

**Composition-Gradient  $\text{Al}_2\text{O}_3\text{:Nb}$  Nanocomposite Thin Films Having Self-healing Corrosion Protection Ability**

K. Sugimoto, M. Yasuda, N. Akao, and N. Hara

Department of Metallurgy, Graduate School of Engineering,  
Tohoku University  
Aza-Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

**INTRODUCTION**

Artificial passivation films, which are formed to simulate the composition, crystal structure, and thickness of passive films on corrosion-resistant alloys, have been expected to use as very thin protective coatings having extremely high corrosion resistance.

In the use for protective coatings, it comes into question whether through pinhole defects exist in the films or not. If pinholes exist, localized corrosion may occur on substrate metal at the site of pinholes. Then, it also comes into question that when the films are broken by mechanical damages, the films should lose the protection ability at the damaged site and corrosion occurs at the site. Therefore, if the films have extremely low pinhole density and high self-healing ability, the films will obtain high confidence as corrosion protection coatings.

The purpose of the present study is to develop  $\text{Al}_2\text{O}_3\text{:Nb}$  nanocomposite thin films with low pinhole defect density and high self-healing ability. To realize this purpose, the relationship between the pinhole defect density and the composition of the films was first examined. Then, based on the result, to satisfy both low pinhole defect density and high self-healing ability, composition-gradient  $\text{Al}_2\text{O}_3\text{:Nb}$  films were formed. The equipment of self-healing ability by alloying Nb has been reported by present authors on  $\text{Al}_2\text{O}_3$  films (1) and  $\text{Fe}_2\text{O}_3\text{:Cr}_2\text{O}_3\text{:Ta}_2\text{O}_5$  films (2).

**EXPERIMENTAL**

$\text{Al}_2\text{O}_3\text{:Nb}$  films ca. 150 nm thick with various composition were prepared on a Fe film substrate 200nm thick on a glass slide by ion-beam sputter deposition technique. The distribution of composition inside the films was also changed. The composition of the films prepared was analyzed by ICPS, AES, and XPS. The micro- and crystal structures were analyzed by TEM and ED.

The pinhole defect density of the films was evaluated from the density of pits formed at the site of the pinhole on the Fe film substrate after the films were immersed in 0.1 M NaCl, because the films are insoluble and the Fe film substrate is soluble in the solution.

The self-healing ability was evaluated from the repassivation behavior of potential and current of the  $\text{Al}_2\text{O}_3\text{:Nb}$  film / Fe film substrate specimen just after giving a knife-scratch in 0.1 M NaCl. In the measurement system, the specimen was connected to an Au auxiliary electrode via an OP amplifier and short-circuit current and potential between the Fe film and the Au electrode appear just after knife-scratching.

**RESULTS**

The pinhole defect density of  $\text{Al}_2\text{O}_3\text{:Nb}$  films increased with increasing Nb content and attained a maximum at 15 mol% Nb. Then, it gradually decreased with increasing Nb content. This means that, to use the films as corrosion-protection coatings, decreasing Nb content is needed for decreasing pinhole defect density. However, increasing

Nb content is needed for increasing self-healing ability. To solve this contradiction, composition-gradient  $\text{Al}_2\text{O}_3\text{:Nb}$  films were introduced.

Four types of composition-gradient  $\text{Al}_2\text{O}_3\text{:Nb}$  films were prepared. The types of films were expressed according to the change in Nb content from the top of film to the bottom of film, like Nb content (top)-Nb content (bottom). Here, Nb content is given in mol%. The films prepared were 13(top)-95(bottom) Nb, 0(top)-96(bottom) Nb, 58(top)- 0(bottom) Nb, and 0(top) - 91(middle)- 0(bottom) Nb.

Among these films, the film 0(top)-96(bottom) had good self-healing ability as shown in Fig.1. There was no pitting on a knife-scratch line and also on a free surface. The other films showed more or less pitting on these parts.

**SUMMARY**

The pinhole defect density of  $\text{Al}_2\text{O}_3\text{:Nb}$  films increases with increasing Nb content. The addition of metallic Nb component is, however, needed to give the self-healing ability to  $\text{Al}_2\text{O}_3\text{:Nb}$  films. The composition-gradient  $\text{Al}_2\text{O}_3\text{:Nb}$  film of 0(top)-96(bottom) Nb is the best solution to satisfy both the good self-healing ability and the good corrosion-protection ability.

**REFERENCE**

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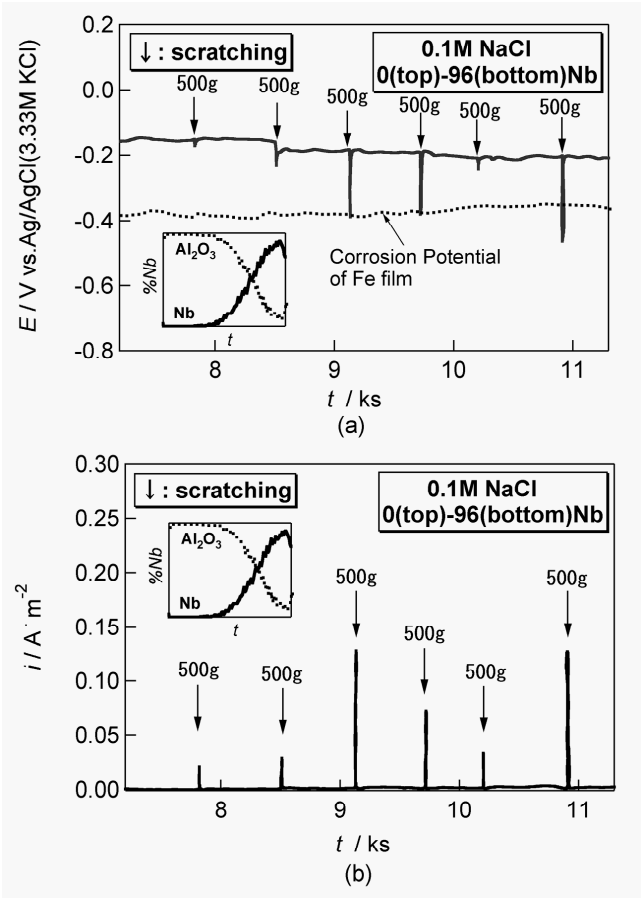


Fig. 1 Potential  $E$  (a) and current density  $i$  (b) as a function of time  $t$  for 0 (top)-96 (bottom) Nb film 154 nm thick on Fe substrate film coupled with Au auxiliary electrode after scratching in aerated 0.1 M NaCl.