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IDEAL TENSILE STRENGTH OF METALS ON THE BASIS OF A GENERALIZED VAN DER WAALS EQUATION

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On the basis of a generalized Van der Waals equation a method is developed to calculate the thermodynamic stability boundary of a condensed phase. For a number of metals the limits of ideal tensile strength during their uniform tension at T = 0 K, T = 293 K, and at the melting temperature are calculated. The character of the temperature dependence of the strength is considered.

Ideal strength of metals is usually evaluated on the basis of concepts of strength of crystals [1, 2]. Below we consider this problem from notions of the thermodynamic stability of a liquid phase. This method can be justified by the fact that in the crystal–liquid phase transition forces of intermolecular attraction change insignificantly and the ideal tensile strength of a liquid or amorphous phase is close to the strength of a crystal [3]. In order to calculate the strength of a liquid phase, use can be made of equations of state for liquids and gases, the simplest of which is the Van der Waals equation.

Thermodynamic Stability Boundary of a Condensed Phase. To increase the accuracy of the Van der Waals equation, in [4, 5] we suggested its three-parametric modification

$$p = \frac{RT}{V - b} - \frac{a}{V^n}. \tag{1}$$

The additional parameter n, introduced by us, determines the character of intermolecular attraction forces and the thermodynamic similarity of substances [5].

The thermodynamic stability boundary of the liquid phase (spinodal) [6] is determined by the condition $(\partial p/\partial V)_T = 0$. Having applied this condition to Eq. (1), we obtain the spinodal equation in V- and T-coordinates:

$$T = \frac{an\,(V - b)^2}{RV^{n+1}}. \tag{2}$$

Substitution of (2) into (1) gives the spinodal equation in p- and V-coordinates

$$p = \frac{a\,[(n - 1)\,V - nb]}{V^{n+1}}. \tag{3}$$

To calculate the spinodal of the given substance by formulas (2) and (3), it is necessary to know values of the parameters a, b, n, which are usually calculated using parameters of a critical point [5]; however for many metals this point is not determined accurately. In the present work, a, b, n for metals are calculated from the experimental results for the molar volume (density) of the liquid phase and the heat of its evaporation in the region of temperatures not higher than the normal boiling point. From Eq. (1) it follows that the molar evaporation heat is equal to [7]

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TABLE 1. Parameters of the Generalized Van der Waals Equation

Metal	n	$b \cdot 10^6$, m^3/mole	a, J/mole$\cdot$(m^3/mole)$^{n-1}$
Zn	1.644	9.189	43.74
Pb	1.500	18.36	394.0
Al	1.357	10.57	1827
Cu	1.383	7.158	1270
Fe	1.395	7.100	1346
Ni	1.376	6.781	1662
Pt	1.310	9.127	4462
Mo	1.297	9.037	5680
W	1.264	9.400	10,270

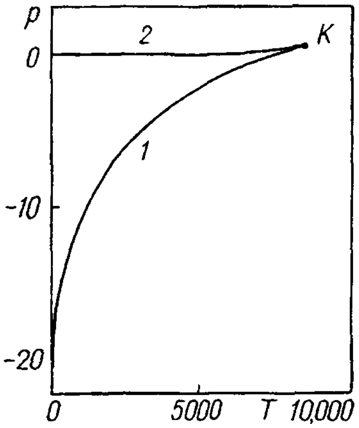

Fig. 1. Diagram of states of iron in the region of liquid–vapor phase transition: 1) spinodal, 2) binodal, K, critical point. p, GPa; T, K.

$$\Lambda = \frac{a}{n-1}\left(\frac{1}{V^{n-1}} - \frac{1}{V_\mathrm{v}^{n-1}}\right) + p\,(V_\mathrm{v} - V)\,, \tag{4}$$

where the index v refers to the vapor phase; V without an index is the liquid phase.

In the region of low temperatures a vapor can be considered as an ideal gas; then when $pV_\mathrm{v} = RT$, $V_\mathrm{v} \gg V$, and $pV \ll RT$, from Eq. (4) it follows that

$$\Lambda = \frac{a}{(n-1)\,V^{n-1}} + RT\,. \tag{5}$$

Under the same conditions Eq. (1) takes the form

$$\frac{a}{V^n} = \frac{RT}{V-b}\,. \tag{6}$$

Having applied Eqs. (5) and (6) to the melting point and to the normal boiling point, we obtain:

$$b = \frac{V_1 V_2 (r_1 - r_2)}{r_1 V_2 - r_2 V_1}\,, \tag{7}$$

$$n - 1 = \frac{V_1}{r_1 (V_1 - b)}\,, \tag{8}$$

TABLE 2. Ideal Strength $-p_{s0}$ of Metals with Uniform Tension at $T = 0$ and Strength Parameters at $T = 293$ K

