

Corrosion Potential Imaging at the Interface of Coating/Metal by a New Electrochemical Technique

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As the corrosion reactions of metals beneath coating are mainly electrochemical in nature, a number of the electrochemical techniques, including dc and ac methods, have been used to study the corrosion behavior of coated metals^[1~3]. One of the most advantages of the electrochemical techniques are not only able to in situ evaluate the corrosion performance for a coated metals, but also to study the mechanism of corrosion process at the interface of metal/coating. The great attempts have been made to measure the potential distribution at the interface of metal/coatings^[4~8]. The potential imaging at the interface of coating/metal is possible to provide a deeper insight into the process of water and corrosion related ions through the coatings, corrosion reaction mechanism of metals beneath organic coating and the defects distribution in the coatings and its effects on the corrosion initiation of coated metals. Information on the interfacial potential is useful for studying the physicochemical process at the interface, coating inhomogeneity and mechanism of corrosion reactions of coated metals. However the conventional electrochemical techniques are not suited for measuring the corrosion potential at the interface of metal and coating because of the polymer film with high resistance on the metal surface. Thus, there is a need to develop a new electrochemical technique to map the corrosion potential distribution at the interface of metal/coatings.

The technique consists of 64-electrode array and micro-computer aided mapping system. The electrode, which are imbedded in an epoxy mounting compound, are made of 0.3 mm diameter, epoxy-insulated steel wires, and assembled as a 8 × 8 array. After fabricating, the imbedded, insulated electrodes (probe) are cut perpendicular to the wire length, leaving the ends of the 64 wires exposed. After polishing and cleaning, the coating to be studied is applied on the probe cross section, and a corrosion cell is then attached on the probe coated surface. By removing the coating after each use, the 64-electrode array probe can be used repeatedly. The corrosion potential mapping system includes an analog switch with multi-channel inputs, an analog/digital converter, and a personal computer. The experimental arrangement is shown in figure 1. When the analog multi-channel switch is on, all 64 electrodes

of the array connect one with the others, simulating a continuous piece of steel having a surface area equal to the total area of the cross sections of all 64 electrodes when the analog multi-channel switch is off, all of the electrodes of array disconnect temporally (approx. 1ms). During this period, the corrosion potential value of the each of the 64 electrodes is measured, referred to a platinum electrode in the solution. The experiment procedure of the multi-channel switch is controlled by a microcomputer. The analog multi-channel switch is always maintained in the 'on' state, unless the corrosion potential acquisition for the 64 individual electrodes is performed under the microcomputer management. The corrosion potential for each individual electrode is acquired for several times and averaged. The format of data is processed to fit 'Surfer' software to plot in three dimensional stereo map or potential contour.

Figure 2 is the corrosion potential imaging for the specimen with a gentle scribe on the nitro lacquer coating. It is indicated that the anodic site of corrosion reaction locates on the scribe line when immersed in 0.5 mol/L NaCl solution for 4 hours. The corrosion potential at anodic position shifts negatively from -40 mV at beginning to -620 mV at 72 hours immersion. The interfacial corrosion reactions develop rapidly at the location of scribe defects. Corresponding to the peak on the corrosion potential map, a green corrosion products under the coating appear at defect site in the early

Fig. 1 Experimental arrangement for the measurement of corrosion potential distribution at the interface of polymeric coating/metals

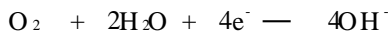
Fig. 2 Corrosion potential imaging for the nitro lacquer coating with gentle scribe defect on the array electrode at different immersion time in 3% NaCl solution, a: 4 h, b: 24 h

stage of immersion. Corrosion under the coating grows speedily at this position because the scribe defect provides a pathway for water and corrosion related ions into the interface of coating/metal. The location for both anodic and cathodic area and their variation with time are illustrated clearly by the corrosion potential imaging.

