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Effect of Pressure on the emf of Chromel–Alumel and Platinum–Platinum 10% Rhodium Thermocouples

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A differential technique has been used to measure the absolute effect of pressure on the emf of Chromel–Alumel and Pt–Pt10Rh thermocouples. The experiments were conducted in a solid pressure medium piston–cylinder apparatus to 35 kbar and 1000°C. Extrapolation of these data shows Chromel–Alumel to read as much as 28°C high at 50 kbar and 1200°C and Pt–Pt10Rh as much as 28°C low at 50 kbar and 2000°C. Graphs are presented which show correction voltage versus temperature for various pressures.

INTRODUCTION

The problem of temperature measurement in high-pressure studies has become more acute as the range of accessible pressures and temperatures has expanded. The high strengths required to contain tens of kilobars has led to extensive use of internally heated pressure cells. Such cells require temperature measuring techniques capable of accurately sensing interior temperatures through large temperature and pressure gradients. No such technique has yet proven to be free of problems.

By far the best technique to date is the use of thermocouples. Their small size and simplicity make them particularly well suited to high-pressure work. Although thermocouples have been studied extensively at room pressure, their behavior in typical high-pressure environments has not been well determined.

The emf of a thermocouple arises from the temperature dependence of the Fermi energies of the metals which make up the thermocuple. Because the Fermi energy of a metal is pressure sensitive, the calibration of a thermocouple changes with pressure. Insufficient progress has been made in the theoretical understanding of the thermoelectric effect to accurately predict this pressure dependence. A review of some of the effects involved here is presented by Bourassa *et al.*[1]

This paper presents our measurements of the absolute corrections for the effect of pressure on Pt–Pt10Rh and Chromel–Alumel thermocouples extrapolated to 50 kbar, and the maximum usable temperature of each thermocouple based on detailed measurements to 35 kbar and 1000°C.

Effects other than pressure contribute to the change in calibration of thermocouples as they are commonly used in high-pressure applications.[2] Among these are cold working of the thermoelements, electrical shunting, diffusion between thermoelements, and chemical contamination.

Figure 1 shows schematically a typical high-pressure thermocouple installation. The high-temperature junction and part of the wire, over which a substantial fraction of the temperature drop occurs, are subjected to pressure. The thermoelectric emf's generated in these pressurized sections of the thermocouple differ from those generated at 1 atm. Also, new junction emf's are introduced at the pressure seal where the compressed and uncompressed segments of the thermoelement wires meet.

The voltage of a thermocouple may be thought of as being generated over a given temperature interval without specific reference to the junction (Peltier) and gradient (Thompson) emf's separately:

$$E=\int_{T_o}^{T_J}\sigma_{ab}dT, \qquad (1)$$

where T_o and T_J are the reference and hot junction temperatures, respectively. The relative Seebeck coefficient σ_{ab} includes both the junction and gradient effects and is commonly known as the "thermoelectric power." The emf of a thermocouple is given by an integral over temperature of some coefficient σ_{ab} which depends both on pressure and temperature. Thus the emf is effected by the composition and/or the state of stress of the thermoelements only where there is a temperature gradient.

The effect of pressure is to modify this coefficient over the temperature interval which takes place under pressure. Thus the emf of a pressurized thermocouple is given by

$$E'=\int_{T_o}^{T_S}\sigma_{ab}dT+\int_{T_S}^{T_J}\sigma_{ab}'dT, \qquad (2)$$

where σ'_{ab} is the pressure-modified Seebeck coefficient and T_S is the pressure seal temperature.

The effect of pressure is the amount by which the second term differs from the emf which would have been produced at 1 atm over the same temperature range:

$$\Delta E=\int_{T_S}^{T_J}(\sigma_{ab}-\sigma'_{ab})dT. \qquad (3)$$

This is the voltage we seek in preparing correction tables for thermocouples used at high pressure.

The relative Seebeck coefficient applies to a pair of thermoelements a and b. It is the difference of two absolute Seebeck coefficients, each of which applies to only one thermoelement:

$$\sigma_{ab}=\sigma_a-\sigma_b. \qquad (4)$$

The voltage change introduced by pressurizing the