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Preparation and Characterization of Nano-Structured SiO_2 Thin Films on Carbon Steel

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Abstract: Nano-structured SiO_2 thin films were prepared on the surface of carbon steel for the first time by LPD. The compositions of the films were analyzed by XPS, and the surface morphology of the thin films were observed by AFM. The thin films were constituted by compact particles of SiO_2, and there was no Fe in the films. In the process of film forming, the SiO_2 colloid particles were deposited or absorbed directly onto the surface of carbon steel substrates that were activated by acid solution containing inhibitor, and corrosion of the substrates was avoided. The nano-structured SiO_2 thin films that were prepared had excellent protective efficiency to the carbon steel.

Keywords: Carbon steel, sodium silicate, nano-structured SiO_2 thin films, AFM.

In modern material science, nano-structured thin films have attracted many interests and have many promising applications, which include perfect ability of optical, electrical, and catalytic applications. Nano-structured thin films embedded between different materials, such as carbon steel, impart the substrates with the ability of anti-corrosion and anti-abrasion without changing the macro-structure of the substrate material[1]. There have been a number of isolated studies in order to fabricate nano-structured thin film by different methods, such as PVD[2], CVD[3], LPD[4], sol-gel[5], LB[6], SA[7]. Successful application of these novel methods, however, mainly exerted on the materials such as Si wafer, glass, and copper[2-7]. The liquid phase deposition (LPD) process was invented in 1988[8] and meliorated in 1991[4] by H. Kawahara *et al*. and has been used for the preparation of nano-structured SiO_2 films on the surface of optical glass using H_2SiF_6 solution containing saturated SiO_2. By LPD process, uniform films could be prepared on the irregular samples. However, this method is difficult to utilize onto metallic substrates, such as carbon steel, because the solution used for film forming was acidic, which could lead the carbon steel to corrosion. So far no report was found to demonstrate the preparation of nano-structured SiO_2 films on carbon steel. In this paper, nano-structured SiO_2 thin films were derived through LPD method by using common water glass and the resulting films had excellent protection to the substrates.

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The carbon steel substrates used in this paper are A3 steel standard samples (50 mm ×10 mm×2 mm). The substrates were polished, degreased in alcohol and cleaned with deionized water. Substrates were dipped into hydrochloric acid solution (AP, pH=5) containing 10 g/L hexamethylene-tetramine (AP) for 5 min, and dipped immediately into water glass solution (AP, 5000 mg/L, modulus: 3.1). After immersing for 24 h at 55℃, and heating for 30 min at a constant temperature of 100℃, the resulting films were prepared on the surface of substrates. Multi-layer films were fabricated by repeating the steps above.

The compositions of the resulting thin films were determined using X-ray photoelectron spectroscopy (XPS. MicroLab MKII, VG Co. Ltd.). The conditions for XPS analysis were: exciting source: X-ray of Mg $K\alpha$; density of ion current: 10 mA/cm^2; energy of ion current: 1.6 keV; pressure: 3×10^{-4} Pa. Atomic Force Microscope (AFM, Nanoscope Ⅲa Multi-mode, Digital Instruments Co. Ltd.) was used to characterize the surface morphology of the thin films and the diameters of particles in the films. The protective efficiency and the tight grade of the films were measured by observing the appearance of corrosion points formed on the substrates when they were dipped in deionized water for 72 h.

Figure 1 presents an AFM surface morphology image of nano-structured SiO_2 thin films deposited once and twice, respectively. As seen from **Figure 1a,** AFM image of once-deposited film shows that the film was constituted by a large number of particles with compact and sequential arrangement. The particles are spherical in their appearance, and have diameters between 30 nm to 50 nm. It is also found from **Figure 1a** that a few of interspaces exists among the particles of the once-deposited film. The comparison of **Figure 1b** and **Figure 1a** on the size of the particles and the morphology indicates that the diameters of particles of the twice-deposited film are also mostly in the range of 30~50 nm, whereas, there are no interspaces to be found in the twice-deposited film, suggesting that the arrangement of the particles of the twice-deposited film was more compact than that of the once-deposited film.

