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Thermophysical Measurements on Solid and Liquid Rhenium[1]

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A fast resistive heating technique was used to measure such thermophysical data of solid and liquid rhenium as enthalpy, specific heat, thermal volume expansion, and electrical resistivity. The measurements are performed with heating rates of slightly more than 10^9 K · s^{-1} up to states of superheated liquid rhenium (7500 K).

KEY WORDS: electrical resistivity; enthalpy; high temperatures; pulse method; rhenium; specific heat; thermal expansion.

1. INTRODUCTION

The abundance of rhenium and its importance for technical applications are small compared to those of other metals. This might be the main reason why the thermophysical data reported on this element are relatively sparse. Nevertheless, the thermophysical behavior of rhenium is of interest: its melting temperature (3453 K) is the second highest, immediately following that of tungsten.

The investigation of rhenium at high temperatures, especially of its liquid phase, can hardly be performed by conventional steady-state heating techniques. The interactions of the specimen with the surroundings and the heat losses can be suppressed only by a fast pulse heating method.

Several authors have demonstrated the applicability of a submicrosecond resistive pulse heating method using wire-shaped samples which are part of a fast RCL–discharge circuit [1–3]. A detailed description of our experimental setup is given in the preceding paper of this volume [4].

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Heating rates of about 10^9 K · s^{-1} allow to complete the measurements before MHD instabilities occur and provide the advantage that the good cylindrical geometry of the water-embedded metal samples lasts far into the liquid state. Therefore, it is also possible to investigate superheated liquid rhenium above the normal boiling temperature, 5870 K.

Measurements were performed up to 7500 K, results are given for the heat of fusion, the specific heat, and the mutual dependencies among electrical resistivity, enthalpy, thermal volume expansion, and temperature.

2. EXPERIMENTAL

The wire samples of rhenium (purity of at least 99.9%; Goodfellow, Cambridge, England), 0.25 mm in diameter and 39 mm long, are coaxially mounted between brass jaws in a discharge vessel filled with water at atmospheric pressure. This arrangement prevents peripheral gas discharges, so that the entire amount of electrical energy will be imparted into the wire sample.

The heating current is obtained from an energy storage capacitor bank of 5.4 μF, charged up to either 5 or 6 kV (to vary the heating rate in a small interval), switched by a spark gap. The discharge circuit has an inductance of 180 nH, a resistance of 26 mΩ, and a short circuit ringing period of 6.2 μs.

A coaxial ohmic voltage divider, developed by Fucke [5], a small induction coil placed between the inner and the outer part of the transmission line (with subsequent RC integration), and a fast pyrometer (operating at $\lambda = 801.7$ nm; photodiodes BPX 65, Siemens) serve for the measurement of three basic quantities: The voltage drop $U(t)$ across the wire, the discharge current $I(t)$, and the temperature-dependent radiation intensity of the wire surface $J(t)$. In addition, the volume change of the sample during the heating process is determined by a shadowgraph method which, in principle, is based on the weakening of the intensity of a light beam by the expanding wire (described in [4]). In order to obtain the relevant ohmic voltage drop the inductive part is substracted by calculations based on the dI/dt signal, as suggested by Gathers et al. [6]. The complete measuring system has a rise time of less than 10 ns. The oscilloscopic recording is done with four 200-MHz oscilloscopes (Tektronix Type 475).

3. DATA REDUCTION

Figure 1 shows, in a flow chart, how the various thermophysical properties can be derived from the original basic quantities, which were obtained from time-resolved measurements.

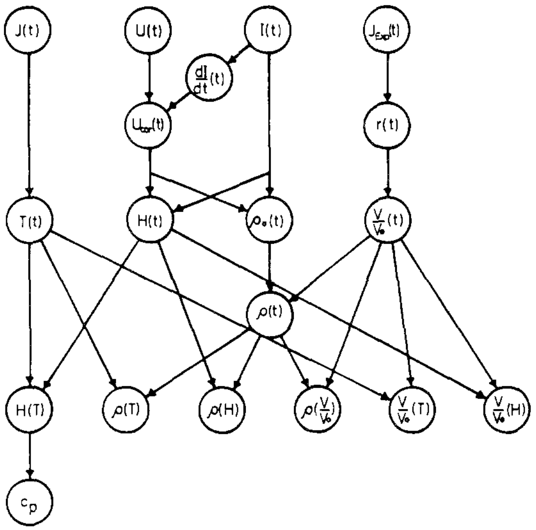

Fig. 1. Survey of measured and derived quantities. J, radiation intensity; U, voltage; I, current; J_{Exp}, radiation intensity of the specimen expansion measurement; r, specimen radius; T, temperature; H, enthalpy, ρ_0, electric resistivity without considering volume expansion; ρ, electric resistivity; V/V_0, volume expansion; c_p, specific heat.

