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Effect of surface geometrical configurations induced by microcracks on the electron work function

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Abstract

Fracture or failure of materials usually results from the initiation and propagation of microcracks. In particular, surface behavior of a material such as wear and/or corrosion depends strongly on the geometry of microcracks. In this study, the effect of microcrack configurations on the local surface electronic activity, which can be represented by the electron work function (EWF), were investigated using the theoretical approach and the Kelvin probing technique. We proposed a micro capacitor model to calculate variations of the EWF with respect to the geometrical parameters of microcracks. It was demonstrated that the EWF depended strongly on the position, angle and orientation of microcracks. Using a scanning Kelvin probe, measurements of the EWF were conducted to verify the theoretical calculations. The experimental observations showed basic agreement with the calculated results. This model could be useful for thorough understanding of the electronic mechanisms responsible for electrochemical and mechanochemical behaviors of a surface containing microcracks.

Keywords: Work function; Microcrack; Kelvin probe; Corrosive wear

1. Introduction

The damage or failure of a material subjected to mechanical loads may manifest itself through two main modes: rapid fracture or gradual wear [1–3]. Microcracks, whether pre-existing or initiated and propagated by external forces, have an important influence on these two modes and thus play a crucial role in determining the service life of a material [4,5]. For example, pre-existing surface flaws, inside blowholes and fissures, and microstructural defects and cavities always make material fracture or failure occur at a lower stress than it would for a perfectly crystalline material [4]. Even for a perfect crystalline material, dislocations can be initiated when the mechanical load reaches a critical level [4,6]. Accordingly, the dislocation pile-ups associated with the local high stress may lead to the occurrence of microcracks, which is the origin of unexpected fracture or invariable wear. In particular, if a material is worn in a corrosive medium, obviously, surface microcracks will also affect corrosion behavior; meanwhile, surface corrosion can further enhance wear rate [7–9]. In this case, the combined effects of wear and corrosion may become more severe, and hence render the total material loss much greater than those caused by corrosion and wear, respectively [10,11]. It is therefore necessary to relate microcrack history (initiation and propagation) and geometry to corrosion behavior in order to completely understand the mechanism of corrosive wear.

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The effect of the geometrical parameters of microcracks on corrosion behavior has been investigated experimentally and theoretically over the past few decades [12–15]. However, because of the size effect of microcracks and electrochemical reactions at microcrack tips, micro-mechanisms responsible for corrosion behavior still remain unclear. As a result, experimental observations from different researchers are inconsistent. For example, while there is hardly any correlation between microcrack geometry and the corrosion parameter [16], it was argued that a manifest correlation between microcrack width and the corrosion rate of steel was observed [17]. On the other hand, a corrosive medium can give rise to the initiation and propagation of microcracks due to the early formation and development of corrosion pits, subsequently assisting in the failure of whole material. Studies involving this early stage of microcracks are now becoming increasingly important [18–20]. However, this stage of microcracks is related to various factors such as the nature of the material (composition, microstructure and microsegregation), electrochemical conditions (pH, temperature, electrode potential, etc.), and applied stresses [20]. It is therefore important, but difficult, to predict microcrack behaviors under corrosive conditions (i.e., the location and growth rate of microcracks).

In general, linear elastic fracture mechanics and elastic–plastic analytical methods as well as microstructural fracture mechanics approaches can be used to predict initial microcrack development and growth [18–22]. However, in some sense, the microcrack behavior in a corrosive medium is governed by the corrosion mechanism. Anodic dissolution or corrosive embrittlement can cause localized damage giving rise to sites at which microcracks may develop [5]. Such mechanochemical behavior in the vicinity of a microcrack tip cannot be treated using the above-mentioned approaches that do not involve the microcrack tip chemistry [23,24]. Since electrochemical mechanisms are responsible for corrosion behavior, electronic parameters of a local surface should be taken into account in order to gain a thorough insight into the microcrack behavior in a corrosive medium.

As a fundamental parameter of electronic structures, the electron work function (EWF), which usually refers to the minimum energy required to remove an electron from the interior of a solid to a position just outside the solid [25], can be related to the electronic activity of a solid surface. The EWF reflects the electronic energy level of a metal surface and is therefore related to electrode potentials or corrosion potentials [26–29]. The EWF can be easily determined using the Kelvin probe technique, which has been applied to study corrosion and related electrochemical behavior [28], such as the kinetics of corrosion-driven delamination processes [29], due to its high sensitivity to change in the EWF (<10 mV) and high spatial resolution (down to a few tens of nanometers) [30]. Recently, attempts have been made to investigate material behaviors (e.g., plastic deformation [31], friction [32], wear [33], adhesion [34], surface roughening [35] and interfacial bonding [36]) using a scanning Kelvin probe.

In the present study, we investigate experimentally and theoretically the local configuration effect of microcracks on the EWF in order to model the electronic activity of a complex surface. The objective is to employ the Kelvin probing technique for characterizing the local surface potential distribution of a surface containing microcracks under corrosive conditions, from which corrosion activity and further corrosive wear rate may be evaluated.

2. Modeling

Generally, the EWF (Φ) is represented as [30,33]

$$\Phi = E_0 - E_F, \quad (1)$$

where E_0 is the energy of electron in infinity and E_F is the Fermi energy.

The principle of the Kelvin probe method to measure the EWF is exquisitely simple: namely, the formation of a capacitor, allowing electronic conduction and detection of the charge transfer [25,30,32,33]. In practical operations, the Kelvin capacitor (C) consists of the two plates face to face. By vibrating one plate (Kelvin probe tip) relative to the other (sample surface) at a frequency f, current flow is generated in the external circuit, as shown in Fig. 1. This current can be described in terms of the geometry of the capacitor and the contact potential differences between the two metals. The current in the external circuit is given by [30,33]

$$i = C(\mathrm{d}V/\mathrm{d}t) + V(\mathrm{d}C/\mathrm{d}t), \quad (2)$$

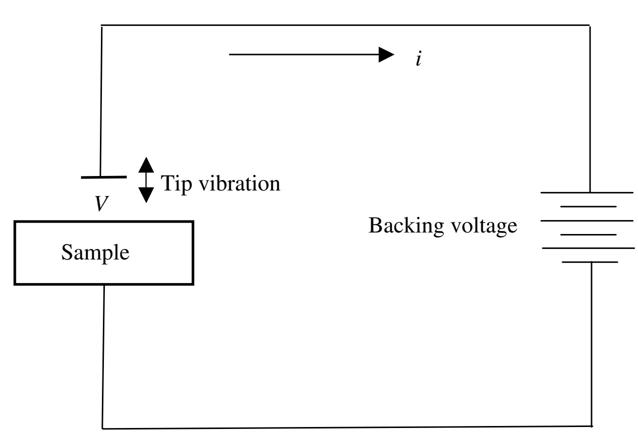

Fig. 1. Schematic diagram illustrating the principle of the Kelvin probe method to measure the EWF.