Dependence of erosive wear of metallic materials on temperature via the electron work function

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Mechanical properties of metals are intrinsically correlated to the electron behavior, which is largely reflected by the electron work function ($\varphi$). Since the work function varies with temperature, the dependence of material properties on temperature could be predicted via variations in work function with temperature. Combining a hardness – $\varphi$ relationship and the dependence of work function on temperature, a temperature-dependent model for predicting solid-particle erosion is proposed. Erosive wear losses of copper, nickel and X70 low-carbon steel as sample materials were measured at different temperatures; results of the tests are in agreement with the theoretical prediction. This study demonstrates a feasible electronic base for looking into fundamental aspects of wear phenomena, which would also help develop alternative methodologies for tribo-material design.

Keywords: temperature, work function, wear

1. Introduction

Intrinsic mechanical properties of metallic materials, e.g., Young's modulus, yield strength, hardness and ductility, are fundamentally determined by their electron behavior [1-6]. The electronic behavior is largely reflected by the electron work function (EWF), which is the minimum energy required to remove an electron from a metal [7]. This parameter can be used in material design and modification. For instance, EWF can be used to select appropriate alloying elements for solution-strengthening and to identify beneficial
and detrimental phases in multiphase alloys. These capabilities of EWF have been demonstrated by recent studies \[8,9\]. It should be indicated that mechanical properties of materials are strongly affected by their microstructure, which complicates the dependence of the properties on the electron behavior. However, the mechanical properties of a material are largely governed by its overall electron work function, which is linked to the roles that individual phases and interphase boundaries play in determining the properties.

Electron work function is temperature dependent \[10-12\]. Thus, the dependence of material properties on temperature could be established via the dependence of work function on temperature. In this article, the dependence of material loss on temperature, caused by wear, is proposed by combining a work function dependent erosion model and the temperature dependent work function. Solid-particle erosion tests were performed for a few sample materials at various temperatures. Results of the experimental testing are in good agreement with the theoretical predictions. The wear loss - temperature dependence would help select tribo-materials and guide engineering materials for effective applications at different temperatures.

2. Temperature-dependent wear model \( W_L(T) \)

2.1 Sliding/abrasive wear

For sliding/abrasive wear of metallic materials, their wear loss is largely dependent on hardness as Archard's equation expresses \[13\]:

\[
W_L = K \frac{L}{H} \tag{1}
\]

where \( L \) is the normal load, \( L \) the sliding distance, and \( H \) is the hardness of the surface under wear attack; \( K \) is the wear coefficient. Hardness is correlated to the work function \[14\],

\[
H = C \varphi^6 \tag{2}
\]

where \( C \) is taken as a constant \[15\]. For self-containing, a brief description of the derivation
of the relationship between the work function and temperature given by ref. [16] is presented here. This relationship is derived by generalizing the Lennard-Jones potential between two atoms for solids, which is given as

$$\varphi(r) = -\varphi_e[(\frac{r}{r_e})^{12} - 2(\frac{r}{r_e})^6]$$  \hspace{1cm} (3)$$

where $r$ is the distance between the two atoms and $r_e$ is their equilibrium distance.

At non-zero temperatures, atoms oscillate around their equilibrium positions. Letting $\chi = \frac{\langle r - r_e \rangle}{r_e}$ represent the relative atomic oscillation amplitude, $\varphi(r)$ can be written as

$$\varphi(r) = -\varphi_0[(1 + \chi)^{-12} - 2(1 + \chi)^{-6}] \approx \varphi_0 - 36\chi^2\varphi_0$$ \hspace{1cm} (4)$$

The temperature dependent $\chi$ varies as [16-18] $\chi = \frac{1}{\gamma_e} \frac{3\varphi_0}{k_B T}$, where we may have $g = 252\frac{\varphi_0}{r_e^2}$ and $f = 36\frac{\varphi_0}{r_e^2}$. Thus, $\chi$ becomes

$$\chi = \left(\frac{7}{48}\frac{k_BT}{\varphi_0}\right)^{\frac{1}{2}}$$ \hspace{1cm} (5)$$

Combining equations (4) and (5), we have

$$\varphi(T) = \varphi_0 - 36\left(\frac{7}{48}\frac{k_BT}{\varphi_0}\right)^2\varphi_0$$ \hspace{1cm} (6)$$