Starting with current $I(t)$ and considering the inductive part of $U(t)$ (obtained using the quantity dI/dt), one obtains the corrected value $U_{\text{cor}}(t)$ for the ohmic voltage drop. These two values, $U_{\text{cor}}(t)$ and $I(t)$, allow the evaluation of the enthalpy $H(t)$ and of the electrical resistivity $\rho_0(t)$, the subscript zero indicating that a thermal expansion of the specimen during the heating process has not yet been taken into account (values which are sometimes useful for comparison to results of other authors).

The last row on the right-hand side of Fig. 1 shows how the volume change $V/V_0(t)$ of the specimen follows from the shadowgraph technique and makes it possible to obtain the corrected value for the electrical resistivity $\rho(t)$.

The first row starts with the surface radiation intensity $J(t)$. The temperature is obtained using the relation

$$T = c \Big/ \lambda \ln \left\{ 1 + \frac{\varepsilon(T)\, J_{\text{m}}}{\varepsilon_{T_{\text{m}}}\, J} [\exp(c/\lambda T_{\text{m}}) - 1] \right\} \tag{1}$$

where λ is the wavelength, ε is the emissivity, c is the second radiation constant, and the subscript m indicates the values at the melting transition.

The evaluation is based on the assumption that ε always has the same value as at melting temperature: $\varepsilon(T) = \text{const} = \varepsilon_{T_m}$, $\varepsilon_{T_m} = 0.39(\lambda = 0.8\ \mu)$ [7], value not relevant in this case.

By elimination of the quantity time, one is able to show the mutual dependencies among enthalpy, temperature, electrical resistivity, and volume expansion, as presented later. From the $H(T)$ diagram the specific heat is derived numerically.

4. RESULTS

4.1. Heat of Fusion and Specific Heat

Figure 2 presents enthalpy as a function of temperature. During the melting transition the enthalpy changes from $H_s = 0.52\ \text{MJ} \cdot \text{kg}^{-1}$ to $H_l = 0.67\ \text{MJ} \cdot \text{kg}^{-1}$, yielding $\Delta H = 0.15\ \text{MJ} \cdot \text{kg}^{-1}$ for the latent heat of fusion. A least-squares fit was made for the liquid range $3453\ \text{K} < T < 7500\ \text{K}$, which can be represented by

$$H = -0.1642 + 0.250 \times 10^{-3}\, T \tag{2}$$

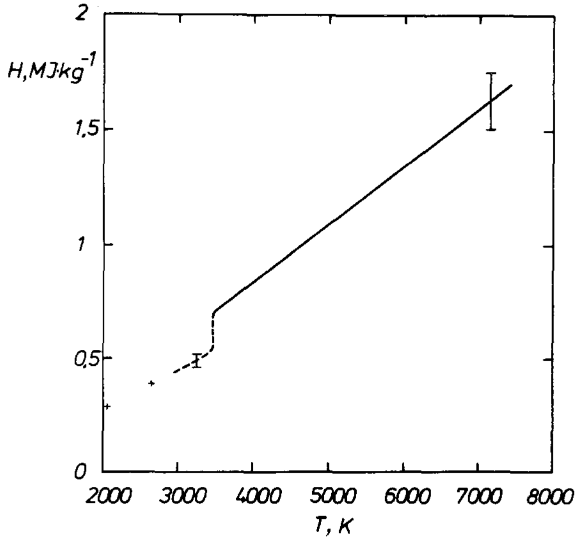

Fig. 2. Enthalpy H versus temperature T. Line, this work (full line corresponding to polynomial fit). (†) Conway and Hein [8].

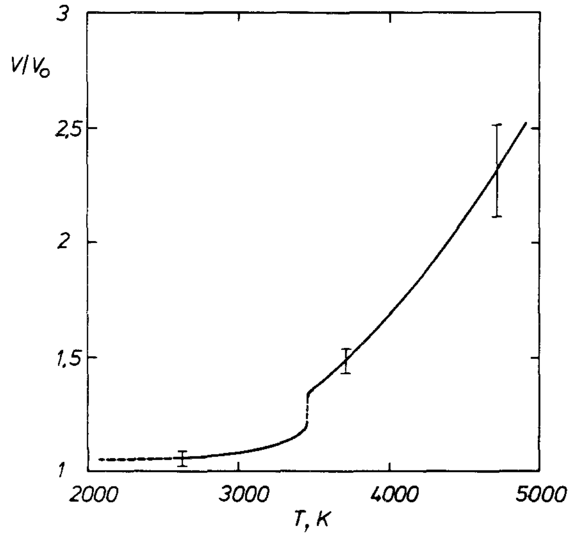

Fig. 3. Thermal volume expansion V/V_0 versus temperature T.

where H is in $\mathrm{MJ \cdot kg^{-1}}$. In all the following diagrams the curves corresponding to the fitted polynomials are drawn as full lines.