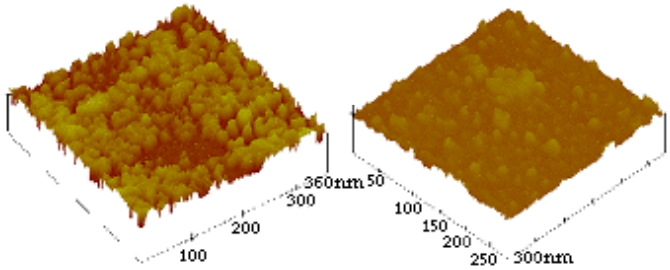
The compositions of once-deposited film were analyzed by XPS, and the results are shown in **Figure 2**. By analyzing the binding energy and the comparative chemical displacement, XPS analysis shows that Si element exists in the once-deposited film, and its binding energy is: Si2s: 154 eV; Si2p: 103.4 eV. So the substance containing Si in the film must be SiO_2 because of these experimental measurements are consistent with the characteristic binding energy of SiO_2 in the standard XPS spectrum.

According to the standard XPS spectrum, the characteristic binding energy of Fe^{3+} is 710.4 or 711.3 eV. However, there is no peak appeared in experimental analysis, suggesting no Fe exists in the film. So the process of films forming must be that the SiO_2 colloid particles were deposited or absorbed on the surfaces of carbon steel substrates directly by activating with acidic solution containing inhibitor, thus avoided the appearance of Fe^{3+} and the corrosion of the substrates.

As for the results of the observation by AFM and the analysis by XPS, the process of the formation of nano-structured SiO_2 thin films was depicted as below: positive ions were carried on the surfaces of carbon steel substrates because of the absorption of H^+ and the inhibitor, leading to the absorption and deposition of the SiO_2 colloid particles on

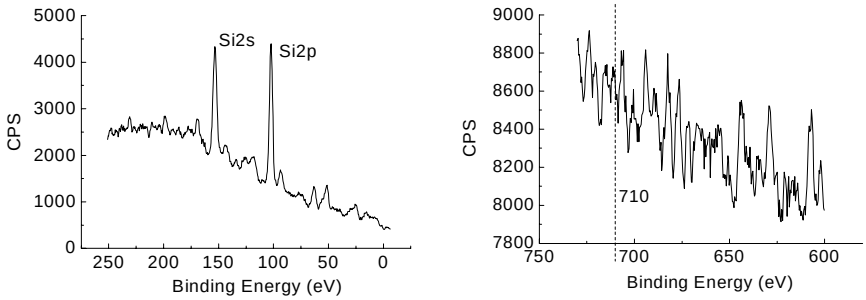
the substrates. The hydrochloric acid solution containing inhibitor also activated the surfaces of the SiO_2 thin films that formed previously and provided positive ions to the

Figure 1 AFM image of nano-structure of SiO_2 thin film



(a) once-deposited (b) twice-deposited

Figure 2 XPS patterns of SiO_2 thin film



（a）Si **（b）Fe**

surface, leading the SiO_2 colloid particles with negative ions to absorb and deposit again, thus resulted in the formation of multi-layer films.

Tight grade of the thin films is a crucial factor to influence the diffusion of dissolved oxygen from the corrosion media, deionized water, to the substrates, and so to the corrosion of the substrates. The tighter arrangement of the particles of the thin films had, the better protective efficiency of the films was acquired. The effects of the conditions of the films forming process, such as the varieties and composition of activating agent, activating time, modulus of water glass, concentration of film forming solution, temperature and time for dipping and for drying, on the protective efficiency were investigated, and the best protective films were prepared under the conditions mentioned in this paper. The samples with SiO_2 thin films showed good ability of anti-corrosion. The time when the first corrosion point appeared was elongated with the increasing of the times of film forming. When dipped in deionized water under room temperature, it was only 5 min that corrosion was observed on the surface of the samples without the protection of the thin films, and severe corrosion was found after 72 h dipping. However, the times when the first corrosion point appeared were 14 h, 18 h,

>72 h, >72 h for nano-structured SiO_2 thin films deposited once, twice, thrice and quartic, respectively. The carbon steel substrates with the nano-structured SiO_2 thin films could be kept from corrosion for 5 months when dipped in the deionized water. With the repeating films forming process, the structure of the resulting films became tighter, and thus led to better protective efficiency.

Acknowledgments

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