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# Superheating of solid and liquid metals in the process of pulse heating

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## Abstract

During the process of pulse heating metallic conductors using a current, the enthalpy of the metals is measured at the initial point of melting and at the initial point of the electrical explosion. From these data, the value of the superheating of the solid phase above the temperature of equilibrium melting and the value of the superheating of the liquid phase above the normal boiling point have been estimated.

## INTRODUCTION

From the theory of thermodynamic equilibrium and phase stability [1], it follows that each first-order phase transition is characterized by the presence of not only stable phases, but also of metastable phases. At fixed temperature and pressure, the free energy of the metastable phase is more than that of the corresponding stable phase. Supercooled metastable phases (supersaturated vapour, supercooled liquid) are readily formed during the cooling of a material. However, superheated metastable phases are formed with difficulty. In the process of slow heating of metals, superheating of the solid phase by only 1–2 K above the equilibrium melting point, has been observed for tin [2], and for gallium and bismuth [3]. Neglecting the low values of this effect, many scientists have considered that significant superheating of the solid phase above the point of its equilibrium with the liquid phase is impossible under real conditions [1,4].

Significantly greater success was achieved when the superheating of non-metallic liquids was investigated [5]. Under atmospheric pressure, many organic liquids were superheated up to temperatures of $T = 0.90T_c$, where $T_c$ is the critical temperature of the liquid. But for metallic liquid phases, superheating during slow heating was observed up to much lower temperatures relative to $T_c$.

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To investigate the superheating of thermodynamic phases, it is necessary to use high-speed pulse heating. Under such conditions of heating, the phase is superheated up to the temperature at which the phase transition rate attains a value corresponding to the rate of heat supply. Experiments with pulse heating of metallic samples using a current have indicated the possibility of significant superheating of the solid as well as the liquid phase above the temperature of the phase equilibrium [6–10]. This paper describes the results of the latest investigations of this problem.

## SUPERHEATING OF SOLID PHASE

For the investigation of the superheating of a solid phase, two experimental arrangements were used [6,11]. In the first, a metallic conductor was heated by a current pulse of duration 0.1–0.4 ms during the discharging of the batteries of electrolytic capacitors. In the second, "rectangular" current pulses of duration 0.4 ms were obtained by using an artificial line. Specimens were 0.5–1.2 mm in diameter and 4–8 cm long, their heating rates were $10^6$–$10^7$ K $s^{-1}$. During the heating process, oscillograms of current and voltage were recorded for the specimen. The start of melting was fixed at time $t_1$ by the break point on the voltage oscillogram. From the oscillograms, the molar enthalpy $H_1$ of the metal at this point was calculated using the formula

$$H_1 = A/m\left(\int_0^{t_1} IU \, \mathrm{d}t - 0.5LI^2\right) \tag{1}$$

where $m$ is the mass of the specimen, $A$ is the molar mass of the metal, $I$ and $U$ are the current and voltage at the time $t$, and $L$ is the inductance of the specimen. The accuracy of the $H_1$ measurements was 2%.

The values of $H_1$ were found to be higher than the enthalpy data $H_s$ of the solid phase at the point $T_f$ of its equilibrium with liquid phase. From the surplus enthalpy $\Delta H_1 = H_1 - H_s$ and the heat capacity $C_s$ of the solid phase at $T = T_f$, the value of the superheating of the solid phase, $\Delta T_1 = T_1 - T_f = \Delta H_1/C_s$, in the pulse-heating process was calculated. Values of $T_f$, $H_s$ and $C_s$ are taken from Hultgren et al. [12].

The results of the experiments on the superheating of solid metals above the melting point are presented in Table 1.

All the metals investigated, with the exception of gallium, had polycrystalline structures; the gallium specimens were monocrystals in which the *b*-axis is aligned with the current direction.

The solid phases with the greatest superheating were lead and indium, whose molar entropy of melting values $\Delta S_f$ are the lowest. From the kinetic theory of melting, it follows that, at a given value of superheating, the velocity of the displacement of the solid–liquid interphase boundary is proportional to $\Delta S_f$. We have investigated the melting of lead–bismuth

TABLE 1

Superheating of solid phase at the beginning of melting

| | Purity (%) | Heating rates $dT/dt \times 10^{-6}$ ($K\,s^{-1}$) | Surplus enthalpy $H_l - H_s$ ($J\,mol^{-1}$) | Superheating $T_l - T_f$ (K) | Relative superheating $(T_l - T_f)/T_f$ (%) |
|---|---|---|---|---|---|
| Pb | 99.9995 | 2–11 | 1180 | $40 \pm 4$ | 6.7 |
| In | 99.9997 | 1–5 | 1120 | $37 \pm 3$ | 8.6 |
| Bi | 99.9997 | 11 | 700 | $23 \pm 5$ | 4.3 |
| Ga | 99.9999 | 1.3 | 433 | $16 \pm 2$ | 5.2 |
| Ag | 99.98 | 2–4 | 1680 | $52 \pm 22$ | 4.2 |
| Zn | 99.98 | 4–6 | 810 | $27 \pm 14$ | 4.0 |
| Ni | 99.93 | 3.3 | 2400 | $66 \pm 28$ | 3.8 |
| Pt | 99.93 | 8.1 | 1700 | $49 \pm 31$ | 2.4 |

solid solutions by pulse heating [13]. The superheating of the solid phase was found to increase with the increasing concentration of bismuth in lead. This can be explained because the surface-active admixture of bismuth in lead decreases the velocity of the displacement of the interphase boundary.