The derivative of the above polynomial gives $c_p = 250\ \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$ for the specific heat of liquid rhenium.

The values for $H(T)$ for the solid state of rhenium are taken from the work of Conway and Hein [8], which is cited by Hoch [9].

4.2. Relative Volume Change

The measured thermal volume expansion data can be summarized by two polynomial least-squares fits,

$$V/V_0 = 2.1572 - 0.8375 \times 10^{-3}\,T + 0.1595 \times 10^{-6}\,T^2 \qquad (3)$$

valid for the solid state in the range $2600\ \mathrm{K} < T < 3453\ \mathrm{K}$, and

$$V/V_0 = 2.0949 - 0.9464 \times 10^{-3}\,T + 0.2104 \times 10^{-6}\,T^2 \qquad (4)$$

for the liquid state of rhenium in the range $3453\ \mathrm{K} < T < 5000\ \mathrm{K}$. The results for both ranges are plotted in Fig. 3.

4.3. Electrical Resistivity

With the knowledge of the relative volume change of the specimen it is possible to determine the actual electrical resistivity, using the relation $\rho = \rho_0 V/V_0$.

At the melting transition, the resistivity changes from $\rho_s = 120\ \mu\Omega \cdot \mathrm{cm}$ to $\rho_l = 137\ \mu\Omega \cdot \mathrm{cm}$, giving an increase of $\Delta\rho = 17\ \mu\Omega \cdot \mathrm{cm}$.

For the liquid phase a least-squares fit by a fourth-degree polynomial is necessary to describe the curves satisfactorily,

$$\begin{aligned}\rho = {} & -1.0023 \times 10^3 + 0.7222\ T - 0.1191 \times 10^{-3}\ T^2 \\ & - 0.5957 \times 10^{-8}\ T^3 + 0.2204 \times 10^{-11}\ T^4\end{aligned} \tag{5}$$

in the range $3453\ \mathrm{K} < T < 5100\ \mathrm{K}$, with ρ in $\mu\Omega$ cm. As a numerical fit for ρ_0 the polynomial

$$\rho_0 = 0.1791 \times 10^3 - 0.0435\ T + 0.7690 \times 10^{-5}\ T^2 - 0.4421 \times 10^{-9}\ T^3 \tag{6}$$

is found, valid for $3453\ \mathrm{K} < T < 7000\ \mathrm{K}$.

In Fig. 4 the curves for the uncorrected and the corrected (for thermal

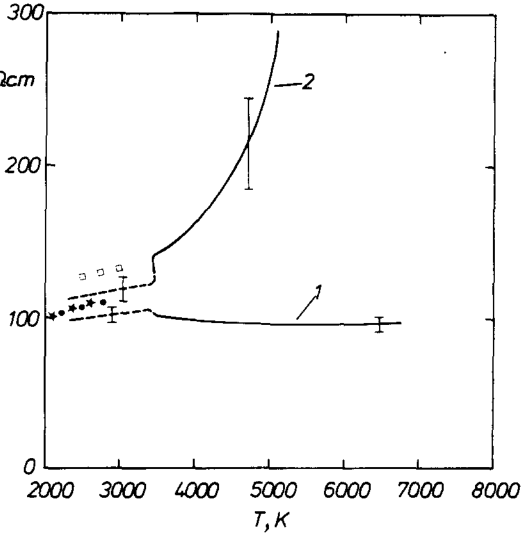

Fig. 4. Electrical resistivity versus temperature (1) without consideration of thermal volume change and (2) including correction for thermal volume change. (★) Gaines and Sims [10]. (□) Agte et al. [11]. (●) Taylor and Finch [12].

expansion) resistivity (ρ_0, ρ) are shown, and for comparison the values of Gaines and Sims [10], Agte et al. [11], and Taylor and Finch [12] are added.

