows operating at a high static pressure of the surrounding gas.

References
[1] Khishchenko K V 2016 J. Phys.: Conf. Ser. 774 012001
[2] Stroev N E and Josilevskiy I L 2016 J. Phys.: Conf. Ser. 774 012040
[3] Senchenko V N, Belikov R S and Popov V S 2015 J. Phys.: Conf. Ser. 653 012100
[4] Pierson H O 1996 Handbook of Refractory Carbides and Nitrides: Properties, Characteristics, Processing, and Applications (Westwood, NJ: Noyes Publications)
[5] Turchanin A G and Turchanin M A 1991 Termodynamika Tugoplavkikh Karbidov i Karbonitridov (Moscow: Metallurgiya)
[6] Tot L 1974 Karbidy i Nitridy Perekhodnyh Metallov (Moscow: Mir)
[7] Khar’kova A M and Velikanova T Ya 1987 Powder Metall. Met. Ceram. 26 994–7
[8] Sims C T, Craighead C M and Jaffee R I 1955 JOM 7 168–79
[9] Glushko V P and Gurvich L V (eds) 1979 Termodinamicheskiye Svoystva Individual’nykh Veshchestv vol 2 (Moscow: Nauka)
[10] Thevenin Th, Arles L, Boivineau M and Vermeulen J M 1992 Int. J. Thermophys. 14 441–8
[11] Zinov’yev V E 1989 Teplofizicheskiye Svoystva Metallov pri Vysokikh Temperaturakh (Moscow: Metallurgiya)
[12] Kraftmakher Ya 2004 Modulation Calorimetry. Theory and Application (Heidelberg: Springer Verlag)
[13] Buchnev L M, Smyslov A I, Dmitriyev A F, Kuteynikov A F and Kostikov V I 1984 Dokl. Phys. 278 1109–11