It is well recognized that the polymeric coatings applied on the substrate are usually non-uniform and with numerous different kinds of defects in the coatings, and also at the interface between coatings and substrate surface. The defects in the coatings are of strong effects on the corrosion initiation beneath coatings. The defects often play a determined role in the degradation process for polymeric coated metals in some cases. The corrosion images indicate that there exist a number of different kinds of defects in the coating including the intrinsic defects, and damages in the service. Corrosion always initiates at the defect sites, by which the water and the corrosion related ions preferentially reach to the interface to promote the corrosion process. In situ mapping of the defects in the coatings and investigating the effects of inhomogeneities on the initiation and development of degradation for a protective coating system are one of the most important projects in modern coating science and technology. Accordingly, the corrosion potential mapping by the array electrode can be as an unique and useful technique for studying the inhomogeneities of polymeric coated metals.

It is noted, from the direct mapping of corrosion potential at the interface (Fig. 3), that the cathodic reaction is always accompanied with the anodic reaction, and cathodic zone locates near by the anodic sites during the corrosion process of metal under the organic

coatings. The electrochemical reactions of the corrosion process happen at anodic and cathodic location in the neutral NaCl solution is typically as follows:



The corrosion potential imaging is not only able to locate the anodic area and cathodic position, but also to follow their development with the immersion time. The anodic reaction leads to the dissolution of the steel. The corrosion products may be different depending on the micro chemical environments at the interface of coating/metal. The corrosion products

Fig. 3 Corrosion potential imaging at the interface of the nitro lacquer coating and array electrode at different immersion time in 3% NaCl solution, a: 72 h, b: 136 h

beneath coating are green (ferrous oxides) at beginning because of oxygen deficiency, then became dark yellow (ferric oxides) for further oxidation. The reduction of oxygen at cathodic area produces an alkali environment under the coating, which will result in the delamination of coating on a substrate. The anodic area grows with the development of coating debonding from metal surface at the cathodic location. This is a degradation characteristic for the organic coated metals, which is revealed by the array electrode technique for the first time.

The array electrode and the microcomputer aided measuring system, as a new electrochemical technique, for imaging the corrosion potential at interface of the polymeric coating/metal have been developed. It is suitable to be applied to in situ image the inhomogeneities in the polymeric coatings, to follow the transport process of water and the corrosion related ions through the coatings, and to study the corrosion mechanism of initiation and propagation of metals beneath the coatings. The relevant and direct information provided by this unique technique will be very helpful for further understanding the physicochemical process associated with degradation of organic coated metals.

Key words Potential imaging, Interface of polymeric coating/metal, Array electrode, Corrosion mechanism under coatings

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一种测量聚合物/金属界面腐蚀电位分布 的电化学新方法

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摘要 在绝大多数环境下, 聚合物/金属界面的腐蚀破坏的本质是电化学过程, 因此, 不少电化学技术, 包括直流稳态技术和交流阻抗技术等被广泛用于研究金属/聚合物界面的腐蚀破坏机制, 评测有机涂层的耐蚀性能。然而, 由于聚合物/金属界面腐蚀破坏的“闭塞”条件和聚合物膜层的高绝缘性, 传统的电化学方法均不能直接获得聚合物/金属界面二维空间的腐蚀电位分布, 难以直接研究聚合物/金属界面的腐蚀破坏过程及相关的影响因素。聚合物/金属界面腐蚀电位的测量有助于研究聚合物/金属等复合材料界面腐蚀破坏机理, 评测有机聚合物涂覆层的耐蚀性能。本文提出一种微计算机控制的阵列电极技术, 用于原位测量金属/聚合物界面电位分布。首次建立了 8×8 阵列电极和微机控制的阵列电极测量系统, 可直接测量聚合物/金属界面腐蚀电位的二维分布。由此可深入研究有关腐蚀物种在聚合物相内传输过程, 聚合物涂层的不均一性及缺陷分布, 以及聚合物/金属界面腐蚀的发生、发展机制。应用阵列电极技术首次在原位获得聚合物涂层的缺陷分布及不均一性, 并考查了聚合物涂层缺陷对诱导聚合物/金属界面腐蚀破坏的关系。阵列电极技术还首次提供了在聚合物/金属界面腐蚀破坏发展过程中阴、阳极同时存在, 共同发展的直接的实验证据。

关键词 腐蚀电位显象, 聚合物/金属界面, 阵列电极技术, 涂层下腐蚀机理