4.4. Relationship Between Properties

For convenience and practical use the remaining figures present other possible graphic plots of the values derived by the least-squares fits: relative volume change versus enthalpy (Fig. 5), electrical resistivity versus relative volume change (Fig. 6), and electrical resistivity versus enthalpy (Fig. 7). The corresponding polynomial fits are

$$V/V_0 = 0.9964 + 0.3135\,H - 1.0332\,H^2 + 1.353\,H^3 + 0.7244\,H^4 \qquad (7)$$

for $0 < H < 1.1$ MJ · kg^{-1},

$$\rho = 29.7373 + 71.907\,V/V_0 + 5.6942(\mathrm{V}/V_0)^2 \qquad (8)$$

for $1.1 < V/V_0 < 3$,

$$\rho_0 = 123.51 - 22.323\,V/V_0 + 4.753\,(V/V_0)^2 \qquad (9)$$

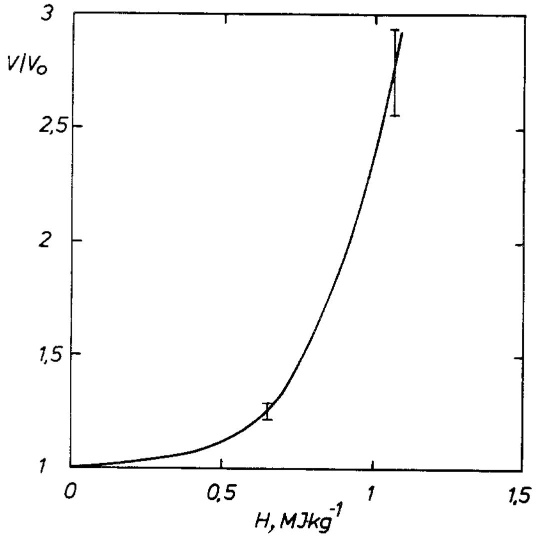

Fig. 5. Thermal volume expansion versus enthalpy.

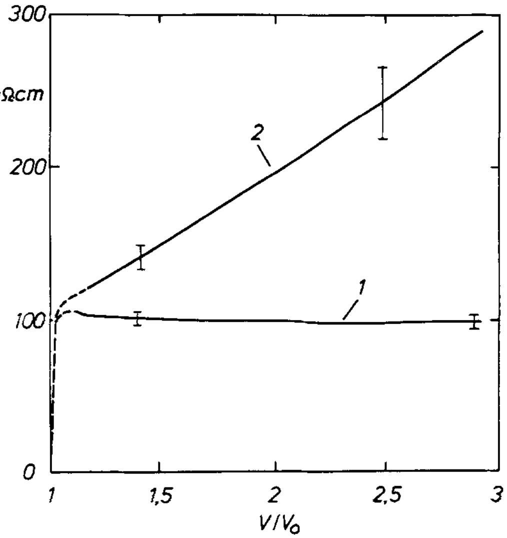

Fig. 6. Electrical resistivity versus thermal volume expansion (1) for uncorrected resistivity data and (2) for corrected data.

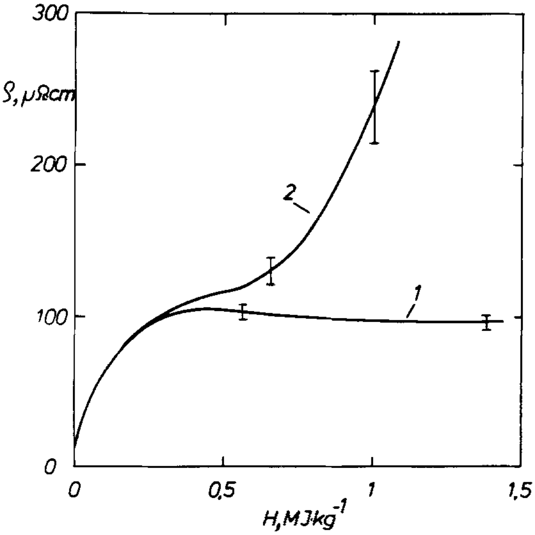

Fig. 7. Electrical resistivity versus enthalpy (1) for uncorrected resistivity data and, (2) for corrected resistivity data.

for $1.1 < V/V_0 < 3$,

$$\rho = 14.859 + 591.305\,H - 1.356 \times 10^3\,H^2 + 1.326 \times 10^3\,H^3 - 0.338 \times 10^3\,H^4 \tag{10}$$

for $0 < H < 1.1\ \mathrm{MJ \cdot kg^{-1}}$,

$$\rho_0 = 15.76 + 0.5581 \times 10^3\,H - 0.113 \times 10^4\,H^2 + 0.7336 \times 10^3\,H^3 \tag{11}$$

for $0 < H < 0.7\ \mathrm{MJ \cdot kg^{-1}}$,

$$\rho_0 = 102.7 - 1.838\,H \tag{12}$$

for $0.7 < H < 1.5\ \mathrm{MJ \cdot kg^{-1}}$.

