ELECTRICAL EXPLOSION OF CONDUCTORS UNDER PRESSURE AND THE METAL – NONMETAL TRANSITION

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UDC 537.528:537.312.67:541.126

By analysis of the thermodynamic and electrical properties of the liquid-metal phase during continuous change, it is shown that the metal–nonmetal transition line must coincide with, or be in the immediate neighborhood of, the spinodal–quasispinodal line. The law of corresponding states is adequately satisfied for this line. The dependence of the relative electrical resistance R/R_0 on the enthalpy $H = H_T - H_0$ (R_0 and H_0 are the values at $T_0 = 298°K$) was measured for Cu, Ag, Au, and Al during heating of a wire sample by a current pulse having a duration less than 10^{-4} sec at pressures p up to 15 kbar. The effect of pressure on the relative resistance R/R_0 and the enthalpy H of these metals in the solid and liquid states was studied. It is shown that for p > (1-3) kbar the line for the pressure dependence of the initiation of an electrical explosion of a conductor corresponds to the line for the transition of metal into nonmetal. The critical temperature and critical pressure for Cu, Ag, Au, and Al were evaluated by using this relation.

1. Electrical explosion of a conductor is considered from the viewpoint of the thermodynamics and kinetics of the transition of liquid metal into vapor at high heating rates. One can expect [1, 2] that during heating of a conductor under pressure by a current pulse with a duration of 10^{-5}–10^{-7} sec the initiation of an electrical explosion, following which the electrical resistance of the metal rises sharply and a shock wave is produced in the surrounding medium, will be located in the neighborhood of the upper limit for the existence of the liquid-metal phase under continuous change. This boundary in the variables pressure, p, and volume, V, is determined [3, 4] by the spinodal

$$\left(\frac{\partial p}{\partial V}\right)_T = 0, \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T > 0 \text{ for } p < p_c \tag{1.1}$$

the critical point

$$\left(\frac{\partial p}{\partial V}\right)_T = 0, \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0 \text{ for } p = p_c \tag{1.2}$$

and the quasispinodal (curve of supercritical transitions)

$$\left(\frac{\partial p}{\partial V}\right)_T < 0, \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0 \text{ for } p > p_c \tag{1.3}$$

(p_c is the critical pressure, and T is temperature). Since the derivative $(\partial p/\partial V)$ is inversely proportional to the fluctuations of the specific volume ΔV^2 [5]

$$-\left(\frac{\partial p}{\partial V}\right)_T = kT / \overline{\Delta V^2} \tag{1.4}$$

(k is the Boltzmann constant), the fluctuations rise sharply upon approach to this boundary from the liquid side in view of Eqs. (1.1)-(1.4). This leads to an abrupt drop in the electrical conductivity of the liquid metal because of the localization of atomic conduction electrons, which are in locations with reduced den-

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 5, pp. 16-22, September-October, 1974. Original article submitted April 22, 1974.

sity. Another reason for the reduction in electrical conductivity is the scattering of conduction electrons by fluctuations of charge concentrations in the liquid metal. Thus, during a continuous change in the liquid-metal phase, the transition into a vapor is accompanied by an electronic transition of metal into nonmetal.

Sharp increase of electrical resistance in liquid mercury near the quasispinodal and critical point was confirmed experimentally [6]. As follows from Eqs. (1.1) and (1.4), the increase in electrical resistance should occur in the neighborhood of the spinodal but it is impossible to observe this phenomenon during slow heating of a liquid metal because of the difficulty of achieving a large amount of superheating of the liquid phase. The possibility of arriving in a region of metastable liquid metal has been discussed for electrical explosions of conductors in air [2].

Calculation of the spinodal for mercury from the formula in [7] and calculation of the quasispinodal for the supercritical region from published data [6] show that the spinodal–quasispinodal line in the reduced coordinates $\pi = p/p_c$ and $\tau = T/T_c$ (the subscript c refers to critical parameters) can be represented approximately by the straight line

$$\pi = 11.1\ \tau - 10.1 \tag{1.5}$$

The spinodal calculated from the formula in [7] for cesium, as well as experimental data for the spinodals of a number of organic liquids [8], are described by the equation

$$\pi = 10\tau - 9 \tag{1.6}$$

which is close to Eq. (1.5). This indicates the satisfaction of the law of corresponding states for the spinodal–quasispinodal line of various liquids.

Since density fluctuations reach maximum values when crossing the spinodal–quasispinodal line, one can assume this line coincides with the metal–nonmetal transition line. In favor of this assertion is the rough agreement of the relative critical density in a number of metals with the density at the metal–nonmetal transition point calculated for a model consisting of conducting spheres in a dielectric medium [9].

