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A novel method to measure the residual stress in a corrosion film formed on metallic substrates

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ABSTRACT

This paper theoretically proposed a series of formulae for a novel tensile testing method to extract the residual stress in the surface film on metallic substrates. Finite element calculations were conducted to verify the accuracy and reliability of the proposed formulae. From the tensile stress–strain curves of metallic substrates with and without a surface film, one can evaluate the residual stress in the film using these formulae. A tarnish film on a brass substrate formed after immersion in Mattsson's solution was tested to demonstrate these methods, and the obtained residual stress showed a low difference below 6.8%.

1. Introduction

Residual stress in a film is a key characteristic related to its mechanical properties. Many techniques have been proposed to measure the residual stress in films by researchers for over a century, such as X-ray or electron diffraction techniques [1–3] and beam bending methods [4–21].

Corrosion product film-induced stress and the residual stress in films deposited by electrolysis are important in the corrosion research and the electrolysis industry. However, the X-ray diffraction technique is not suitable to measure the residual stress in the corrosion product film due to the amorphous nature. The beam bending method is widely used to measure the stress in the corrosion product film [4–15] or electrolysis layer [16–21] on a metal substrate, based on the formula:

$$\sigma = \frac{Et^2\delta}{3(1-\nu^2)L^2 d} \quad (1)$$

where δ is the deflection at the free end of the foil, E and ν are the Young's modulus and Poisson's ratio of the metal substrate, L and t are the length and thickness of the substrate and d is the thickness of the film layer where the stress is generated.

The beam bending method was first proposed by Stoney [16] to measure the stress in metallic films deposited by electrolysis. It has been widely used to determine the stress in films formed on metallic materials during the anodic oxidation [4–11] and stress corrosion cracking [12–15] processes. However, mechanical assumptions and geometric restrictions must be taken into account before the beam bending method is applied. Eq. (1) is only valid for a film with thickness much smaller than the substrate; typically a thickness ratio of 1/20 is acceptable [21]. Additionally, the length-to-width ratio has to be as large as possible so that the influence of transverse deformation can be neglected [22].

In using the beam bending method, a metallic strip specimen is coated on one side with a lacquer to make that side inert. One end of the strip is fixed, and a small mirror is attached to the free end. When the uncoated side of the strip specimen is exposed to the solution, a film is formed on the uncoated surface and a stress is generated in the film that causes the strip to bend and the free end to move. By measuring the deflection of the free end of the strip using a laser beam, the stress in the film can be extracted using Eq. (1). However, in practice, the beam bending method is actually quite troublesome. Experimental error is introduced into the measured stress that causes significant scatter due to the uncontrolled lacquer characterization (such as the thickness and the mechanical properties of the lacquer) on the inert side, and the reflection of the laser beam.

The flow stress in metallic materials is only dependent on plastic strain. If a metallic strip is loaded above its yield stress σ_Y, the inter-atomic bonds stretch. If the load is then removed, the inter-atomic bonds recover to their initial state and any plastic strain (σ_{pl}) remains, as shown in Fig. 1. Prior to unloading, the total strain for the flow stress σ_f is $\varepsilon_f = \varepsilon_{pl} + \varepsilon_{el}$ ($\varepsilon_{el} = \sigma_f/E$, E is Young's modulus). When the specimen is reloaded, the dislocation generation and movement does not occur again until the applied stress reaches the flow stress σ_f prior to unloading. During repetitive

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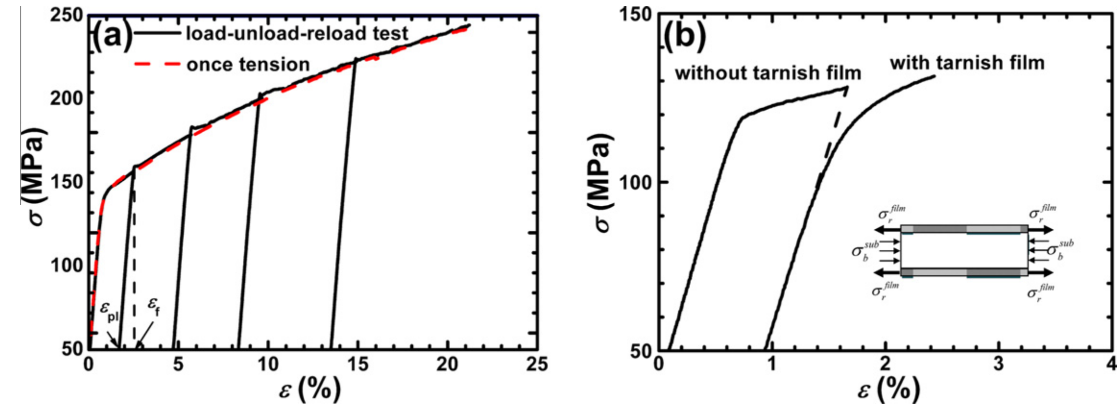

Fig. 1. The stress–strain curves for the load-unload cycle of an H62-brass (a). The stress–strain curves of an H62-brass with and without and with tarnish film formed by immersing in Mattsson's solution for 3 h and dried in air after washing with deionized water (b).

loading and unloading, a stress–strain curve is created similarly, as shown in Fig. 1a.