This approach can be generalized for solids by considering the interaction with other adjoining atoms. The second term in equation (4) (after the negative sign) can be generally expresses as

$$36\varphi_0\sum_r \frac{<r_i - r_e>^2}{r_e} = \xi\varphi_0\left(\frac{<r_i - r_e>}{r_e}\right)^2 = \eta\varphi_0\left(\frac{k_BT}{\varphi_0}\right)^2$$ \hspace{1cm} (7)$$

where $<r_i - r_e> \approx <r_i - r_{eq_i} > + <r_{eq_i} - r_e> = <r_i - r_{eq_i} > + (i-1)a$ and $<r_i - r_{eq_i} >$ is average deviation or displacement of atom $i$ away from its equilibrium position; $a$ is the lattice
parameter and \( r_{\text{e}} \) is the nearest neighbour distance. \( w_i \) is an energy contribution factor that counts the influence of \( i\)th neighbour atom on the square of relative oscillation amplitude, \( x^2 \). These distant dependent contributions from the nearest, \( 2^{\text{nd}} \) and \( 3^{\text{rd}} \) neighbor atoms are \( W_{r\text{e}} = 1, W_{2r\text{e}} = 0.031, W_{3r\text{e}} = 0.0027, \ldots \) (determined based on the Lennard-Jones potentials for \( r_{\text{e}}, 2r_{\text{e}}, 3r_{\text{e}}, \ldots \)). \( \varphi(T') \) then becomes

\[
\varphi(T') = \varphi_0 - \gamma \frac{\xi L_{e} \gamma^{\alpha}}{w_i} \tag{8}
\]

\( \varphi_0 \) is the work function at room temperature \( (T' = 295 K) \), \( \gamma = \xi \left(\frac{\gamma^{\alpha}}{L_{e}}\right)^2 \) and

\[
\xi = \frac{36}{\chi_1} \sum_i \left(\frac{<r_i-r_{\text{e}}^2>}{r_{\text{e}}^2}\right)^2
\]

where \( \chi_i = \frac{<r_i-r_{\text{e}}^2>}{r_{\text{e}}^2} = \alpha_L T' \) and \( \alpha_L \) is the thermal expansion coefficient of the metal.

\( \xi \) is dependent on the crystal structure. For FCC structures with \( r_{\text{e}} = a/\sqrt{2}, \) \( \xi \) is expressed as \[15\]

\[
\xi_{\text{FCC}} = \frac{36}{\chi_1} \sum_i \frac{w_i (\chi_1 + \sqrt{2}(i-1))}{1 + \sqrt{2}(i-1)} \tag{9}
\]

For BCC structures with \( r_{\text{e}} = \sqrt{3}a/2, \) \( \xi \) becomes

\[
\xi_{\text{BCC}} = \frac{36}{\chi_1} \sum_i \frac{w_i (\chi_1 + \sqrt{3}(i-1))}{1 + \sqrt{3}(i-1)} \tag{10}
\]

Combining equations (1),(2) and (8), the wear loss per distance becomes:
\[ W_L = K \frac{FL}{H} = K \frac{FL}{Cq^6} = K' \frac{FL}{(q_0 - \gamma (k_B T)^2/q_0)^6} \]  \hspace{1cm} (11) \\

where \( K/C = K' \). Since the interaction between atoms decreases rapidly with the atomic spacing, only the interaction between neighbouring atoms is considered i.e. \( N \) is equal to the coordination number for a crystal. Volume loss – temperature curves for X70-Steel, Copper and Nickel are plotted and shown in figure 2, which well follow the trend predicted by eq.(11). The constants in eq. (11) are substituted with \( \alpha \), where \( \alpha = K'fL \). The values for \( \alpha \) are determined from fitting the experimental data as materials behave differently and exhibit different \( K' \) and \( \gamma \). These values are presented in table 1.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Crystal structure</th>
<th>( N )</th>
<th>( \alpha [10^{-7} \text{ eV}^6 \text{m}^2] )</th>
<th>( \beta [10^{-1} \text{ Kg eV}^6] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>X70 Steel</td>
<td>BCC</td>
<td>8</td>
<td>1.95</td>
<td>3</td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>12</td>
<td>3.5</td>
<td>8</td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>12</td>
<td>5</td>
<td>8.5</td>
</tr>
</tbody>
</table>

2.2 Erosive wear

The relationship between erosive wear and work function has also been established. Again, for self-containing the derivation is also briefly described here. For a ductile material, the contact area created by the impingement of particle, \( A_c \), may be expressed as:

\[ A_c \propto \frac{\varepsilon}{N} \]  \hspace{1cm} (12)
$F$ represents the impact force. $H$ is the hardness of the material. During erosion process, the impact force comes from the kinetic energy of solid particle associated with its moment change when striking the target surface:

$$v' = -m \frac{d\sigma_y}{dt} \quad (13)$$

where $m$ is the mass of the particle, and $\nu_y$ represents the vertical component of the velocity of the particle. Thus we have

$$m \frac{d\sigma_y}{dt} = -HA_c$$

$$m \left( \frac{dy}{dt} \right) \cdot d\nu_y = -HA_c \cdot dy$$

$$\therefore \quad \int_u^v m\nu_y \cdot d\nu_y = - \int_0^d HA_c \cdot dy = - \int_u^d HA_c(y) \cdot dy$$

