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Electron work function, adhesion, and friction between 3d transition metals under light loads

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Abstract

Adhesion and friction between metallic materials are of importance to many dynamic mechanical systems, particularly to those at nano- or micro-scales. Under light loads, friction is mainly dependent on the adhesion between two surfaces in contact, to which valence electrons have the predominant contribution. However, the correlation between the electronic behavior and adhesion as well as friction has not been well established.

This paper reports the authors' recent studies on the correlation among electron work function (EWF), adhesion and friction of transition metals. The EWF is the minimum energy required to remove an electron from the Fermi level. This parameter characterizes the electronic behavior of metals and can be determined experimentally. In this study, the metal–metal friction under light loads was evaluated employing a micro-tribometer. It was demonstrated that adhesion and friction of the transition metals were closely related to their electron work functions. The adhesion between two different metals in contact could be expressed as a function of their EWFs and electron densities. Consequently, the friction between the two metals under light loads could be estimated based on these two parameters.

Keywords: Electron work function; Adhesion; Friction; Metals

1. Introduction

Adhesion has attracted extensive interest because of its importance to many surface processes, such as friction, wear, and adsorption [1]. Adhesion could be particularly important to nano/micro devices. In this case, the light contact force and smooth contact surfaces render the friction to be dominated by adhesion, and mechanical plowing is less important [2,3]. Fundamental understanding of adhesion between two metals could therefore be necessary for operation and optimization of nano/micro-devices.

Considerable efforts have been made to fundamentally investigate adhesion and friction between two metals using experimental and theoretical approaches. Rabinowicz correlated friction coefficients of clean metals to their ratios of adhesion energy to hardness [2]. Buckley examined the adhesion between (0 1 1) face of iron and surfaces of other metals, and showed that the chemical reactivity of the metals was directly related to their adhesion behavior [4]. He also demonstrated that metals with larger percentages of d valence bond character had lower friction coefficients [1]. Sikorski [5] investigated the adhesion of different metals by applying the twist-compression bonding method under normal atmospheric conditions and showed that high friction was always accompanied with strong adhesion, which was influenced by melting point, crystal structure, mutual solubility and hardness, etc. Calculations of adhesive force from first principles have also been made [6–11], which shed light on the adhesion mechanism; however, clear correlation between adhesion of metals and their fundamental properties, e.g., the electron behavior, has not yet been established.

Different mechanisms have been proposed regarding the adhesion between two metals; it is undoubted that the intrin-

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sic adhesion largely depends on the surface electronic configuration and properties [4,12–14]. The electron behavior of a metal can be characterized by its electron work function (EWF), the minimum energy required for an electron to escape from the Fermi level to a point just outside the bulk metal [15]. The EWF is one of fundamental electronic properties of a metallic surface, which can be measured quantitatively and is related to various properties of metals and semiconductors as well as many surface processes, such as adsorption, contamination, surface segregation and friction [16–18]. Studies have been conducted to investigate the relationship between EWF and metal–ceramic adhesion. It was observed that higher EWF corresponded to lower adhesive force for metal–ceramic contact [19,20]. Since ceramic is relatively inert, the EWF of the metal therefore largely determined the adhesion and friction for the metal–ceramic contact. For metal–metal contact, the situation is complicated. In this case, the EWFs of both metals are of importance to adhesion because charge transfer exists between the two different metals, which results in an internal electric field [6,9,21].

The objective of this work is to investigate the relationship between the EWF and adhesion for 3d transition metals. Transition metals and their alloys are widely used in engineering practice, often involving dynamic metal–metal contact [22]. The interaction between transition metals is more complicated than simple metals because of their electronic configurations [6]. The adhesion behavior of transition metals is a topic of both practical and theoretical interests. Due to the difficulty in direct determination of adhesion between the metals, in this work, friction was used as a parameter to evaluate the adhesion behavior. This is acceptable when the contact load is light. It is known that the friction force is the summation of two contributions: the adhesive force and the deformation force. The ratio of these two contributions varies with the contact condition especially the contact force [23–25]. Our previous study has demonstrated that under light loads, adhesion plays a predominant role in controlling the friction force [20].

2. Experimental procedure

2.1. Samples preparation

Materials under the study were 3d transition metals provided by Alfa Aesar and Strem Chemicals Companies (Table 1), respectively. All metal samples (plates) were annealed in Argon atmosphere at temperatures above their recrystallization points for 1 h and slowly cooled down in furnace. The annealing temperatures for the metals are listed in Table 2 .

