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Note

Point-Defect Formation and Temperature Coefficient of Electrical Resistivity of Platinum and Platinum–(10 wt%) Rhodium Alloy in the Range 1100–1900 K

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Measurement of the temperature coefficient of electrical resistivity of platinum and platinum–(10 wt%) rhodium alloy was performed by the modulation method in the temperature range 1100–1900 K. Nonlinear change in the temperature coefficient of resistivity of metals at high temperatures can be explained by the formation of equilibrium point defects. The enthalpy of point-defect formation in platinum ınd platinum–rhodium alloy has been determined to be 1.6 ± 0.3 and 1.8 ± 0.3 eV, respectively. The modulation frequency was 0.2 Hz; the amplitude of the temperature oscillation was about 10 K. The accuracy of the temperature coefficient of resistivity measurements was about 1%.

KEY WORDS: modulation method; platinum; platinum–rhodium alloy; point defects; temperature coefficient of electrical resistivity.

1. INTRODUCTION

Modulation methods are widely known to be used for thermophysical measurements [1, 2]. They are characterized by a high sensitivity and may be applied over a wide temperature range. These methods are especially advantageous at high temperatures for studying vacancy formation in equilibrium. This phenomenon leads to essential changes in the temperature dependence of the specific heat, thermal expansion coefficient, and temperature coefficient of resistivity (TCR). The enthalpy of point-defect

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formation and the equilibrium concentration of defects are estimated from these properties.

This paper deals with results of the high-temperature behavior of the temperature coefficient of resistivity in platinum and platinum–(10 wt%) rhodium alloy obtained by the modulation method.

2. EXPERIMENTAL

The wire samples were heated by AC current modulated at a low frequency (Fig. 1). The sample temperature and its resistance oscillate around some mean value. For the TCR measurements the method suggested in Ref. 3 was used. The thermocouple leads were welded to the central part of the sample, which is about one-third of its total length, and the specimen was connected to the direct (DC) current source. The amplitude of the periodic oscillations of the voltage due to temperature oscillations was $U = I_0(dR/dT)\theta$. The voltage due to the thermoelectric power was $U = \alpha\theta$. Where I_0 is the direct current, dR/dT is the temperature derivative of

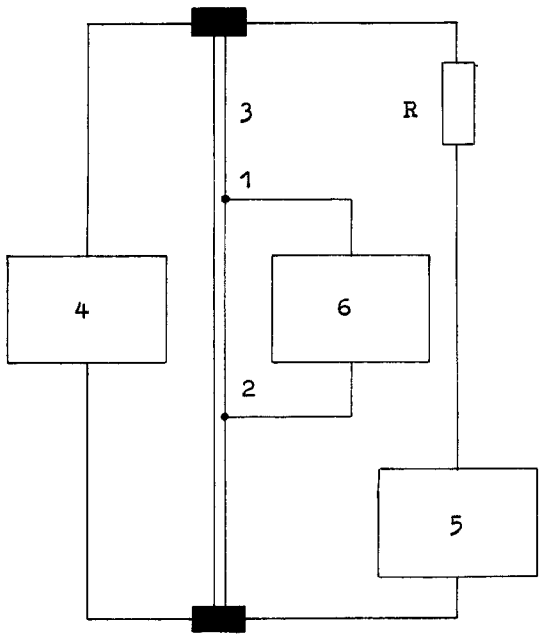

Fig. 1. Block diagram of the apparatus for TCR measurements. (1, 2) Thermoelectric wires; (3) sample; (4) modulated current source; (5) DC current source; (6) zero indicator (compensation indicator).

resistance, θ is the amplitude of temperature oscillations, and α is the sensitivity of the Pt–Pt/Rh thermocouple. The thermal emf is changed simultaneously with the temperature of the sample when the temperature modulation frequency is less than 1 Hz. The thermal emf oscillations were compensated by the AC component of the voltage across the central part of the sample, related to the resistance oscillations. The equality of these voltage amplitudes, $I_0(dR/dT)\theta = \alpha\theta$, was obtained by adjustment of the DC current, and it was determined with a compensation indicator, switched between the thermocouple leads.

The measurement error of the temperature derivative of resistivity was determined by the error of the compensation and was about 1%.

The samples under examination were 0.5 mm in diameter and 100 mm long. The temperature coefficient of resistivity of platinum and platinum–rhodium alloy has been measured in the temperature range 1100–1900 K. The modulation frequency was 0.2 Hz. The amplitude of the temperature oscillations was about 10 K.

