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Determination of the Critical Point of Gold[1]

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Wire-shaped gold specimens are placed in a new, improved high-pressure vessel, which is part of a fast capacitor-discharge circuit and in which static pressures above 600 MPa can be reached with distilled water as the pressure-transmitting medium. The specimens are self-heated resistively by a current pulse. The current through the specimen, the voltage drop across it, and its temperature are recorded as a function of time with submicrosecond resolution. The radial expansion of the specimen is determined with a CCD camera. Experiments are performed at different pressures. When the critical pressure is exceeded, there is no liquid–gas phase transition; hence, no sudden change in the thermal expansion rate is observed. The results for temperature, pressure, and specific volume at the critical point of gold are as follows: $T_c = 7400 \pm 1100$ K, $p_c = 530 \pm 20$ MPa, and $v_c = 0.13 \pm 0.03 \times 10^{-3}$ $\text{m}^3 \cdot \text{kg}^{-1}$.

KEY WORDS: critical point; electrical resistivity; enthalpy; gold; high pressure; high temperature; liquid metals.

1. INTRODUCTION

For more than 10 years our laboratory has performed experimental investigations of critical point data up to pressures of about 450 MPa. Using our original pressure vessel, we have completed studies of lead [1], indium [2], and zinc [3]. By extrapolating the measurements, the original pressure vessel was also used to investigate the critical point data on iron [4] and cobalt [5]. We now have available a new pressure vessel with a capability to reach pressures up to 800 MPa, which allows us to investigate

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metals requiring higher static pressures, such as gold and silver (see, e.g., Ref. 6). This paper describes critical point measurements made on gold.

2. EXPERIMENTAL

Gold specimens in the shape of wires of nominal diameter 0.5 mm and length 40 mm were resistively volume heated to the end of the liquid phase by passing a large current pulse through them. The pulse-heating system is described in an earlier paper [7]. The gold samples, supplied by Goodfellow Metals, were 99.99+% pure by weight and had the following impurities (ppm) as reported by the manufacturer: Pb, 1; Fe, 1; Cu, 3; Mg, <1; Pd, 2; Pt, 3; Ag, 10; and Si, <1.

During the heating period, the current through the sample, voltage across the sample, and surface radiation from the sample were measured as functions of time. Since the main emphasis of this work was to investigate the strong volume expansion of the sample as a function of surrounding pressure from 0.1 to 600 MPa, which occurs in the vicinity of the spinodal line in the phase diagram, the expansion of the sample radius was monitored with a fast-framing CCD camera. The camera records images of the central portion of the sample and is described in Ref. 3.

3. RESULTS

3.1. Previous Data for Gold

The mutual dependences of enthalpy, electrical resistivity, density, and temperature have been presented in a previous paper [8] and are listed here again in the form of least-squares fits.

The least-squares fit for specific enthalpy versus temperature in the range $1337\ \mathrm{K} < T < 4300\ \mathrm{K}$ is

$$H = 1.57 \times 10^{-4} T \tag{1}$$

where H is in $\mathrm{MJ \cdot kg^{-1}}$. From this fit, a value of $157\ \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$ ($7.39\ \mathrm{cal \cdot mol^{-1} \cdot K^{-1}}$) is obtained for c_P, the specific heat capacity at constant pressure.

The density d versus enthalpy for the range $0.21\ \mathrm{MJ \cdot kg^{-1}} < H < 0.6\ \mathrm{MJ \cdot kg^{-1}}$ is given by

$$d = 19033 - 9193.7H \tag{2}$$

where d is in $\mathrm{kg \cdot m^{-3}}$.