The samples were then lightly polished using a slurry containing aluminum oxide powder (0.05 μm). After polishing, the samples were ultrasonically cleaned in reagent grade acetone (10 min) and reagent alcohol (5 min). All tests were carried on the polished surfaces without etching in order to (1) reduce the probability of formation of surface films, and (2) to minimize the orientation effect on friction measurement. Friction tests were performed under unlubricated condition in ambient environment [($22 \pm 2\,^{\circ}C$, $45 \pm 5\%$ relative humidity (RH)].

Table 1
Composition of 3d transition metals under study

Metal	Purity (%)
Ti	99.2
V	99.5
Cr	99
Mn	99.9
Fe	+99.97
Co	+99.9
Ni	+99.9
Cu	+99.9

2.2. Friction measurement

Coefficients of friction of the metals in contact with Fe were measured using a universal micro-tribometer (UMT) provided by CETR, California, USA. Before the friction test, a small plate of iron with dimensions 4 mm × 4 mm × 1.2 mm slid reciprocally on a bigger dissimilar or similar metal sample under a load of 40 mN for six passes. The bigger samples had various dimensions (plates) with their surface areas large enough for the sliding process. The sliding distance was 6 mm for each pass and the sliding speed was 4 mm/s. The aim of this reciprocal sliding process was to remove a possible oxide scale or an adsorption layer on the surface. Single-pass sliding tests were then performed under different constant loads from 1 to 40 mN at a sliding speed of 3 mm/min over a sliding distance of 6 mm. Both normal load (F_N) and frictional force (F_L) were measured during the single-pass sliding process. Friction coefficients ($\mu = F_L/F_N$) of the transition metals against iron were obtained by averaging three measurements or more to ensure the consistency of the friction measurements.

3. Results and discussion

3.1. Friction measurement under light loads

Adhesion and friction of metals are surface phenomena and depend on physical and chemical properties of the met-

Table 2
Annealing temperature

Metal	Annealing temperature (°C)
Ti	500
Fe	500
Co	500
Ni	500
V	630
Cr	630
Mn	390
Cu	390

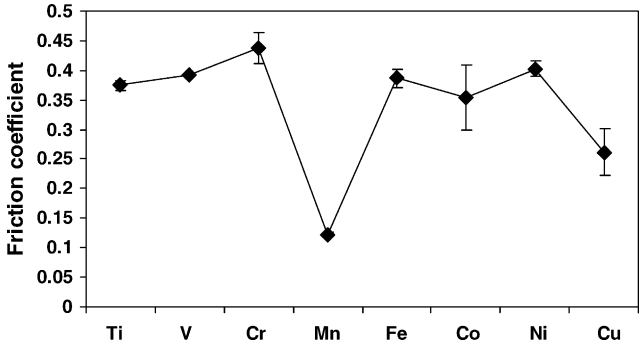

Fig. 1. Friction coefficients of 3d transition metals in contact with iron (under 30 mN).

als in contact, the contact force and surface condition, e.g., contamination [26]. When a friction test is performed in the ambient environment, the existence of oxide and adsorption is almost unavoidable [1,26]. Therefore, before each friction test, the top sample (iron) was slid on the bottom sample under a relatively large load (40 mN) to produce metal–metal contact in order to minimize the influence of oxide film or surface contamination on friction [5,26]. The combination of normal and tangential forces may remove contaminated surface layers so that direct metal–metal contact with clean and fresh surfaces could be obtained [5,27,28].

Microstructure and crystal structure certainly affect adhesion. As mentioned earlier, for a polished surface, the orientation effect could be minimized so that the determined adhesive force was more a measure of the atomic interaction, which largely depended on the electronic configuration of the tested metal.

Fig. 1 presents friction coefficients of 3d transition metals in contact with Fe measured under a low load (30 mN). Comparing with previously reported EWFs of the metals (Fig. 2) [29], there is no obvious relationship between EWFs of the individual metals and the measured friction coefficients. This is understandable, since in the present case, the adhesion and thus friction between two different metals under a light contact force are affected by the EWFs of both metals in contact. In order to explain the adhesion between two different metals based on their electronic behaviors, the adhesion between the two metals and their EWFs needs to be correlated.

3.2. Theoretical consideration

When two surfaces are brought into contact, the adhesion or the pull-off force is usually analyzed in terms of surface energy rather than the force [30]. Surface energy is an important property of materials: the energy required to form a surface, and is therefore closely related to the cohesive energy [1]. The surface energy is largely determined by the surface electronic structure [1,4,16]. Many models have been proposed to predict surface energies of solid surfaces [1,31,32]. Miedema [33] suggested an equation to relate the surface energy of a metal to its electronic properties, which has received experimental and theoretical supports [16,34]. This semi-empirical equation has the following form [33]:

$$\gamma_0^{\mathrm{s}} = \frac{n_{\mathrm{ws}}^{5/3}}{(\varphi^* - 0.6)^2} \quad (1)$$

where γ_0^{s} is the surface energy of a metal at 0°K, n_{ws} the electron density at the boundary of the Wigner–Seitz cell and φ^* is the parameter approximately equal to EWF of a metal and related to its electronegativity [29,33,35–38].

