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Influence of SiO_2 in TiO_2 matrix on tribological properties of TiO_2

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Abstract

TiO_2 thin film was grown on a glass substrate by sol–gel process followed by high temperature treatment at 500°C. TiO_2 films demonstrated a very good wear resistance, endurance life and enhancing tribological characteristics. Energy Dispersive X-ray Spectroscopy (EDS) was used to indicate elements that contain in the film. EDS result showed that besides Ti, O and Si elements there is a small amount of Ca, Na, Mg elements diffused from the glass substrate. X-ray Diffraction (XRD) analysis indicated that TiO_2 films contain only anatase phase. The morphologies of the original and worn surfaces of the samples were analyzed by means of Scanning Tunneling Microscope (STM) and Scanning Electron Microscopy (SEM). The tribological properties of TiO_2 thin film sliding against the AISI-52100 steel pin were evaluated with a pin on disk system. The results indicate that TiO_2 films are superior in reducing friction and resisting wear compared with that of glass substrate. SEM observation of worn surfaces indicates that the glass wear is characteristic of brittle fracture and severe abrasion. The superior friction reduction and wear resistance of multilayer TiO_2 films are attributed to slight plastic deformation as well as good adhesion of the film to the substrate.

Keywords: Thin film; TiO_2; SiO_2; Tribological properties; Sol-gel.

1. Introduction

There is a great scientific and technological interest in the sol–gel ceramic films because of their excellent tribological and mechanical properties [1, 2]. TiO_2 is well known as a functional film, and its functional properties have been widely studied [1-4]. Recently, tribological investigation of TiO_2 film has attracted a lot of attention [1]. Therefore, the physical and mechanical properties of the films have been largely focused on [2]. At the same time, the tribological investigations of ceramic films used as micro-device materials are drawing much attention of both tribologists and scientists engaged in material science [2, 5]. Although, these materials have shown good tribological properties, there still remain considerable challenges in reducing wear and improving adhesion on various substrates [1, 2]. Numerous studies indicated that the fine-grained ceramics have a lower wear rate than the coarse-grained one in both sliding [1]. The addition of La_2O_3, CeO_2, CuO, Fe_2O_3, SiO_2, or other oxides into anatase TiO_2 can improve the thermal stability and prevent the growth of titania grains [1, 7-9]. Additionally, the presence of some dopants could increase the adhesion and mechanical stability of thin film on substrates, which are a key issue in device reliability [1, 3].

TiO_2 films have been produced by several techniques such as: physical vapor deposition, chemical vapor deposition, pulsed laser deposition, magnetron sputtering, and electro deposition. However, the application of these techniques are limited to the production of small scale films because of the cost of production and the need of a complex experimental set up [5, 8]. The sol–gel technique is regarded as a cost effective method for the production of TiO_2 films and involves simple processing steps [2, 5, 8]. The sol–gel process is a wet chemical method based on the hydrolysis/polycondensation of metal precursors, which leads to a large variety of oxide materials [8, 10]. Some papers have reported the sol-gel deposition of TiO_2 films for decreasing the friction coefficient of surface.

In this paper, TiO_2:SiO_2 thin films were deposited on glass substrate via the sol-gel method. The tribological properties of the films were investigated. The friction coefficient and wear life of the thin films were discussed in details.

2. Experimental

2.1. TiO_2:SiO_2 film preparation

For the preparation of the target solution, Tetraisopropoxy titanium (TTIP), tetraethyl orthosilicate (TEOS), ethanol, hydrochloric acid, and acetylacetone (ACAC) were commercially obtained and used without further purification [1-4].

Nanostructure of TiO_2 was prepared by the following method. TEOS (1 ml) was mixed rapidly with 20 mL ethanol for 15 min. Then, the solution was dropped slowly to 67 mL ethanol containing 0.5 mL HCl 1M and 1 mL deionized water under continuous stirring for 1 hr. Meanwhile, TTIP (7 mL) was dissolved into 89.5 mL of ethanol and magnetically stirred for 30 min. Then, ACAC (2 mL) was added to stabilize TTIP solution [1, 2]. The pre-hydrolyzed TEOS solution was poured into the matrix of TiO_2 sol and stirred for 30 min [1]. The pure TiO_2 film was prepared by the same procedure without adding TEOS. Finally, the sols were aged in a sealed beaker for 24 hr [1]. The films were deposited on glass substrates (25 mm×75 mm×2 mm) by the dip coating method with a speed of 5 mm/s. These films were dried at room temperature for 15 min, followed by calcinations at 500 ˚C for 4 h and finally cooled in the oven to room temperature [2]. The double- and multi-layer films are obtained by repeating the above procedures properly.