The least-squares fit to the data of the uncorrected electrical resistivity for the range of $0.148\ \mathrm{MJ \cdot kg^{-1}} < H < 0.21\ \mathrm{MJ \cdot kg^{-1}}$ is

$$\rho_0 = -0.2019 + 2.371H \tag{3}$$

(r_0 in $\mu\Omega \cdot \mathrm{m}$) and that for the range $0.21\ \mathrm{MJ \cdot kg^{-1}} < H < 0.6\ \mathrm{MJ \cdot kg^{-1}}$ is

$$\rho_0 = 0.1216 + 0.8308H \tag{4}$$

3.2. Critical Point Data

The gold sample is rapidly heated from the solid state into the region of a metastable superheated liquid in less than 100 μs. In the phase diagram the binodal line is the equilibrium curve for liquid and vapor, whereas the spinodal line represents the boundary of thermodynamic stability. Using high heating rates we can superheat liquid metals up to the spinodal line [9]. Close to the spinodal line a sudden increase in the number of homogeneous vapor nuclei in the superheated liquid leads to a "jump" from this unstable region into the gas phase, see, e.g., Refs. 10 and 11. This jump is accompanied by a large increase in volume and is called the phase explosion. This powerful expansion produces a shock wave in the surrounding medium. At that moment, the surface temperature starts to decrease due to the cooling of the liquid phase, as it loses the more energetic atoms to the vapor phase [12]. In addition, as the conducting part of the sample is reduced, a sharp increase in the electrical resistivity is observed.

Experiments are performed at different ambient, static pressures. As the pressure is increased, the phase explosion becomes weaker. This is because the difference in specific volume between the liquid and the gas phase decreases as the critical pressure is approached. For the same reason, the shock wave produced by sudden boiling when the spinodal line is reached becomes weaker. The sharp rise in electrical resistivity occurs at higher enthalpy values and is not as sharp as at the lower pressures. When the critical pressure is exceeded, there is no distinction between the liquid and the gas phases, hence, no phase transition. The phase explosion does not occur, and no shock wave is produced. The rise in electrical resistivity becomes weaker and occurs even later but does not necessarily disappear completely.

In the present work a fast-framing CCD camera was used to monitor the sample geometry and to observe the relative strength of the phase explosion as a function of the ambient pressure. Figure 1 shows a picture with 2×9 frames in a row. Starting with the top frame, which is triggered at a prechosen instant, the second frame shows the same spot of the sample after 10.13 μs. The time interval between two consecutive frames is adjustable and was always set to 10.13 μs for these experiments. Figure 1, at an surrounding pressure of 101 MPa, shows a typical phase explosion in the eighth frame from the top, 70.9 μs after the start of the experiment. In Fig. 2, at a surrounding pressure of 405 MPa, the liquid phase is maintained stable up to 81 μs after the start of the experiment, for the same discharge parameters as in Fig. 1. The phase explosion that follows is much weaker than that at 101 MPa, in agreement with the discussion above. In Figs. 3 and 4, at a surrounding pressure of 524.8 and 538.0 MPa, respectively, no phase explosion is observed. This leads to the conclusion

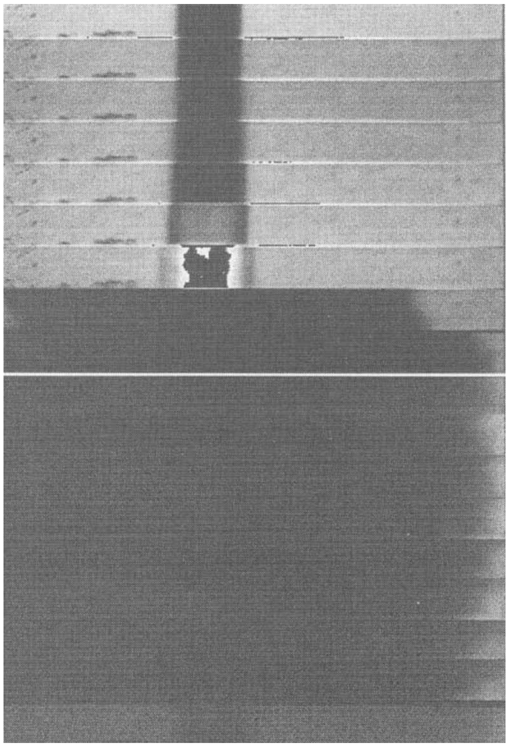

Fig. 1. Phase explosion of a gold sample, picture taken with a fast framing CCD camera. The phase explosion can be seen in the eighth frame from the top, 70.9 μs after the start of the experiment. The surrounding pressure is 101 MPa. Time between any two consecutive frames is 10.13 μs.