This semi-empirical equation suggested by Miedema includes EWF and electron density, which has also been applied in analyzing the heat for forming solid alloys [29,35]. These two parameters are properties of pure metals and related to the strength of metallic bonds. When two metals are brought into contact, electrons will flow from one metal to the other with a lower Fermi energy, resulting in a dipole layer at the interface [6,9,21]. In addition to reconstruct the Fermi surface at the interface, the electronic density must be continuous at the boundary between two corresponding Wigner–Seitz cells [29,36]. Therefore, the interaction between the two metals is related to the differences in EWF and the electron density between the two metals. For a metal in vacuum, its surface energy is only determined by the EWF and electron density of the metal [33]. Fig. 3 presents surface energies of 3d transition metals, calculated using Eq. (1). The incorporation of EWF into sur-

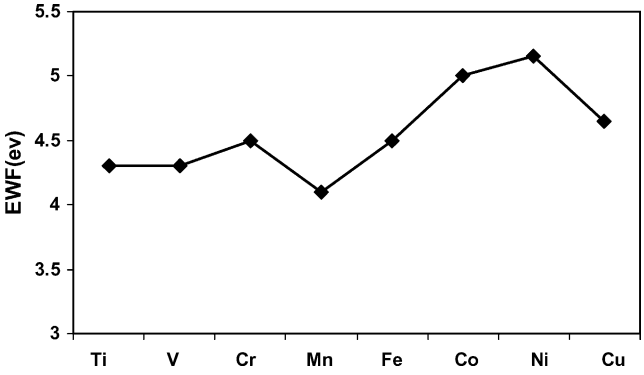

Fig. 2. EWFs of 3d transition metals from ref. [29] (Miedema's data).

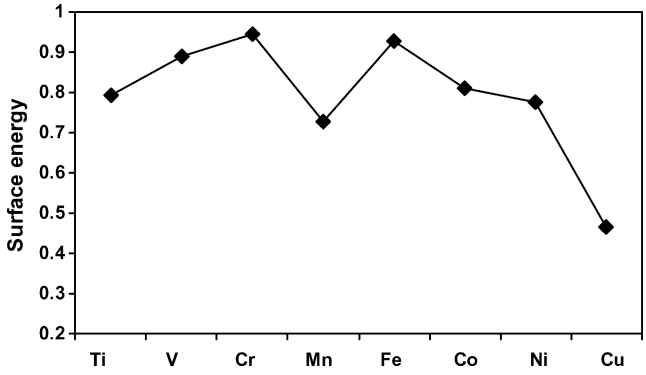

Fig. 3. Surface energy (dimensionless) calculated using Eq. (1).

face energy calculation can also be found in other models [31,32].

In order to separate two bonded surfaces (per unit area), a minimum energy, i.e. the adhesion energy is required [2,5]. The adhesion energy for a pair of metals A and B, may be expressed as a function of surface energies, γ_A^0, γ_B^0, of the metals A and B and the interfacial energy γ_{AB}^0 (Eq. (2)). The latter is the summation of the average interfacial configuration energy (γ^{geom}) and the chemical interaction energy (γ^{chem}) of the two metals (Eq. (3)) [39,40]:

$$-\Delta\gamma_{AB} = \gamma_A^0 + \gamma_B^0 - \gamma_{AB}^0 \quad (2)$$

$$\gamma_{AB}^0 = \gamma^{chem} + \gamma^{geom} \quad (3)$$

The average interfacial configuration energy is approximately expressed as [39,40]:

$$\gamma^{geom} = 0.15(\gamma_A^0 + \gamma_B^0) \quad (4)$$

So, the adhesion energy may be represented as:

$$-\Delta\gamma_{AB} = 0.85(\gamma_A^0 + \gamma_B^0) - \gamma^{chem} \quad (5)$$

Since γ^{chem} is a relatively small contribution to the total adhesion energy, it may be ignored in approximate calculations [39].

If EWF and n_{ws} are available, the adhesion energy for a pair of metals can be calculated based on Eqs. (1) and (5). Fig. 4 presents the result of such calculated adhesion energies between Fe and 3d transition metals. The values of EWF and electron densities come from ref. [38].

3.3. Further discussion

The frictional force results from two main sources. One is the adhesive force (F_{adh}) from the chemical interaction and the other is the mechanical force (F_{def}) involving asperity-plowing and deformation [23–25]. Under low loads, F_{adh} plays the main role in generating the frictional force, while under high loads F_{def} becomes predominant.