Metal	$-p_{s0}$, GPa	$-p_s$, GPa	$\frac{p_s}{K_T}$, %	$V_s \cdot 10^6$, m^3/mole	$\frac{V_s - V_b}{V_b}$, %	α_s, MPa/K	σ_m, GPa
Zn	8.33	4.87	7.92	10.8	13.3	5.27	1.66
Pb	5.03	3.19	7.53	21.3	12.9	2.84	0.32
Al	10.3	7.02	8.90	12.2	12.5	5.20	2.67
Cu	16.6	11.5	7.62	8.18	11.9	8.16	2.76
Fe	20.4	14.6	8.53	8.00	10.7	9.20	6.42
Ni	21.5	15.4	8.54	7.64	10.7	9.68	4.62
Pt	17.8	13.2	–	10.2	10.6	7.46	3.70
Mo	19.7	14.8	5.85	10.1	10.2	5.66	5.62
W	23.3	18.1	6.03	10.4	9.23	8.45	7.24

$$a = (n - 1)\, RT_1 r_1 V_1^{n-1}\,, \tag{9}$$

where $r_1 = \Lambda_1/RT_1 - 1$, $r_2 = \Lambda_2/RT_2 - 1$. The values of a, b, n, calculated from formulas (7)-(9) for a number of metals, are given in Table 1. The data for T_1, T_2, Λ_1, Λ_2, V_1 are taken from [8] and for V_2, from [9]. The calculation shows that for all the metals tabulated in Table 1 the parameter $n < 2$.

From the system of Eqs. (5) and (6), written for two points on a saturation line, expressions of type (8) and (9) follow also for the second point. Application of formulas (8) and (9) to the normal boiling point gives values which differ from these presented in Table 1 by no more than by 0.2% for n and no more than by 5% for a.

Figure 1 illustrates the p–T-diagram for states of iron in the region of the liquid–vapor transition. The spinodal of the liquid phase is calculated by means of a numerical solution of Eqs. (2) and (3) at the values of n, b, a given in Table 1. The spinodal goes through the regions of negative and positive pressures and terminates at the critical point K. The parameters of this point ($T_{cr} = 8310$ K, $p_{cr} = 271.6$ MPa, $V_{cr} = 43.1 \cdot 10^{-6}$ m^3/mole) are found from formulas obtained in [5] at the same values of n, b, a. The binodal is determined by extrapolation to the critical point of the experimental data [8] for the temperature dependence of the saturated vapor pressure. Between the binodal and spinodal a region of a metastable liquid (an extended or superheated liquid) is located. At the given temperature the value of the pressure p_s on the spinodal defines the rupture strength limit of the liquid phase during its uniform tension (on a decrease in the pressure with respect to the binodal). The rupture of the liquid is manifested as an intense process of origination of homogeneous cavitation centers when approaching the spinodal from the side of the region of the metastable liquid [6]. In cooling below the melting point (under conditions that eliminate a crystallization process) the supercooled liquid goes to the amorphous state; therefore in the region of low temperatures the value of $-p_s$ determines the tensile strength limit of the amorphous phase.

Strength of Metals at Characteristic Points of the Temperature Scale. The amorphous phase has the greatest limiting tensile strength $-p_{s0}$ at a temperature of absolute zero (see Fig. 1). According to Eqs. (2) and (3), this strength is determined by the formula

$$-p_{s0} = \frac{a}{b^n}\,. \tag{10}$$

For a number of metals (Table 2) from formula (10) we calculated the ideal strength $-p_{s0}$ with uniform tension at $T = 0$; by means of a numerical solution of Eqs. (2) and (3) we obtained the values for the strength $-p_s$ at $T = 293$ K; in calculations we used the data for a, b, n from Table 1. When $T = 293$ K, the ratio of $-p_s$ to the isothermal modulus of the bulk elasticity K_T [10] for these metals is equal to 6–9%. For $T = 293$ K from Eq. (2) we also calculated the molar volume on the spinodal V_s and from Eq. (1), the volume on the binodal V_b at $p = 0$. The relative increase in the volume of the amorphous phase $(V_s - V_b)/V_b$ during its uniform tension at the instant of rupture is 9–13%.