4.5. Estimate of Errors

As already reported in an earlier publication [13], the uncertainties of current and voltage measurements are estimated to be within 2% each, giving uncertainties of 5% for enthalpy and electrical resistivity, without considering volume corrections.

The uncertainty of the temperature measurements on rhenium is assumed to be less than 10%. For lower-melting metals the measurements of sample expansion with the help of the shadowgraph method are generally more accurate than in the case of rhenium because of the higher temperature of the specimen itself. Therefore an uncertainty of 15% for the ratio V/V_0 is assumed for the worst case, which consequently increases the uncertainty limits for the volume-corrected electrical resistivity up to about 20% for the highest temperatures achieved.

The uncertainty of the specific heat is estimated not to exceed 20%.

5. DISCUSSION

There are few data of other authors available for a comparison with our thermophysical values for rhenium up to the melting point. For the liquid phase only one value is reported.

In the *Rare Metals Handbook* [14], $\Delta H = 0.177\ \mathrm{MJ \cdot kg^{-1}}$ is reported for the latent heat of fusion, our value being $\Delta H = 0.15\ \mathrm{MJ \cdot kg^{-1}}$ (see Fig. 2).

Conway and Hein [8] present $H(T)$ values up to 2641 K, obtained by means of a drop technique. Although our data for solid rhenium start with $T = 2900$ K, an extrapolation down to lower temperatures shows good agreement with the ones mentioned above.

For the liquid metal no reference for $H(T)$ could be found. Sherwood et al. [15] assumed $242\,\mathrm{J\cdot kg^{-1}\cdot K^{-1}}$ for the specific heat of liquid rhenium. This value is only 3.5% lower than ours ($250\,\mathrm{J\cdot kg^{-1}\cdot K^{-1}}$ valid up to 7500 K).[3]

The good agreement between the dynamic and the steady-state data is an indication that our samples are close to thermodynamic equilibrium, at least at the temperatures up to the melting point and immediately above it. Considerations similar to those made by Seydel et al. [1] and Fucke [19] show that inhomogeneities caused by skin effect, heat losses, and instabilities can be neglected during the whole time interval of our measurements.

To prove this as a first step we intend to perform measurements with heating rates down to $10^8\,\mathrm{K\cdot s^{-1}}$. Small changes in the heating rate (1.0–$2.5\times10^9\,\mathrm{K\cdot s^{-1}}$) did not show a significant influence on the measured data.

Conway and Losekamp [18] report thermal linear expansion data for rhenium up to 2500 K. However, using heating rates $>10^9\,\mathrm{K\cdot s^{-1}}$, we could find only a radial expansion of the wire sample (in agreement with Fucke [19]). Thermal volume expansion versus temperature is shown in Fig. 3.

When discussing the dependence of the electrical resistivity on the temperature (Fig. 4), it should be pointed out that the uncorrected values (ρ_0) in the liquid phase decrease slightly with increasing temperature. This is in contrast to all other metals we have investigated so far (Nb, Ta, Ni, Fe, Cu), which show a slight increase in ρ_0 until the wire explodes at the end of the liquid phase. However, this discrepancy is within our uncertainty limits. The resistivity jump upon melting, $\rho_l/\rho_s = 1.14$, is similar to that of other refractory metals.

The values of Gaines and Sims [10] and those of Taylor and Finch [12] (measured up to 2000 K, extrapolated up to 2800 K), are somewhat lower than the values in this work; the values of Agte et al. [11] (extrapolated up to 3000 K) are somewhat higher.

In Figs. 5–7 the trend of the rhenium values is similar to that in corresponding diagrams of other metals we had investigated so far.

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[3] For temperatures up to the melting point the following c_p values were found: Conway and Hein [8] (cited by Hoch [9], [16]) report $c_p = 163\,\mathrm{J\cdot kg^{-1}\cdot K^{-1}}$ for 2600 K; Sherwood et al. [15], $c_p = 213\,\mathrm{J\cdot kg^{-1}\cdot K^{-1}}$ for 2700 K; Taylor and Finch [12], $c_p = 161\,\mathrm{J\cdot kg^{-1}\cdot K^{-1}}$ for 3120 K; Gaines and Sims [10], $c_p = 201\,\mathrm{J\cdot kg^{-1}\cdot K^{-1}}$ for 2600 K; and Fillipov [17], $c_p = 194\,\mathrm{J\cdot kg^{-1}\cdot K^{-1}}$ for 2500 K.

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