In our experiments, the length of time at which the solid phase stayed in the superheated state was from 7 to 25 μs. From the theory of homogeneous nucleation in the solid phase, it follows that the stationary establishment time for this process is around 0.2 μs. Thus, it can be concluded that, in our experiments, the superheated solid phase was metastable.

Despite significant superheating of the solid phase of nickel before its melting (Table 1), a displacement of the Curie point was not discerned for this metal during pulse heating: this can be explained by the fact that the ferromagnetic–paramagnetic phase transition in nickel is not characterized by the presence of metastable phases.

To determine whether the values obtained here for the superheating of the solid phases (Table 1) are higher than the limits, we calculated the range of the relative superheating of solid metals in which homogeneous formation of liquid phase nuclei is possible. It was found to be equal to 18–22% relative to the melting temperature $T_f$, which is much higher than the values given in Table 1.

The polymorphic $\alpha$–$\beta$ transition process of titanium and zirconium was investigated at the heating rate of $8 \times 10^6\ K\,s^{-1}$. The beginning and end of

TABLE 2

Superheating of the $\alpha$-phase of titanium and zirconium

| | Purity (%) | $H_\alpha$ ($kJ\,mol^{-1}$) | $H_\alpha - H'_\alpha$ ($J\,mol^{-1}$) | $T_\alpha - T_{\alpha\beta}$ (K) | $(T_\alpha - T_{\alpha\beta})/T_{\alpha\beta}$ (%) |
|---|---|---|---|---|---|
| Ti | 99.74 | 28.5 | 3120 | $92 \pm 18$ | 8.0 |
| Zr | 99.76 | 30.5 | 5500 | $160 \pm 17$ | 14.1 |

this transition were fixed by the break points of voltage oscillogram. The enthalpy of the $\alpha$-phase $H_\alpha$ at the beginning of the transition, calculated from the oscillograms, was found to be higher than its value $H'_\alpha$ at the equilibrium point $T_{\alpha\beta}$ of the $\alpha$ and $\beta$ phases. We calculated the superheating of the $\alpha$-phase using the formula $T_\alpha - T_{\alpha\beta} = (H_\alpha - H'_\alpha)/C_\alpha$, where $C_\alpha$ is the heat capacity of the $\alpha$-phase at the temperature $T_{\alpha\beta}$ and $T_\alpha$ is the temperature of the $\alpha$-phase at the beginning of the transition during pulse heating. The results are presented in Table 2.

## SUPERHEATING OF THE LIQUID PHASE

To investigate the superheating of liquid metal, a third experimental arrangement was used [14]. The duration of the current pulse was 10–40 $\mu$s; specimens were 0.2–0.5 in diameter and 4–6 cm long, heated at rates of $10^8$–$10^{10}$ K $s^{-1}$. Under such heating conditions, the beginning $t_1$ and end $t_2$ of melting, and also the starting point $t_3$ of the electrical explosion of the conductor were fixed on the oscillograms. After the point $t_3$, the current in the conductor drastically decreased as a result of the increase in the resistivity of the metal [15]. Homogeneous heating of the conductor after the point $t_3$ is impossible because of the development of electrothermal instabilities in it. The enthalpy of the liquid metal $H_3$ at the initial point of its electrical explosion was calculated from the oscillograms. The temperature of the metal at this point was estimated from the formula

$$T_3 = T_f + \frac{H_3 - H_L}{C_L} \tag{2}$$

where $H_L$ is the enthalpy of the liquid phase at the melting point $T_f$ and $C_L$ is the heat capacity of the liquid phase at this point. We calculated the value of the superheating of the liquid phase at the point $T_3$, relative to the normal boiling point $T_b$ of the metal. Values for $T_f$, $H_L$, $C_L$ and $T_b$ are taken from Hultgren et al. [12].

Data for the liquid-phase superheating were also obtained from experiments performed on the first experimental arrangement, with pulse heating of specimens under pressure [16]. In these experiments, $H_3$ was found to increase linearily with an increase in pressure. In this case, the value of the superheating at atmospheric pressure was defined by the enthalpy obtained by extrapolating $H_3$ to atmospheric pressure.

The influence of different factors (heat losses, magneto-hydrodynamic instabilities of the specimen) on the results of the enthalpy measurements was considered: the errors in the enthalpy measurements did not exceed 4%.

The results of the experiments on superheating the liquid metals are presented in Table 3.