TABLE 3. Parameters of Ideal Metal Strength at the Melting Point

Metal	T_l, K	$-p_s$, GPa	$V_s \cdot 10^6$, m^3/mole	$\frac{V_s - V_b}{V_b}$, %	α_s, MPa/K
Zn	629.7	3.32	12.0	20.1	2.97
Pb	600.6	2.51	22.0	18.2	1.80
Al	933.3	4.80	13.9	22.0	2.49
Cu	1357	6.51	9.92	24.9	3.01
Fe	1809	7.45	10.0	25.9	2.84
Ni	1726	9.48	9.48	25.5	3.08
Pt	2042	7.07	12.9	25.6	2.23
Mo	2890	6.33	13.8	30.8	1.76
W	3680	7.48	14.5	31.9	1.63

From the elasticity theory [11] it follows that the strength p_s during uniform tension and the strength σ_m during uniaxial tension for isotropic solids (amorphous solids) are expressed by the formula

$$\sigma_m = - p_s(1 - 2\nu) . \tag{11}$$

Table 2 presents values of σ_m calculated using the parameter $-p_s$ and data for ν from [10]. The theoretical strength of metals σ_m during uniaxial tension at $T = 293$ K is comparable with the real strength of thread-like crystals; according to [1, 12], the maximum values of σ_m (GPa) for these crystals are equal to: 0.89 for Zn; 2.27 for Al; 4.41 for Cu; 13.1 for Fe; 2.90 for Ni; 13.0 for W. The values of σ_m (Table 2) calculated by us are also close to the experimental data [13] obtained by a method of rear spall in the process of dynamic tension of metals: 4 for Cu, 6.5 for Fe, 5.5 GPa for Ni.

Table 3 presents the results of calculations for the melting temperature T_l of different metals: the strength $-p_s$ and the molar volume V_s of the liquid phase on the spinodal. The relative volumetric deformation $(V_s - V_b)/V_b$ during the rupture of liquid metals at this point amounts to 20–30%. The strength of metals $-p_s$ is here 2–3 times lower than the strength $-p_{s0}$ at $T = 0$ (Table 2).

Temperature Dependence of the Strength. As the temperature rises, the spinodal curve form (see Fig. 1) shows a sharp decrease in the strength of the condensed phase. In the region of low temperatures, when the pressure on the binodal is close to zero, the strength of the liquid is equal to $-p_s$ and its temperature dependence is characterized by a derivative along the spinodal $\alpha_s = dp_s/dT_s$. Differentiating Eqs. (2) and (3), we obtain

$$\alpha_s = \frac{dp_s}{dT_s} = \frac{R}{V_s - b} . \tag{12}$$

From Eq. (12) it follows that the temperature strength coefficient α_s is inversely proportional to the free volume $V_s - b$ on the spinodal. When $T = 0$, $\alpha_s = \infty$, since $V_s = b$. The values of α_s for $T = 293$ K are presented in Table 2 and for the melting point of metals, in Table 3.

At temperature above the normal boiling point the tensile strength of the liquid is determined by the difference in the pressures $p_b - p_s$. At a certain temperature $T_{s,p=0}$ the pressure on the spinodal becomes equal to zero and the strength of the liquid at this point is numerically equal to the pressure of the saturated vapor. It follows from Eqs. (2) and (3) that this temperature is determined by the formula

$$T_{s,p=0} = \frac{a}{Rb^{n-1}} \frac{(n-1)^{n-1}}{n^n} . \tag{13}$$

The volume on the spidonal at this point is

$$V_{s,p=0} = \frac{nb}{n - 1}. \qquad (14)$$

According to Eqs. (12) and (14), the slope of the tangent to the spinodal is here of the form:

$$\alpha_{s,p=0} = \frac{R}{b\,(n - 1)}. \qquad (15)$$

When $T \geq T_{s,p=0}$, the pressure p_s on the spinodal is positive; as the temperature rises, the strength of the liquid $p_b - p_s$ decreases and tends to zero on approaching the critical point K (see Fig. 1).

NOTATION

p, pressure; V, molar volume; T, absolute temperature; R, gas constant; a, b, n, parameters of the generalized Van der Waals equation; Λ, molar heat of evaporation; r, dimensionless heat of evaporation; K_T, isothermal modulus of the volumetric elasticity; σ_m, strength limit with uniaxial tension; ν, Poisson coefficient; α_s, temperature strength coefficient with uniform tension. Subscripts: v, vapor; 1, melting point; 2, normal boiling point; cr, critical point; s, spinodal; b, binodal; m, maximum value; 0, absolute zero.

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