2.2. Film characterization

The crystalline phase of the films was identified by a X-ray diffractometer (X'Pert, Bruker) using CuKα radiation (r =1.54056Å). In addition, the grain or crystal size (L) was estimated from the width of lines in the X-ray pattern with the aid of Scherrer's formula [1, 8]:

$$L = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

where L is the crystal size of pure TiO_2, K is a constant (=0.94), λ is the wavelength of X-ray (CuKa = 1.54065Å), β is the true half-peak width, and θ is the half diffraction angle of the centroid of the peak in degree.

Energy dispersive X-ray spectroscopy (EDS; 7353, Oxford, England) was used for elemental analysis. The surface morphology of the thin films was observed by scanning electron microscope (STM; Nama, Iran). The worn surfaces of the films were observed with a scanning electron microscope (SEM; Leo 1450 VP, Zeies, Germany).

2.3. Tribological properties test

The tribological properties of the films were tested with a pin on disk friction and wear tester at a sliding velocity of 90 $mm.min^{-1}$. The counter-part was a fixed AISI52100 steel pin (diameter 5 mm) and the applied normal force was 3N. The chemical composition of the counter-part AISI52100 pin is shown in Table 1. The coefficient of friction and number of sliding passes were recorded automatically. In the whole sliding process, the friction coefficient keeps stable with very little fluctuation for a long period and then rises to a higher stable value. The friction coefficients are recorded as a function of distances that pin passes on the wear. The average friction coefficients were cited in this paper. Prior to the friction and wear tests, all the samples were cleaned in an ultrasonic bath with acetone for 2 min.

Table 1: Chemical compositions of AISI-52100 steel pin

Element	**Fe**	**C**	**Si**	**Mn**	**P**	**S**	**Ni**	**Cu**	**Cr**
Composition (wt%)	**Balance**	**1.03**	**0.22**	**0.31**	**0.01**	**0.01**	**0.07**	**0.06**	**1.39**

3. Results and discussion

3.1 Characterization of the film

Figure 1 shows XRD pattern of TiO_2 and TiO_2:SiO_2 film calcined at 500˚C for 4 hr. For this sample, the diffraction peak of anatase phase was observed. The grain size of TiO_2 can be deduced from the XRD line broadening using the Scherrer equation. Accordingly, the average grain size of TiO_2 and TiO_2:SiO_2 films were estimated to be 33 and 10 nm, respectively. Small proportion of SiO_2 is highly dispersed through the TiO_2 network homogeneously [1]. SiO_2 dopant does restrain the crystallization of TiO_2 and effectively suppress the phase transformation of TiO_2 from anatase to rutile. This strong retarding has been often ascribed to a good chemical homogeneity of the starting gels, i.e., to a high degree of Si–O–Ti bonding, which is believed to be reason of restricting the growth of grains during heat treatment [1, 11-16]. But fewer amount of SiO_2 could not prevent the growth of TiO_2 grain.

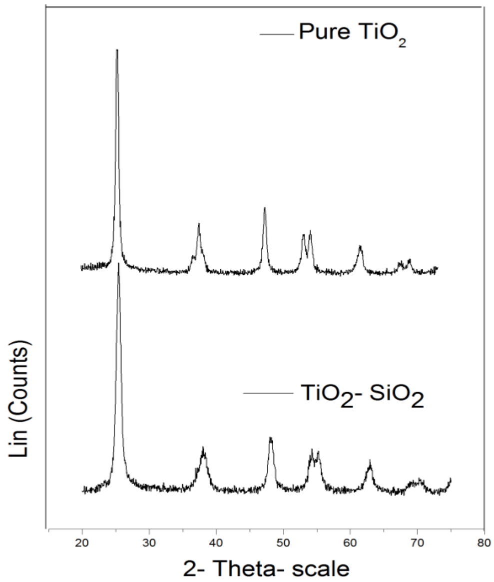

Figure 1. XRD pattern from the TiO_2:SiO_2 film at 500˚C for 4 hr.

The film composition was evaluated by EDS analysis. Figure 2 shows the EDS spectra of TiO_2 and TiO_2:SiO_2 films. EDS result indicated the main peaks of Ti, Si and also small amounts of Na, Ca, and Mg elements diffused from substrate. Diffusing Si element from the glass substrate is the reason of vigorous Si peak. Moreover, the presence of SiO_2 in thin film can destroy the linkage of Ti-O-Ti and change it to Ti-O-Si; this can shift binding energy of Si to higher value [1]. As mentioned before, the formation of Ti–O–Si cross linking bonds in the thin films is believed to restrict the growth of grains during heat treatment [1].