If the particle strikes the surface at 90°, the above integration yields

**Indentation volume**, $V = A_c \cdot d = \frac{m\nu_y^2}{2H}$

If the particle strikes the surface at a certain angle, the horizontal velocity needs to be taken into account, in which case a general relation between the erosion volume loss ($V$) and material’s hardness and thus the work function can be expressed as

$$V = K_{E\psi} \frac{mv^2}{H} = K_{E\psi} \frac{mv^2}{\phi^6} \quad (14)$$
where $K_E$ is an erosion coefficient, which is related to the impingement angle of the particle and other factors such as the size and angularity of particle. When the hardness is converted to work function, this coefficient is replaced by $K_{E\varphi}$. Incorporation of the relation between work function and temperature i.e. equation (8), the erosion volume loss is expressed as a function of temperature via the effect of temperature on work function,

$$V = K_E \frac{mv^2}{H} = K_{E\varphi} \frac{mv^2}{\varphi^6} = K_{E\varphi} \frac{mv^2}{(\varphi_0 - \gamma (k_B T)^2 \frac{1}{\varphi_0})^6} \quad (15)$$

The expression for the erosive mass loss can be realized based on equation (15), since the mass, $m$ and the volume, $V$ are related by the density, $d$ as $m = dV$. The expression for mass loss becomes:

$$\text{Mass loss} = \beta \left( \frac{\varphi}{\varphi_0 - \gamma (k_B T)^2 \frac{1}{\varphi_0}} \right)^6 \quad (16)$$

Where $\beta = K_{E\varphi} m v^2 (1 - \nu^2) d$. Equation (16) is plotted and presented in figure 5. and the values for $\beta$ are fittend and the results for the fit are presented in Table 1.

3. Experimental Observation

3.1 Sliding/abrasive wear

Cu, Ni, X70 steel samples with dimensions of 20×10×5 mm were polished with 800 and then 1200 grit grinding papers, cleaned with distilled water and acetone. Pin-on-disk tests were performed on these samples using a High Temperature Tribometer (CSEM Instrument). A silicon nitride ball in diameter of 3mm was applied to abrade the surfaces of specimens under a normal load of 10 N (the silicon nitride ball was set on a metal cantilever).

During test, the pin moved at a velocity of 2 cm/s along a circle with its diameter equal to 2 mm and the total tavel distance was 37.71m. Temperature was controlled by a heater
attached to the tester. Five temperatures were used for the tests, including the room temperature, 100 °C, 200 °C, 250 °C and 300 °C. In order to minimize oxidation of sample surfaces at elevated temperatures, an Ar gas flow was directed to the sample surface under an aluminum lid that covered a container in which the sample was placed. Pressure of the Ar flow was 25 psi. Each test was repeated 3 times. After the pin-on-disk tests, samples were cleaned with distilled water and alcohol. The wear tracks of specimens were then examined using a 3D optical profiler (Zygo, USA). Volume loss of each sample was determined based on dimensions of the wear track. Results of the tests are illustrated in Fig. 2, in which theoretical curves are also presented (α obtained by fitting to the experimental data). As shown, the volume loss increased as temperature was raised. The dependence of the volume loss on temperature is in good agreement with eq.(11) for all the sample materials.
3.2 Erosive wear

A home-made air-jet erosion tester was used to perform solid-particle erosion tests at elevated temperatures for the sample materials. The pressure of the air flow was kept constant at 40 psi to eject sand particles, corresponding to a sand particle velocity of 55 m/s. The impingement angle was set at 90°. AFS 50-70 sand was used for the tests. The air and sand mixture was delivered through a nozzle of 4 mm in inner diameter and the distance between the nozzle and samples was 20 mm. A balance with an accuracy of 0.1 mg was used to determine the weight loss by weighting each specimen before and after test. Eroded surfaces were examined using a Vega-3 TESCAN Scanning Electron Microscope at 20 kV.

Fig. 3 illustrates weight losses of the materials at different temperatures. As shown, the trend of the material loss with temperature well follows the theoretical prediction using eq. (15). Fig. 4 illustrates eroded surfaces experienced erosion tests at the room
temperature, $373 \, K$, $473 \, K$ and $573 \, K$.

![Graphs of X70 Steel, Copper, and Nickel](image)

**Figure 4** Variations in mass loss of X70 Steel, Copper and Nickel with temperature. The curves represent the theoretical prediction and the data points are from the experimental results. Beta is determined by fitting experimental data.
4. Conclusions

Mechanical properties of metallic materials are intrinsically determined by their electron behavior, which is largely reflected by the electron work function. In this study, temperature-dependent abrasion and solid-particle erosion models were proposed based on the correlation between hardness and electron work function and the dependence of...
work function on temperature. Wear losses of copper, nickel and X70 low-carbon steel as sample materials were measured at different temperatures; results of the tests are in agreement with the theoretical prediction. This work demonstrates a feasible electronic base for looking into fundamental aspects of wear phenomena, which would also help develop alternative methodologies for tribo-material design and development.

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