The transition of liquid mercury into the nonmetallic state has been considered [10] without including the effect of fluctuations on the basis of ideas about the zonal structure of this metal. The following approximate criterion was established for the determination of the transition point:

$$g = N(E_F) / N(E_F)_f = 1/3 \tag{1.7}$$

which corresponds to a specific resistance of mercury of $\sim 300\ \Omega^{-1} \cdot cm^{-1}$; $N(E_F)$ is the density of states at the Fermi level in the liquid metal; $N(E_F)_f$ is the density of states for the free-electron model. If one accepts the criterion (1.7), the metal–nonmetal transition line does not coincide with the spinodal–quasispinodal line for mercury according to the data published [6]. In the pressure range up to 1.7 p_c, it can be represented approximately by a straight line displaced parallel to the line (1.5) toward lower temperatures by an amount 0.05 T_c. Extension of this line into the region of metastable liquid gives the point 0.87 T_c at $p = 0$. Experimental data for the electrical conductivity of potassium in the supercritical region [11] provides a basis for assuming that the metal–nonmetal transition line coincides with the spinodal–quasispinodal line in alkali metals. According to Eq. (1.6), this line intersects the temperature axis at the point 0.90 T_c. These evaluations indicate that the metal–nonmetal transition point T_{t_0} at $p = 0$ is related to T_c by the expression

$$T_{t_0} = bT_c \tag{1.8}$$

where $b = 0.87$ for similarity to mercury, and $b = 0.90$ for similarity to cesium.

Based on these concepts, initiation of an electrical explosion of a conductor, following which the resistance of a liquid metal rises sharply, can be identified with the metal–nonmetal transition point. Such an identification is valid under the following conditions: a) the influence of the magnetic field of the current on sample shape must be eliminated; b) for $p < p_c$, the length of the heating pulse must be so short that vaporization of metal through the sample surface and through the surface of heterogeneous vapor centers can be neglected; at the same time, it must not be so short (less than 10^{-7} sec) as to violate the stationarity of homogeneous nucleation [2].

The possibility of transition of liquid metal into a state with poor conductivity during electrical explosion of a conductor has been pointed out [12]. Experimental confirmation of this hypothesis was obtained from explosion of copper wires in capillaries [13] and from explosion in a plastic medium under pressure [1].

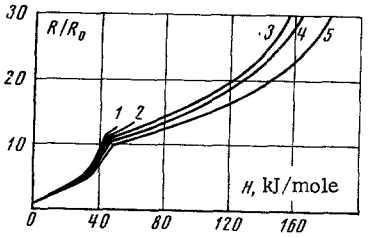

Fig. 1

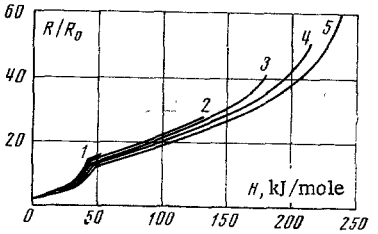

Fig. 2

Since for electrical explosion of a conductor in air there is the danger of its premature rupture by the magnetic field, and the production of a discharge shunting the sample and distorting the oscilloscope trace is not eliminated, electrical explosion of a conductor in a plastic medium under pressure was used in the present work, as was done previously [1], in order to eliminate these factors. In contrast to [1], quantitative results were obtained in the present work because of increased accuracy of pulse measurements. This method provides an opportunity to study the effect of pressure on the high-temperature properties of metals and to obtain the pressure dependence of the initiation of the electrical explosion, which is compared with the metal–nonmetal transition line.

2. By heating a wire sample (0.2-0.3 mm in diameter, 20 mm long) with a current pulse lasting ~100 μsec, oscillographic measurements were made of the dependence of the relative electrical resistance R/R_0 on the enthalpy $H = H_T - H_0$ (H_0 and R_0 are the values at $T_0 = 298°K$) for Cu (99.96), Ag (99.97), Au (99.99), and Al (99.99). For such pulses, the effect of inductive pickup on the shape of oscilloscope traces is insignificant and can be taken into account [14]. A sample enclosed in a pellet of fluoroplast 3 (Teflon) was placed inside a steel chamber of the cylinder-piston type under constant pressure, which varied over a range up to 15 kbar in the different experiments. For a given pressure, the dependence of R/R_0 on H [14] was calculated on a Minsk-22 computer from the oscilloscope traces for sample current and voltage; calculations were performed for temperatures from room temperature (298°K) to the initiation of electrical explosion.