TABLE 3

Enthalpy $H_3$ and temperature $T_3$ of the metals at the initial point of their electrical explosion, and the critical temperature $T_c$ of the metals; $T_b$ is the normal boiling point of the metals according to ref. 12

| | Conditions of the experiments | $H_3$ (kJ mol$^{-1}$) | $T_3$ (K) | $T_3 - T_b$ (K) | $(T_3 - T_b)/T_b$ | $T_c$ (K) |
|---|---|---|---|---|---|---|
| Cu | a | 152 | 4710 | 1870 | 0.66 | 5890 |
| Ag | a | 119 | 3660 | 1220 | 0.50 | 4580 |
| Au | c | 196 | 5970 | 2840 | 0.91 | 7650 |
| Zn | a | 70 | 2350 | 1170 | 0.99 | 2940 |
| Cd | a | 63 | 2230 | 1190 | 1.14 | 2790 |
| Al | c | 107 | 3390 | 600 | 0.21 | 4350 |
| Pb | a | 104 | 3570 | 1730 | 0.76 | 4460 |
| Zr | b | 310 | 7750 | 3070 | 0.66 | 9450 |
| Nb | b | 375 | 9290 | 3530 | 0.85 | 11330 |
| Mo | b | 336 | 8570 | 4270 | 0.74 | 10450 |
| W | b | 460 | 12170 | 6340 | 1.09 | 14840 |
| Pt | a | 250 | 6810 | 2710 | 0.66 | 8510 |

[a] Heating in air.

[b] Heating in water.

[c] Heating in plastic medium under pressure and extrapolation of enthalpy to atmospheric pressure $P_{at}$.

On the $P$–$T$ diagram, the point $T_3$ can be identified with the point beyond which the specific resistance of liquid metal drastically increases. According to experimental data for alkali metals and mercury, the dependence of $T_3$ on pressure $P$ is expressed by the linear function

$$T_3/T_c = 0.095(P/P_c) + 0.78 \tag{3}$$

where $T_c$ is the critical temperature and $P_c$ the critical pressure.

From eqn. (3) and the $T_3$ values from Table 3, we estimated the critical temperature $T_c$ of the metals [17], taking $T_3 = 0.80T_c$ for experiments in air, $T_3 = 0.82T_c$ for experiments in water and $T_3 = 0.78T_c$ for experiments in plastic medium under pressure with extrapolation of enthalpy to $P = P_{at}$. The values of critical temperature for metals obtained in this way are presented in Table 3. The accuracy of these critical temperature estimations is 15%.

Our calculations made on the basis of the theory of homogeneous nucleation of vapour bubbles has shown that, under atmospheric pressure, explosive boiling of superheated alkali metals and mercury takes place at the temperatures $T = (0.88–0.90)T_c$. Hence, it seems that the temperature $T_3$ is not the temperature limit of superheating of metals.

## REFERENCES

1 J.W. Christian, Theory of Transformations in Metals and Alloys, Pergamon Press, Oxford, 1975.

2 S.A. Khaikin and N.P. Bene, Dokl. Akad. Nauk SSSR, 23 (1939) 31.

3 J.D. Mackenzie and R.L. Cormia, J. Chem. Phys., 39 (1963) 250.

4 A.P. Ubbelohde, Melting and Crystal Structure, Clarendon Press, Oxford, 1965.

5 V.P. Skripov, Metastabilnaya shidkost (Metastable Liquid), Nauka, Moscow, 1972; Metastable Liquids, John Wiley, New York, 1974.

6 M.M. Martynyuk and G.E. Guerrero, Zh. Tek. Fiz. 42 (1972) 187.

7 M.M. Martynyuk and G.E. Guerrero, Zh. Fiz. Chim. 48 (1974) 1131.

8 M.M. Martynyuk and V.D. Lyakhovets, Fiz. Tverd. Tela (Leningrad) 16 (1974) 1809.

9 M.M. Martynyuk and V.D. Lyakhovets, Zh. Fiz. Chim., 49 (1975) 237.

10 M.M. Martynyuk, V.I. Tsapkov, O.G. Panteleychuk and I. Karimkhodzaev, Isledovaniie Fizicheskikh Svoistv Metallov (Investigation of Metals' Physical Properties by Pulse Heating Method), People's Friendship University, Moscow, 1972.

11 M.M. Martynyuk and V.I. Tsapkov, Zavod. Lab., 3 (1974) 54.

12 R. Hultgren, P.D. Desai and D.T. Hawkins, Selected Values of the Thermodynamic Properties of the Elements, Am. Soc. Metals, Metals Park, Ohio, 1973.

13 M.M. Martynyuk and V.D. Lyakhovets, in A.E. Galashev (Ed.), Teplofizicheskiie Svoistva Metastabilnykh system, (Thermophysical Properties of the Metastable Systems), Ural Scientific Centre of USSR Academy of Sciences, Sverdlovsk, 1984.

14 M.M. Martynyuk and I. Karimkhodzaev, Dokl. Akad. Nauk Tadzh. SSR, 8 (1971) 14.

15 F. Hensel and E.U. Franck, Ber. Bunsenges., 70 (1966) 1154.

16 M.M. Martynyuk and O.G. Panteleychuk, Teplofiz. Vys. Temp., 15 (1976) 1201.

17 M.M. Martynyuk, Zh. Fiz. Chim., 57 (1983) 810.