Thick Porous Oxide Layer on Fe-Cr and Ni-Cr Alloys Formed by Square Wave Potential Pulse Polarization

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Passive films formed on Fe-Cr alloys, such as stainless steels, have the function to protect the substrate alloy from environmental degradation and accommodate their structure, thickness, and chemical composition to their environment most suitably. Therefore, passive films of Fe-Cr alloys formed in the aqueous environment are usually very thin, compact, and highly Cr enriched. Recently, production of the oxide films with well-ordered structure is one of the objectives to obtain a novel surface function of metallic and/or inorganic materials.

As previously reported[1)-4], extraordinarily thick and porous oxide and/or hydroxide films can be obtained on austenitic stainless steels, Fe-18Cr alloy, and Ni-18Cr alloys by square wave potential pulse polarisation. The material was polarised in 5 kmol/m^3 H_2SO_4 solution at 50 - 80 ℃ with applied potential modulated as square wave. The films formed are classified into two types according to the applied potentials. For the anodic type, Fe and Cr actively dissolve at the lower potential of the square wave, E_L, into Fe^{2+} and Cr^{2+}, then re-oxidised at the higher potential, E_H, to be mainly Cr^{3+} oxide. Alternatively, for the cathodic type, Fe and Cr dissolve at E_H, which is in the transpassive region, then thus dissolved Cr^{6+} ions are reduced into Cr^{3+} oxide at E_L. The thickness of the film was evaluated from the *uv-visible* light reflectance spectra, because the film is thick enough to show the interference colour. Fig.1 shows a TEM image of the stripped film, which is formed on Type304 stainless steel with E_L=-400 mV, E_H=1000 mV, t_H=t_L =0.1 s. The film consists of nano-crystalline oval-shape grains of around 1-4 nm in its size. The film also has large amount of open pathways linking with each others to be penetrated easily by ions or water molecule. The structure of the porous film can be ordered by changing the conditions of the formation process. The porous film consists of nano-scale crystalline of Cr_2FeO_4 spinel oxide covered with dis-ordered Cr hydroxide or oxide. Despite the morphology of the anodic and cathodic porous films are apparently similar, the electronic properties differ depending on the formation conditions. The electronic structure of the films were characterised by Electrochemical impedance and photo-electrochemical response. The electrochemical impedance measurement in Na_2SO_4 solution revealed that the capacitance of the anodic film is fairly larger than that of the substrate steel, and is nearly proportional to the total thickness of the film. Therefore, the film / electrolyte interface, which arises the electrochemical capacitance, distributes whole the cross section of the porous film. Furthermore, the unit structure which consists the porous film connects electrochemically each other, and has space charge layer to yield capacitance on each surface. On the other hand, the capacitance for the cathodic type film was almost equivalent to that of the substrate steel, and was independent of thickness, structure, and other properties. Therefore, the capacitance arose only at the substrate/solution interface, and porous structure of the thick film has no electrochemical connection with substrate. It is noted that the substrate underneath the porous film are in contact with the electrolyte. The photo-electrochemical response measured in sulphuric acid revealed that the anodic porous film has p-type semiconductor property, and that the photo current spectrum is similar to that for ordinary thin passive film, but quantum efficiency is larger depending on thickness[3)].

The square wave potential pulse polarisation was also applied to Fe-Ti alloy to form highly Ti enriched porous oxide film. The thickness of the oxide layer on Fe-Ti alloy is, however, less than 0.1 μm, which is fairly smaller than that obtained for Fe-Cr and Ni-Cr alloys. Nevertheless, a Ti-rich oxide layer which shows a photo-catalytic property as TiO_2 and satisfactory adhesive to the substrate has been obtained[5)].

The square wave potential pulse polarisation process has potential to produce oxide films with various structures, compositions and functions, which might be applied for various surface functional materials, *i.e.*, a carrier of catalyst, oxide electrode, and bio-compatible material.

References

1) S. Fujimoto, T. Shibata, K. Wada and T. Tsutae, *Corros. Sci*., **35**, 147 (1993).
2) S. Fujimoto and T. Shibata, *Materials Science Forum,* **185/188**, 741 (1995).
3) S. Fujimoto, S. Kawachi, T. Nishio and T. Shibata, *J. Electroanal. Chem.*, **473**, 265 (1999).
4) S. Fujimoto, K. Tsujino and T. Shibata, Electrochim. Acta, **47**, 543 (2001).
5) S. Fujimoto and T. Shibata, *Electrochemistry*, **67**, 1156 (1999).

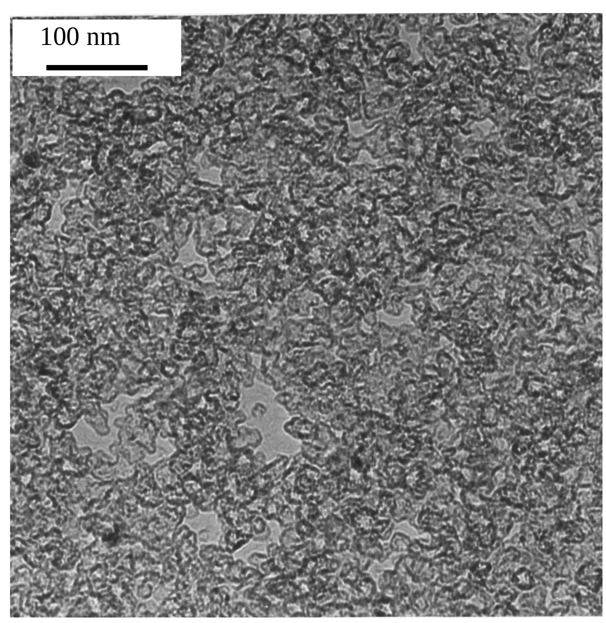

Fig.1 A bright field transmission electron microscopy of the anodic porous film on Type 304 stainless. The specimen was peeled of from the substrate steel.