This relation is shown for copper (Fig. 1) and gold (Fig. 2). Similar curves were obtained for silver and aluminum in the pressure range to 15 kbar. In Fig. 1, curve 1 gives the experimental results in air and curves 2-5, the experimental results in Teflon under various pressures: curve 2, 0.2 kbar; curve 3, 3 kbar; curve 4, 6 kbar; curve 5, 15 kbar. In Fig. 2, curve 1 gives the experimental results in air and curves 2-5, the experimental results in Teflon under pressure: curve 2, 0.2 kbar; curve 3, 1 kbar; curve 4, 3 kbar; curve 5, 6 kbar.

In the curves obtained, the beginning of metal fusion is determined by the point R_1/R_0, H_1 after which the dependence of R/R_0 on H deviates from a linear dependence; the end of fusion is marked by the break at R_2/R_0, H_2. The variation of resistance of the metal during fusion, R_2/R_1, and the heat of fusion $\Lambda = H_2 - H_1$ are determined from these points.

Experiments showed that the values of R_1/R_0, R_2/R_0, and R_2/R_1 for a given metal fell, and those of H_1, H_2, and Λ rose, in proportion to the increase in pressure. For experiments in Teflon under pressures up to 6 kbar, the dependence of these quantities on pressure is close to linear. The effect of pressure on the electrical resistance of liquid metal is greater than for the solid metal; the pressure coefficient of resistance $\beta = -dR/R_0dp$ near the fusion temperature T_2 is almost an order of magnitude greater for the liquid metal than for the solid metal. For the liquid state up to the normal boiling point T_b (the value $H = H_b$ at T_b was taken from [15]), there is a slight increase in the quantity β as the temperature increases. For the four metals studied, a sharp increase in β was observed upon approach to the initiation of an electrical explosion (Figs. 1, 2).

The dependence of R/R_0 on H for a given metal at a given pressure p is characterized by the parameter

$$\delta = (1 / R_0)\ (dR / dH)_p = \alpha_p / C_p \qquad (2.1)$$

where $\alpha_p = (1/R_0)(dR/dT)$ is the temperature coefficient of electrical resistance, and $C_p = (dH/dT)_p$ is the heat capacity at constant pressure. For the solid state, δ is constant. A similar relationship is observed for the liquid state in the range from T_2 to temperatures exceeding T_b. For the solid and liquid states, the quantity δ falls as the pressure increases. The effect of the pressure p on the reduction of α_p is greater than it is for C_p.

TABLE 1

	H_{t0}, kJ/mole	H^*_{t0}, kJ/mole	γ, kJ/mole·kbar	T_c, °K	p_c, bar
Cu	155	145	2.5	5330	420
Ag	120	110	2.0	4110	150
Au	213	196	3.0	7610	2510
Al	112	107	2.2	4140	90

Samples ruptured shortly after fusion in experiments in air and in Teflon at low pressure. This may be caused by the appearance of hydromagnetic instabilities in the liquid cylinder. Values corresponding to a liquid state with $T > T_b$ are observed in Cu, Ag, and Au for $p >$ (1-2) kbar and in Al for $p > 3$ kbar (Figs. 1, 2). Obviously, the pressure is sufficient for suppression of instabilities in the sample when $p > 3$ kbar. Pressure slows down the growth of vapor centers, which facilitates superheating of the liquid above its boiling point when $p < p_c$. Formation of vapor centers is impossible when $p > p_c$.

The initiation of an electrical explosion of a conductor at the point R_t/R_0, H_t, up to which the dependence of R/R_0 on H was calculated (Figs. 1, 2), was marked by a sharp increase in sample voltage and a break in the oscilloscope trace for the current following which the current quickly fell to zero. In the case of suppression of hydrodynamic instabilities, this indicates a sharp drop in the electrical conductivity of the metal after the initiation of an electrical explosion. At this point, a strong shock wave was created in the surrounding medium; the shock front was detected by means of an abrupt rise in the voltage on a barium titanate piezoelectric detector mounted at the bottom of the high-pressure chamber. The amplitude of the shock wave decreased as the pressure increased.

With suppression of instabilities in the liquid sample, the electrical resistance R_t/R_0 at the initiation of electrical explosion amounted to 30-60 for the metals studied, and the value H_t of the enthalpy at this point exceeded estimated data for H_b at T_b [15]. In this case, the dependence of H_t on p was nearly linear with H_t increasing slightly as p increased,

$$H_t = H_{t0} + \gamma p \tag{2.2}$$

where p is the pressure calculated from force on the press and the cross section of the piston of the high-pressure chamber; H_{t0} is the value of H_t obtained by linear extrapolation of the pressure dependence of H_t to zero value of p. Values of H_{t0} and of the derivative $\gamma = dH_t/dp$ for the metals studied are given in Table 1.

