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 \( \frac{\partial p}{\partial V} = 0 \). 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

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

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]
<table>
<thead>
<tr>
<th>Metal</th>
<th>n</th>
<th>$b \cdot 10^6$, m$^3$/mole</th>
<th>$a$, J/mole·(m$^3$/mole)$^{n-1}$</th>
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<tbody>
<tr>
<td>Zn</td>
<td>1.644</td>
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<td>6.781</td>
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<td>Pt</td>
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<tr>
<td>W</td>
<td>1.264</td>
<td>9.400</td>
<td>10,270</td>
</tr>
</tbody>
</table>

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.

\[
\Lambda = \frac{a}{n-1} \left( \frac{1}{V^{n-1}} - \frac{1}{V_v^{n-1}} \right) + \rho (V_v - V),
\]

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 $pV_v = RT$, $V_v \gg V$, and $pV \ll RT$, from Eq. (4) it follows that

\[
\Lambda = \frac{a}{(n - 1) V^{n-1}} + RT.
\]

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

\[
\frac{a}{V^n} = \frac{RT}{V - b}.
\]

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

\[
b = \frac{V_1 V_2 (r_1 - r_2)}{r_1 V_2 - r_2 V_1},
\]

\[
n - 1 = \frac{V_1}{r_1 (V_1 - b)},
\]