

"Influence of surface morphology on corrosion and electronic behaviour" -

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Keywords

Corrosion, Roughness, Work Function, WF, Kelvin Probe

Abstract

Electrochemical or mechanochemical behaviour of a surface, such as corrosion or corrosive wear, is extremely complicated and involves various chemical, physical and mechanical factors. To gain a thorough insight into such a complex phenomenon, it is necessary to understand the role of each factor. In this study, the influence of surface morphology, represented by roughness, on the corrosion and electronic behaviour, represented by the electron work function (EWF), of copper was investigated using an atomic force microscope and a scanning Kelvin probe. Experimental results showed that the corrosion rate increased with an increase in surface roughness, whereas its surface EWF decreased. It was theoretically demonstrated that roughness can decrease the average EWF but increase the fluctuation of the local EWF. Such fluctuation could promote the formation of microelectrodes and, therefore, accelerate corrosion. The study demonstrates that the surface morphology can make a considerable contribution to corrosion and thus corrosive wear.



Figure 1. KP Technology RHC020 Corrosion/Environmental Housing Kelvin Probe System.



Research Area

Electrochemical or mechanochemical behaviour of a surface is extremely complicated and involves various chemical, physical and mechanical factors. For example, surface wear of a material depends strongly on the material properties, external force, surface conditions, and environmental conditions, such as temperature. The involvement of different parameters makes it difficult to investigate the wear mechanism. In particular, when a material is worn in a corrosive medium, i.e. corrosive wear, the failure process becomes much more complicated. In such cases, the combined effect of wear and corrosion can render the total material loss much greater than that caused by corrosion or wear alone.

Corrosive wear is one of the common failure modes encountered in various industries (e.g., mining, petroleum, oilsands and marine transportation) and can cause severe damage to machinery and equipment. It is, therefore, necessary to develop effective approaches to fundamentally investigate corrosive wear and relevant processes.

During a corrosion process, material loss occurs through electrochemical reactions at surfaces. The localised electrochemical reactions may cause pitting, intergranular or intragranular corrosion. From the viewpoint of thermodynamics, the exchange of electrons between a metal and environment constitutes an electric current at the metal surface. It is, therefore, essential to investigate the relationship between the electronic behaviour and corrosive wear in order to understand the synergy of corrosion and wear. As a fundamental characteristic of a solid surface, the electron work function (EWF) usually refers to the minimum energy required to remove an electron from the interior of a solid to a position just outside the solid. The EWF of a metal surface reflects the electronic energy level and is, therefore, related to its electrode potential.

The EWF can be determined using a Kelvin probe, which has been applied to study corrosion and relevant electrochemical behaviour of metals. The Kelvin probe is also used to study the kinetics and mechanism of corrosion-driven delamination processes. Recently, attempts have been made to investigate various material behaviours using the Kelvin probing method. As a complicated wear mode, corrosive wear involves both mechanical and chemical processes. In general, the wearing force on a surface leads to changes in surface roughness and deformation (lattice distortion dislocations). These changes could play crucial roles in determining the corrosion behaviour of the surface and may thus accelerate the wear damage to the surface.

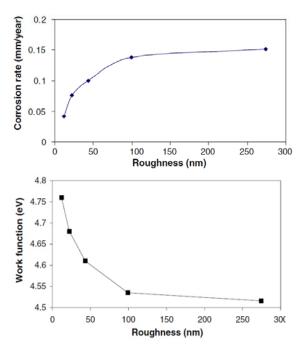
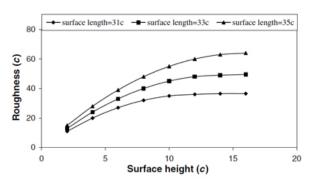


Figure 2. a) Variations in Corrosion Rate to Roughness and b) Variations in EWF to Roughness



It is, therefore, of importance to study the interaction between corrosion and deformation and to establish relationships among electronic behaviour, chemical activity, corrosion and strain, and surface morphology for thorough understanding of the mechanism responsible for



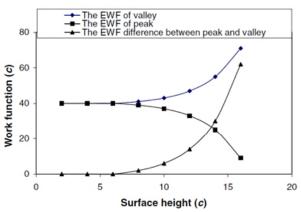


Figure 3. a) Theoretical variations in roughness with respect to the lattice heights for different lattice lengths. b) Theoretical variations in EWF with respect to lattice height when lattice length was set as 33c

corrosive wear. However, conventional testers are not effective characterising corrosive wear. Recent studies have demonstrated that the Kelvin probe is a promising tool for the investigations of corrosion behaviour due to its high sensitivity to changes in the EWF (<10 mV) and high spatial resolution (down to a few tens of nm). It is noted that in these recent studies, the influences of various parameters such as surface composition, solution exposure time, relative humidity, impurity concentration, and interfacial interactions on the measured corrosion /surface potential have been investigated. However, the effect of surface morphology, which may play an important role in determining corrosion behaviour, has never been addressed. The authors have made considerable efforts to investigate various material behaviours using a SKP and to explore theoretically the correlation between the EWF and various factors, including dislocations, grain boundary, crystallographic orientation, deformation, yielding, adhesion, and wear onset.

Use of Kelvin Probe

The EWF of specimens having different roughness before corrosion test was determined using a SKP that was provided by the KP Technology Ltd. The principle of operation and experimental procedure of the SKP system to measure EWF has been described in detail in previous studies. Briefly, the principle for this Kelvin system is exquisitely simple: the formation of a capacitor to allow electronic conduction and to detect the charge transfer. In practical operations, the Kelvin capacitor consists of the two plates face to face. By vibrating one plate (Kelvin probe tip) relative to the other (sample surface) at a certain frequency, the current flow is generated in the external circuit. By nullifying the current with a backing voltage in series with the vibrating Kelvin probe, the sample EWF can be determined. The system had a high-resolution ($<50~\mu\text{eV}$) and the probe spacing could be controlled within 40 nm. In the present study, a gold tip with a diameter equal to 0.1 mm was used, and the scanning area was 0.2~x~0.2~mm; the frequency of the Kelvin probe was set as 173 Hz.



Conclusion

Research was conducted to investigate effects of surface morphology on corrosion behaviour. Experimental results showed that the corrosion rate of copper increased with an increase in surface roughness, while the surface electron work function decreased. Theoretical studies demonstrated that the roughness affected not only the overall EWF of a surface but also its local EWF fluctuation. It is easier for electrons in the vicinity of a peak to escape than those in a valley, so that the peak would be corroded preferentially. The EWF fluctuation increased with an increase in roughness and may also promote the formation of corrosion cell that could further accelerate corrosion of a rough surface. From a thermodynamic point of view, the EWF is closely related to surface potential and could be used to evaluate corrosion behaviour.

Reference

1. Original publication: "Influence of surface morphology on corrosion and electronic behaviour" - W. Li, D.Y. Li

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