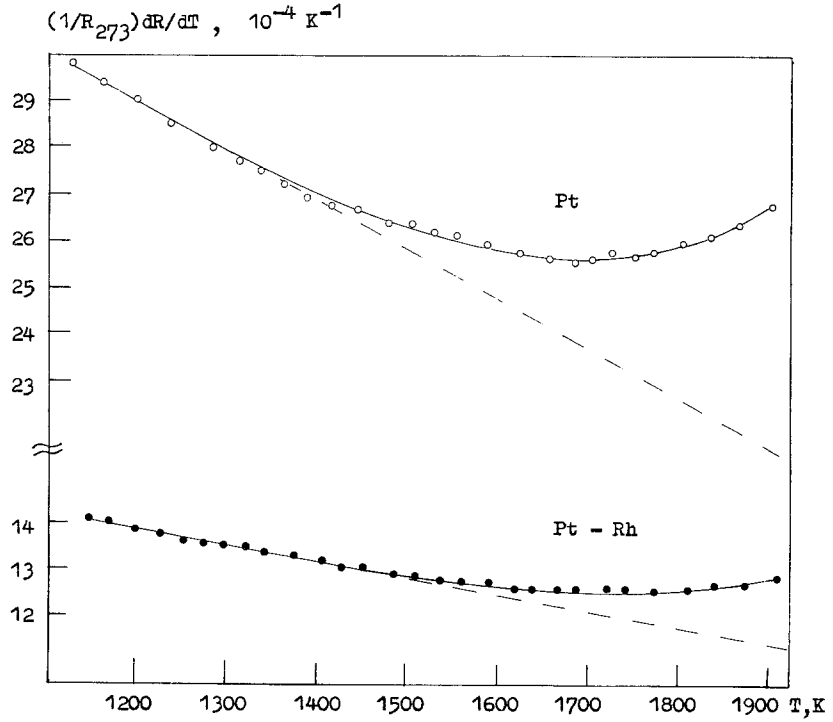

Fig. 2. Temperature coefficient of resistivity of platinum and platinum–(10 wt%) rhodium alloy at high temperatures.

The temperature distribution along the sample was studied with an optical micropyrometer. When the diameter of thermocouple leads was 0.015 mm, the deviation of the temperature from the mean value in the central part did not exceed 2 K.

3. RESULTS AND DISCUSSION

The results of the measurements of the TCR are shown in Fig. 2.

The data for platinum within the experimental error are in agreement with the results obtained earlier [4]. Direct measurement of the temperature coefficient of resistivity of Pt–Rh alloy has not been carried out before.

The nonlinear rise in the TCR of metals at high temperatures can be explained by the formation of equilibrium point defects. The results obtained were approximated by an expression corresponding to the quadratic temperature dependence of the resistance of a vacancy-free lattice and to the exponential rise in the resistance due to the equilibrium vacancies:

$$(1/\rho_{273})\, d\rho/dT = (1/R_{273})\, dR/dT = A + BT + (C/T^2) \exp(-H/kT) \quad (1)$$

where H is the enthalpy of point-defect formation, k is the Boltzmann constant, and T is the absolute temperature.

The coefficients of Eq. (1) were computed by the least-squares method. Since the enthalpy of vacancy formation appears in Eq. (1) in a nonlinear way, several possible values of H were tried. Figure 3 shows the sum of the squared deviations of the experimental points from the approximating curve as a function of the assumed value of the vacancy-formation enthalpy. This quantity has a minimum for platinum at $H = 1.6$ eV, which is close to the values obtained earlier. Estimation of the confidence interval of the enthalpy of point-defect formation was made according to Fisher's criterion [5]. When the level of reliability is 0.95, the uncertainty in the enthalpy of point-defect formation for platinum is about 0.3 eV.

Various values of formation enthalpies were obtained from the measurements of quenched platinum samples. The values for the enthalpy of point-defect formation determined from the most reliable measurements of the excess resistivity are 1.3–1.5 eV [6–11]. These data confirm the suggestion that the nonlinear change in the TCR of platinum is due to the formation of equilibrium point defects in the crystal lattice. The temperature coefficient of resistivity of platinum can be described by Eq. (1) in the range 1100–1900 K, where $A = (4.21 \pm 0.04) \times 10^{-3}\ \mathrm{K}^{-1}$, $B = -(1.08 \pm 0.04) \times 10^{-6}\ \mathrm{K}^{-2}$, $C = (3.78 \pm 1.60) \times 10^{7}$ K, and $H =$