Our previous work [20] demonstrated variations in friction between a sharp ceramic tip and 3d transition metals with respect to the load. Under light loads, friction was largely contributed by adhesion; while under relatively high loads, the friction coefficient was mainly determined by the hardness of the metals. The friction coefficient of the 3d transition metals in contact with Fe under 30 mN (Fig. 1) shows no correlation with the hardness of the metals [20], so the plowing effect should not be dominant. Besides, fairly good agreement between the friction coefficients (Fig. 1) and calculated adhesion energies (Fig. 4) was observed. Therefore, it is believed that in the present study, 30 mN was low enough to have the friction dominated by adhesion between two metal samples with apparent contact area equal to 4 mm × 4 mm. It should be indicated that, if the contact force is too small, e.g., 1 mN, the measured friction is not stable with large fluctuation.

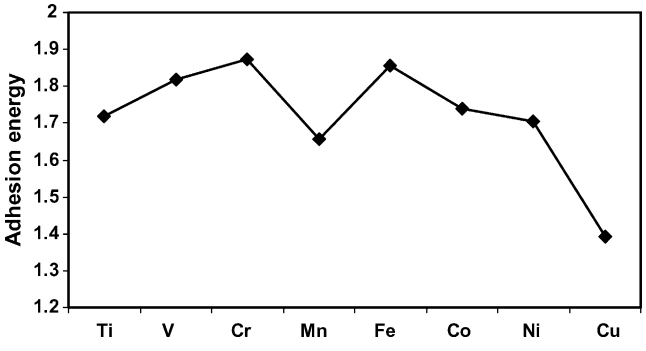

Fig. 4. Adhesion energy (dimensionless) for 3d transition metals in contact with Fe calculated using Eqs. (1) and (5).

In addition, previous studies on friction of 3d transition metals using atomic force microscope [20] showed that adhesion played a predominant role when a metal sample was in contact with a moving ceramic tip (radius: 20–60 nm) under a load within 50 nN. Assuming that the contact area was $\pi r^2 = \pi(40\,nm)^2$ under a load of 50 nN, one may find that the contact stress was approximately equal to $50\,nN/\pi(40\,nm)^2 \approx 1 \times 10^{-2}\,nN/nm^2$. This contact stress is much larger than the contact stress used in the present study. In the present friction measurement, the contact force was 30 mN and the apparent contact area is 4 mm × 4 mm, which resulted in a contact stress in the range of $2 \times 10^{-6}\,nN/nm^2$. This estimation may further support the argument that the measured friction in this study was mainly contributed by adhesion.

According to the definition of adhesion energy, the work required to separate two bonded surfaces is equal to the adhesion energy multiplied by the real contact area [2,5]. The real contact area is affected by mechanical properties of the two contacting solids and the applied load [2,12,24]. For the present friction measurements, the top sample (Fe) had the same apparent surface area. Under low loads, the influence of hardness on the real contact area could be negligible. Or in other words, the real contact area may be roughly the same for all target metals, so the magnitude of adhesion energy should reflect the adhesion between a pair of metals. Therefore, the frictional force determined under low loads mainly results from adhesion and may thus be predicted based on EWFs and electron densities of two metals in contact. Comparing the measured friction coefficients of the 3d transition metals in contact with Fe under 30 mN (Fig. 1) with the calculated adhesion energies (Fig. 4), one may see that these two parameters are basically consistent, although minor discrepancy exists. For example, the calculation (Fig. 4) indicates that the Fe–Cu contact should have a lower friction coefficient than the Fe–Mn contact, which is different from that experimentally determined (Fig. 1). The difference may be explained by considering the fact that Mn is much harder than Cu [20,41] so that the true contact area of the Fe–Mn contact is smaller than that of the Fe–Cu contact [24], thus leading to a lower friction coefficient for the Fe–Mn contact.

In this study, the surface energy was used to connect adhesion to the EWF and the electron density. Although the

relation between surface energy and the electron behavior is very complicated, such a relation may, however, be described using a simple semi-empirical equation such as Eq. (1), which makes it possible to predict, quickly and approximately, the adhesion between a pair of different metals based on their electronic properties.

4. Conclusions

Friction between iron and 3d transition metals under low loads were investigated. Efforts were made to determine the correlation between the electron work functions of the metals and their adhesion and thus friction between the 3d transition metals under light loads. It was demonstrated that the adhesion and friction between two metals under light loads could be predicted based on their electron work functions and electron densities.

The correlation among adhesion, EWF and electron density is of importance to material selection and friction control for nano/micro devices in which friction is dominated by adhesion.

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