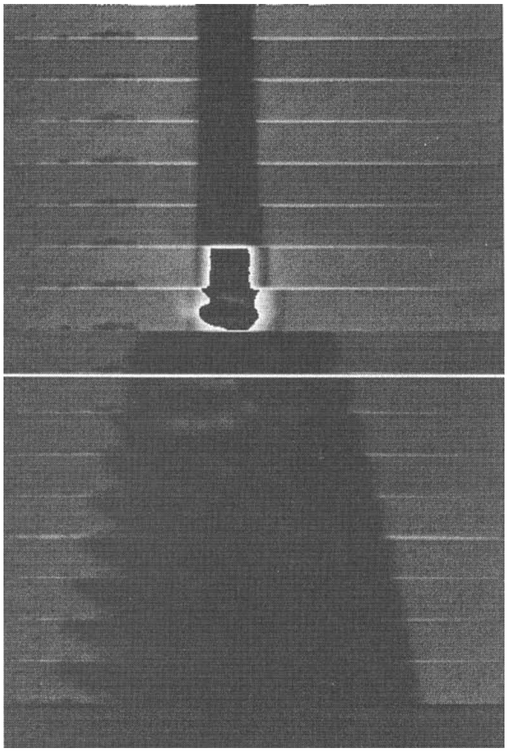

Fig. 2. Phase explosion of a gold wire, picture taken with a fast framing CCD-camera. The phase explosion can be seen in the ninth frame from the top, 81 μs after start of the experiment. The surrounding pressure is 405 MPa. Time between any two consecutive frames is 10.13 μs.

that both experiments were performed at pressures exceeding the critical pressure. Many experiments in this pressure range led to a value of 530 MPa for the critical pressure of gold.

The specific volume at the critical point was determined from expansion measurements with the CCD camera. The value obtained for gold is $(0.13 \pm 0.03) \times 10^{-3}\, \mathrm{m}^3 \cdot \mathrm{kg}^{-1}$.

The temperature at the critical point was determined from pyrometric measurements of the radiance emitted by the sample surface. Because of our pyrometer's high sensitivity, recording temperatures as high as the critical temperature of gold required attenuation of the radiance entering the pyrometer. Therefore, the melting plateau of gold could not be resolved

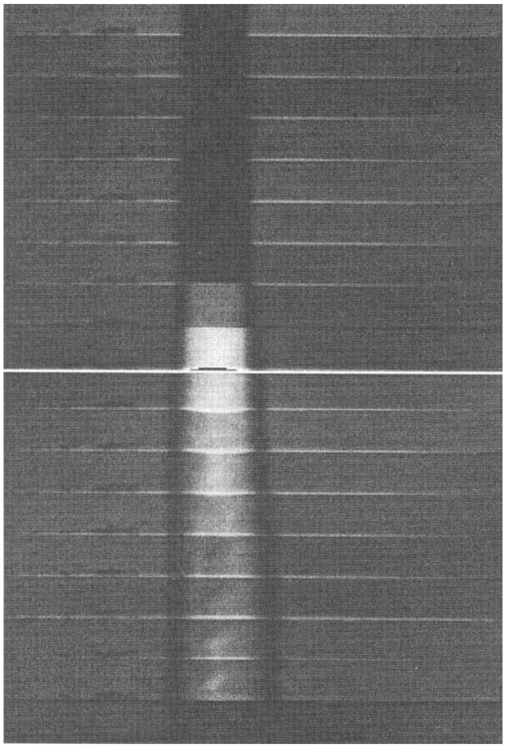

Fig. 3. Short time frames at a surrounding pressure of 524.8 MPa. No phase explosion can be observed. Time between any two consecutive frames is 10.13 μs.

at the same time and its known melting point could not be used to convert the recorded signals to temperature. Instead, the specific enthalpy versus temperature relation, determined for the liquid phase at lower temperatures and given in Eq. (1), was used, under the assumption that the specific heat capacity ($c_p = 157\ \mathrm{J \cdot kg^{-1}\ K^{-1}}$ in the range $1337 < T < 4300$ K) does not change significantly at higher pressures. The time at which the critical temperature was reached was assumed to be the same at which the resistivity curve showed a sharp rise. The value obtained for the critical temperature of gold is 7400 ± 1100 K.