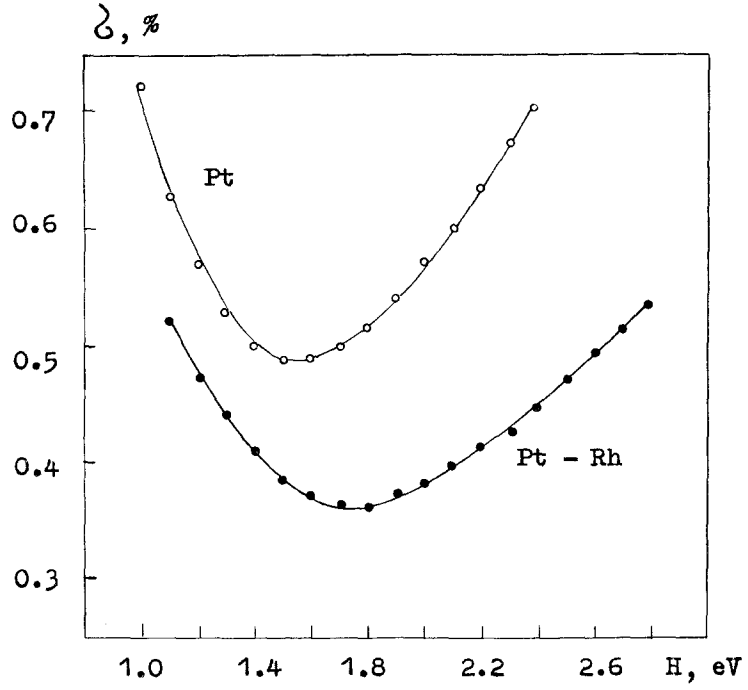

Fig. 3. Determination of the enthalpy of point-defect formation. The X coordinate is the enthalpy of point-defect formation. The Y coordinate is the mean-square error.

1.6 ± 0.3 eV. The excess resistivity due to formation of point defects is $2.3 \times 10^{-6}\ \Omega \cdot$ cm at the melting point.

Study of equilibrium point-defect formation of Pt–Rh alloy has been done in quenching experiments [12]. However, low cooling rates did not permit the preservation of the major portion of the defects in equilibrium at high temperatures. Direct measurements of the TCR of Pt–Rh alloy at high temperatures can be useful for studying the vacancy formation in equilibrium.

The temperature coefficient of resistivity of Pt–Rh alloy can be described by Eq. (1) in the range 1100–1900 K, where $A = (1.78 \pm 0.01) \times 10^{-3}\ \mathrm{K}^{-1}$, $B = -(3.37 \pm 0.14) \times 10^{-7}\ \mathrm{K}^{-2}$, $C = (5.80 \pm 1.80) \times 10^{7}$ K, and $H = 1.8 \pm 0.3$ eV. The excess resistivity corresponding to the point-defect formation is $2.4 \times 10^{-6}\ \Omega \cdot$ cm at the melting point (2095 K).

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REFERENCES

1. Ya. A. Kraftmakher, *High Temp. High Press.* **5**:433 (1973).
2. Ya. A. Kraftmakher, *High Temp. High Press.* **5**:645 (1973).
3. M. Kawai, T. Tahira, K. Kitagawa, and T. Miyakawa, *Appl. Phys. Lett.* **33**:9 (1978).
4. Ya. A. Kraftmakher and E. B. Lanina, *Fiz. Tverd. Tela.* 7:123 (1965).
5. D. Himmelblau, *Process Analysis by Statistical Methods* (New York, John Wiley and Sons, 1974), p. 270.
6. J. J. Jackson, in *Lattice Defects in Quenched Metals* (New York–London, Academic Press, 1965), pp. 467–479.
7. F. Heigl and R. Sizmann, *Cryst. Lattice Defects.* **3**:13 (1972).
8. M. Senoo, H. Mii, J. Fujishira, and T. Takeuchi, *Jap. J. Appl. Phys.* **12**:1621 (1973).
9. M. Charles, J. Hillairet, M. Beyeler, and J. Delaplace, *Phys. Rev.* **B11**:4808 (1975).
10. J. S. Zetts, *J. Bass. Phil. Mag.* **31**:419 (1975).
11. K. Mišek, *Czech. J. Phys.* **B29**:1243 (1979).
12. T. Ricolfi and S. Sartory, *Phys. Lett.* **A26**:141 (1968).

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