3. The weak linear dependence of H_t on p indicates that it may not be similar to the temperature dependence of saturated vapor pressure (binodal). This property of the dependence of H_t on p and the sharp increase of the resistance of the metal near this line under the experimental conditions is evidence that it can be compared with the metal–nonmetal transition line; Eq. (2.2) is comparable with Eqs. (1.5) or (1.6).

This analogy is also confirmed by the value of the specific resistance of the metals studied at the initiation of electrical explosion. If one considers that the volume of copper at that point is more than two times greater than the volume at $T_0 = 298$°K and if one considers that the change in volume of liquid metal during a heating pulse occurs only in the radial direction of a sample [16], the specific resistance ρ_t for the metals studied at the initiation of explosion is 60-120 times greater than its value ρ_0 at $T_0 = 298$°K. This ratio agrees in order of magnitude with the value of ρ/ρ_0 for mercury at the metal–nonmetal transition point [6, 10].

The value of the enthalpy at the initiation of electrical explosion when $p = 0$ is a quantity characterizing the thermodynamic properties of the exploded metal; it must be related to the metal–nonmetal transition point, which is located in the neighborhood of the spinodal when $p = 0$. It is impossible to relate the resultant value of H_{t0} to zero pressure, since it was observed that with pulsed heating of a conductor in Teflon, the medium created at its surface an additional pressure Δp_d, the effect of which appeared in a reduction of R_2/R_0 by $\Delta R_2/R_0$ for experiments in Teflon at low pressure (0.2 kbar) in comparison with R_2/R_0 for experiments in air. The additional pressure is associated with the effects of inertial forces which arise during rapid thermal expansion of a sample in Teflon. The magnitude of Δp_d was estimated with the help of the relation $\Delta p_d = (\Delta R_2/R_0)/\beta_2$, where β_2 is the value of the pressure coefficient of resistance of the liquid metal near the fusion temperature for experiments in Teflon. For Cu, Ag, and Au, Δp_d is 4-6 kbar, and for Al, ~2 kbar.

Including this pressure under the assumption Δp_d remains constant over the entire range of the liquid state, the value of H_{t0} was reduced by an amount $\Delta H_{t0} = \gamma \Delta p_d$, and we thus obtained $H_{t0}^* = H_{t0} - \Delta H_{t0}$

(Table 1). Because of the weak dependence of H_t on p, the correction ΔH_{t0} was no more than 8% of H_{t0}. The correction ΔH_{t0} obtained in this manner was overestimated because Δp_d decreases for some time after the end of sample fusion. The mean-square spread of experimental data for H_t in the region of linear dependence of H_t on p was 5-6% of H_{t0}*.

The value $H_t = 152$ kJ/mole obtained for copper [2] in an explosion in air of a copper wire by a current pulse lasting less than 10 μsec (heating time of liquid phase $\Delta t = 1.6$ μsec) agrees with the present results; it falls between the values for H_{t0} and H_{t0}*. For Au, $H_t = 129$ kJ/mole [2], which was obtained for an explosion in air with $\Delta t = 7.7$ μsec, is less than the value of H_{t0}* in Table 1. This comparison indicates that the heating rate for Cu in [2] was sufficient to heat the liquid metal to the metal–nonmetal transition point before the sample ruptured because of the effect of the magnetic field and the growth of heterogeneous vapor centers. For Au, the heating rate in [2] was less than the minimal rate which ensures attainment of the neighborhood of the spinodal and the production of a strong electrical explosion associated with the transition of metastable liquid into a stable state.

The similarity in reduced coordinates for the spinodal–quasispinodal line and the metal–nonmetal transition line in various materials has been pointed out above [Eqs. (1.5), (1.6), and (1.8)]. If one assumes that Eq. (1.8) is satisfied for the metals studied, one can determine from the values obtained for H_{t0}* a value of T_c,

$$T_c = \frac{T_{t0}}{b} = \frac{1}{b}\left[T_2 + \frac{H_{t0}^* - H_2}{C_2}\right] \tag{3.1}$$

where C_2 is the mean value of the heat capacity of the liquid metal, which is taken at the fusion temperature T_2 with published data [15] taken into account. Values of T_c obtained for $b = 0.87$ are given in Table 1. The table also gives estimates of the critical pressure p_c obtained by extrapolation of the published temperature dependence of the saturated vapor pressure [15] to $T = T_c$.

The evaluations show that under the experimental conditions the linear portion of the dependence of H_t on p should be related to the quasispinodal and that the metal–nonmetal transition line was reached in the region of supercritical states for the metals studied. At low pressures, this line is not reached because of premature rupture of samples through the action of the magnetic field or because of the growth of heterogeneous vapor centers.

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