The critical compressibility factor z_c is given by

$$z_c = \frac{p_c V_c}{R T_c} \tag{5}$$

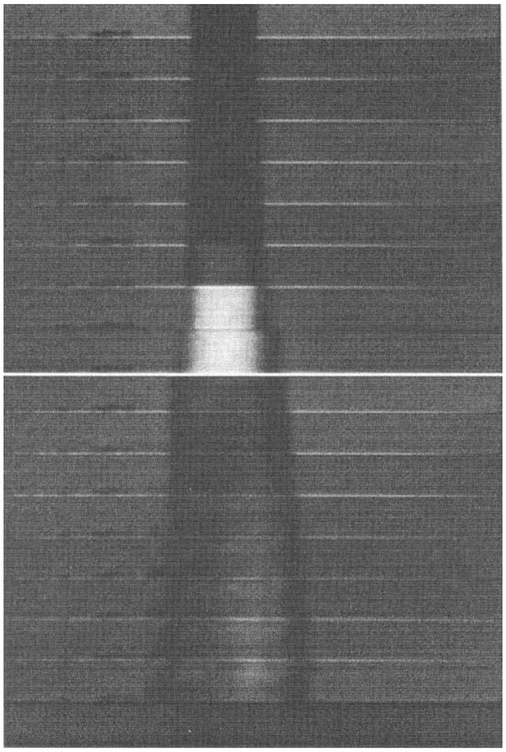

Fig. 4. Short time frames at a surrounding pressure of 538 MPa. No phase explosion can be observed. Time between any two consecutive frames is 10.13 μs.

Table I. Values for the Critical Volume, V_c, the Critical Pressure, p_c, and the Critical Temperature, T_c, of Gold Compared with Literature Data

Investigator (first author)	Ref. No.	T_c (K)	p_c (MPa)	V_c ($m^3 \cdot kg^{-1}$)
This work		7400 ± 1100	530 ± 20	$(0.13 \pm 0.03) \times 10^{-3}$
Gates, 1960	17	5557	37.6	1.82×10^{-3}
Grosse, 1962	18	9500		
Martynyuk, 1974	19	4820		
Morris, 1964	14	8100	462	0.23×10^{-3}
Young, 1971	15	8267	626.5	0.20×10^{-3}
Egry, 1995	16	7520		
Lang, 1977	20	9950		

where p_c is the critical pressure, V_c is the specific volume at the critical point, T_c is the critical temperature, and R is the universal gas constant. Our data (volume expansion measured by means of the fast CCD camera) for gold yield a value of 0.22 for z_c. This result for gold is smaller than values obtained in our laboratory for other metals (0.3 for lead, 0.45 for indium, 0.3 for zinc, and the values of critical compressibility for the alkali metals range from 0.2 to 0.3, as cited in Ref. 13), which confirms that the critical compressibility does not have the same value for different metals.

A comparison of our results with data reported in the literature, all of which were obtained from theoretical models, is given in Table I.

4. ESTIMATION OF ERRORS

Enthalpy is the most accurate quantity of those determined under dynamic conditions. The estimated uncertainty of enthalpy values is $\pm 5\%$. The uncertainties in temperature measurements are $\pm 5\%$ in the melting region, increasing to $\pm 15\%$ at the critical point. The static pressure in the surrounding medium can be measured to within $\pm 2\%$. The estimated uncertainty for the critical pressure, as reported in Table I, is higher because of the additional uncertainty in determining the pressure at which the phase explosion does not occur. The uncertainty in obtaining the specific volume at the critical point from expansion measurements is estimated to be $\pm 20\%$.

5. CONCLUSIONS

Critical point values of pressure, temperature, and specific volume of gold were determined using a rapid, resistive pulse-heating technique in combination with a fast-framing CCD camera.

Compared to values from the literature, the data for T_c of this work match, within the error bars, the values of Morris [14] and of Young and Alder [15]. The value from Egry [16], estimated from surface tension values at the begin of the liquid phase, extrapolated to much higher temperatures, which are not available by means of levitation techniques, shows excellent agreement. Our value for the critical pressure lies between the values of Morris [14] and of Young and Alder [15]. Our measured V_c is the lowest one cited in this table.

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