When a film forms on a metallic substrate, a residual stress σ_r^{film} is generated in the film. According to the force balance, a stress σ_b^{sub} with the opposite sign will be generated within the substrate. When the metallic substrate is placed in tension, the applied stress σ_A, with a balance stressσ_b^{sub}, in the substrate act together to deform the substrate. The stress–strain curve changes compared to the substrate without surface film, as shown in Fig. 1b. Based on the distinguishing characteristics of the stress–strain curves of the substrate with and without the surface film, the residual stress in the film can be extracted.

The objective of this paper is to examine a novel method to measure the residual stress in the film formed on a metallic substrate using tensile tests. A theoretic analysis formula relating the yield and the flow stress in the metallic substrate with and without a surface film and the residual stress in the surface film is derived first. A finite element method (FEM) was used to check the accuracy and reliability of the proposed method. A tarnish film formed on a brass substrate by immersing in Mattsson's solution was tested to demonstrate the proposed method. The residual stress in the film was extracted from the experimental stress–strain curves of the substrate with and without the tarnish film.

2. Theoretical analyses

First, we assume that the residual stress in the film and the balance stress in the substrate are uniformly distributed in the film and the substrate. According to the force balance:

$$\sigma_b^{sub} = -\frac{d}{t}\sigma_r^{film} \tag{2}$$

where d and t are the thickness of the film and the substrate, respectively, as shown in the insert of Fig. 1b. When the metallic substrate with the surface film is placed under an applied stress σ_A, the total stresses in the film and the substrate, respectively, are:

$$\sigma_t^{film} = \sigma_A^{film} + \sigma_r^{film} = \frac{E_{film}}{E_t}\sigma_A + \sigma_r^{film} \tag{3}$$

$$\sigma_t^{sub} = \sigma_A^{sub} + \sigma_b^{sub} = \frac{E_{sub}}{E_t}\sigma_A + \sigma_b^{sub}, \tag{4}$$

where $\sigma_A^{film} = \sigma_A E_{film}/E_t$ and $\sigma_A^{sub} = \sigma_A E_{sub}/E_t$ are the applied stress components in the film and the substrate, and E_t is the reduced Young's modulus of the substrate with the surface film and is defined as:

$$E_t = \frac{d}{d+t}E_{film} + \frac{t}{d+t}E_{sub} \tag{5}$$

When the applied tensile stress reaches a critical value, i.e., $\sigma_A = \sigma_Y^{*sub}$ ((σ_Y^{*sub} is defined as the measured yield stress of the substrate with the surface film), the total stress in the substrate σ_t^{sub} reaches the yield stress of the substrate σ_Y^{sub}, and the substrate with the surface film will yield. In this case, we use Eq. (4) to derive:

$$\sigma_t^{sub} = \frac{E_{sub}}{E_t}\sigma_Y^{*sub} + \sigma_b^{sub} = \sigma_Y^{sub} \tag{6}$$

Combining Eq. (2) with Eq. (6), we find that:

$$\sigma_r^{film} = -\frac{t}{d}\left(\sigma_Y^{sub} - \frac{E_{sub}}{E_t}\sigma_Y^{*sub}\right) \tag{7}$$

Thus, if the yield stress σ_Y^{*sub} of a substrate with a surface film is obtained, and the Young's modulus of the substrate and the film are known, the residual stress in the film can be calculated according to Eq. (7). This method is called the Difference in Yield Stress Method (DYSM) in this paper.

However, in practice, E_{film} and E_t are not well known with sufficient accuracy. A method to derive the residual stress without having to know the Young's modulus is more useful. As shown in Fig. 1a, in the load-unload-reload process of metallic materials, the yield stress for the reloading process is equal to the flow stress prior to unloading. If the film is deposited on the unloading metallic substrate, and the substrate with the film is reloaded to a critical stress of $\sigma_A = \sigma_Y^{**sub}$ σ_Y^{**sub} is the nominal yield stress of the loaded substrate with surface film), the total stress in the substrate σ_t^{sub} will reach the flow stress of the substrate without a film prior to unloading, σ_f, which make the substrate with film to yield. So it can be derived from Eq. (4):

$$\sigma_t^{sub} = \sigma_A^{sub} + \sigma_b^{sub} = \frac{E_{sub}}{E_t}\sigma_Y^{**sub} + \sigma_b^{sub} = \sigma_f \tag{8}$$

Combining Eq. (2) with Eq. (8), we find that:

$$\sigma_r^{film} = -\frac{t}{d}\left(\sigma_f - \frac{E_{sub}}{E_t}\sigma_Y^{**sub}\right) \tag{9}$$

Form Eq. (9), the flow stress is:

$$\sigma_f = \frac{E_{sub}}{E_t}\sigma_Y^{**sub} - \frac{d}{t}\sigma_r^{film} \tag{10}$$

From Eq. (10), we can extract the residual stress in the film from the $\sigma_f \sim \sigma_Y^{**sub}$ curve without knowing E_{film} and E_t. This method is called the Difference in Flow Stresses Method (DFSM) in this paper.