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G-GIXS approach to characterize nano-structure of the titanium surface after chemical treatments

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Introduction

Titanium sheets have been applied for roofs, walls and monuments for more than 10 years even in seaside where stainless steels may suffer pitting corrosion. However, titanium shows discoloration phenomenon in some cases, where a thin titanium oxide film forms on the surface resulting in change of colour caused by interferential colouring depending on thickness of the film. Though it does not deteriorate durability of titanium sheets for exterior materials, it might spoil outward appearance.

Recently it has shown that chemical treatments of titanium sheets are effective for preventing the discoloration of titanium [1,2]. But its mechanism has not been clarified yet because of difficulty to reveal the change of surface after chemical treatments.

Experiments

The surface of titanium sheet was chemically treated using a solution of HNO_3+HF. The surface was analyzed by x-ray photoelectron microscopy (XPS) to determine the thickness and the chemical compositions. Then the nano-scale structure of the surface was investigated by generalized grazing-incidence-angle x-ray scattering (G-GIXS) technique [3], where symmetric and non-symmetric diffraction intensities are measured simultaneously with keeping the incident angle (α_i) near the critical angle (α_c) of total reflection. G-GIXS measurements were carried out at BL-6C at PF, KEK, Tsukuba, Japan. Diffraction patterns were measured in air using a scintillation detector and an image plate with an x-ray of 9.54 keV. Details of conditions were described in the reference [3].

Results and Discussion

XPS has shown that the surface of specimen was covered with a thin (*ca.* few nm) titanium oxide film containing fluorine (F). However, no clear relationship has been shown between the chemical compositions of the films and their discoloration properties.

G-GIXS measurements were carried out for various incident angles (α_i). Figure 1 shows penetration depth as a function of α_i in the conditions of experiments. Figure 2 shows x-ray diffraction patterns of the specimen for two values of α_i: below and above α_c. The broad peaks corresponding to the anatase-type TiO_2 phase were clearly observed in the pattern with α_i = 0.2 deg., as shown reverse triangles in Fig.2. Even though the roughness of metal surfaces after chemical treatments is expected to be a rather rough compared to atomically-flat substrates such as Si-wafers, it was confirmed that the thin oxide film formed on the titanium can be characterized by G-GIXS. This may be because symmetric and non-symmetric diffraction are measured simultaneously in G-GIXS, with enhancing the evanescent wave by controlling α_i.

Diffraction patterns obtained by G-GIXS showed slight but significant differences among specimens which were treated by solutions with different ratios of HNO_3/HF, and the details are being analyzed. G-GIXS approach is expected to give fundamental understanding the mechanism of chemical treatments of titanium surface.

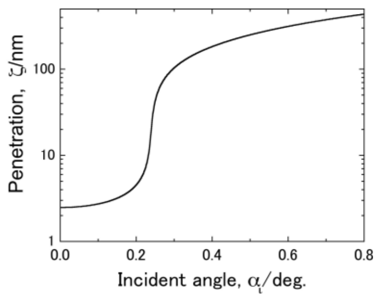

Fig.1 Penetration depth as a function of the incident angle (α_i) in the conditions of experiments.

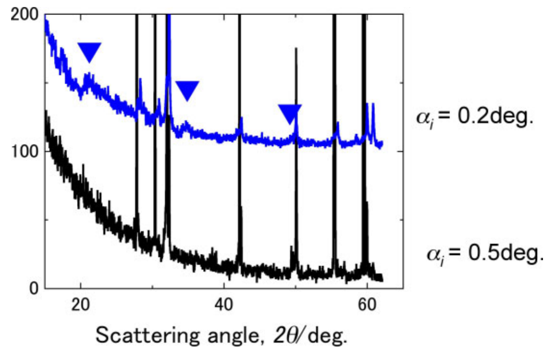

Fig.2 X-ray diffraction patterns of the specimen with incident angles: α_i = 0.2 deg. (above) and 0.5 deg. (below), respectively.

References

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