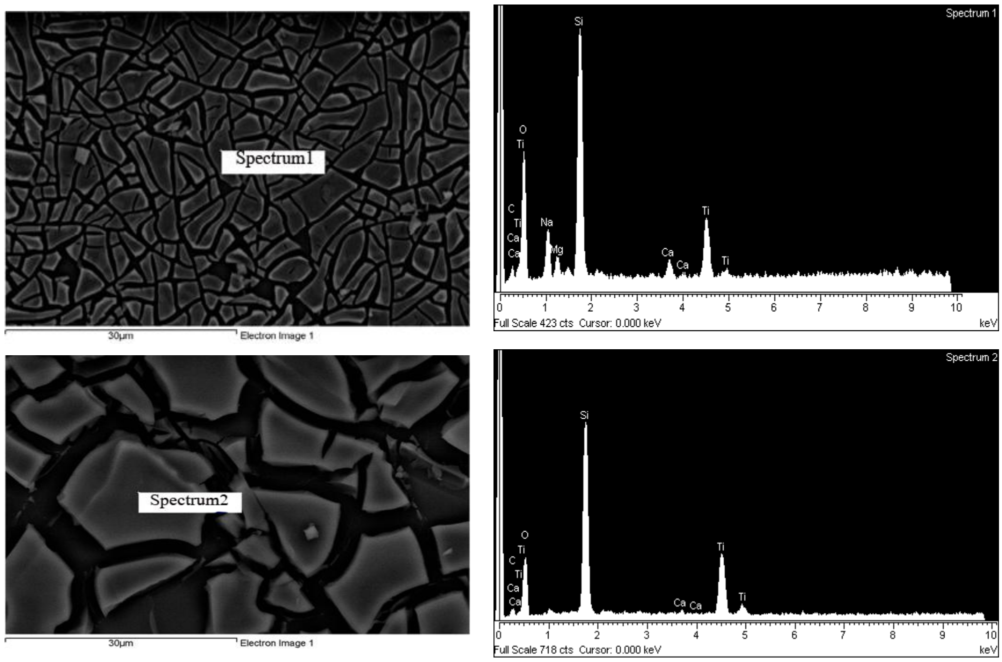

Figure 2. EDS analysis of the films: Spectrum 1) TiO_2, Spectrum 2) TiO_2:SiO_2 film

Figure 3 shows STM image of the TiO_2 and TiO_2:SiO_2 film. Growing up of the particles appears on the surface of multilayer film. The surface of TiO_2:SiO_2 films are smothering than TiO_2 films and adhesion of these films is more stable on the glass substrate.

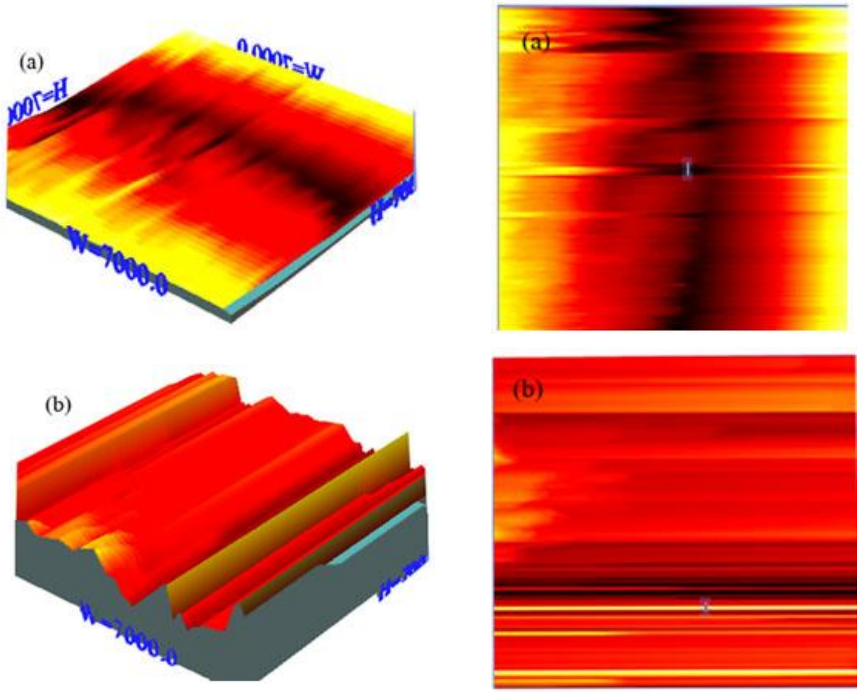

Figure 3. STM image of the films: (a) TiO_2:SiO_2, (b) TiO_2 thin film.

3.2. Tribological properties

Figure 4 shows the resulting friction coefficient for TiO_2 and TiO_2:SiO_2 multilayer films. For the glass substrate, the friction coefficient increase shrilly under 3 N only after several cycles, this is denote that the glass slide registers poor wear resistance. With explore in the results, 11-layer TiO_2:SiO_2 film sliding against AISI52100 pin exhibited much lower friction coefficient and longer wear life under low loads. Average friction coefficient of the films after 69 and 76 meters is shown in Table 2.

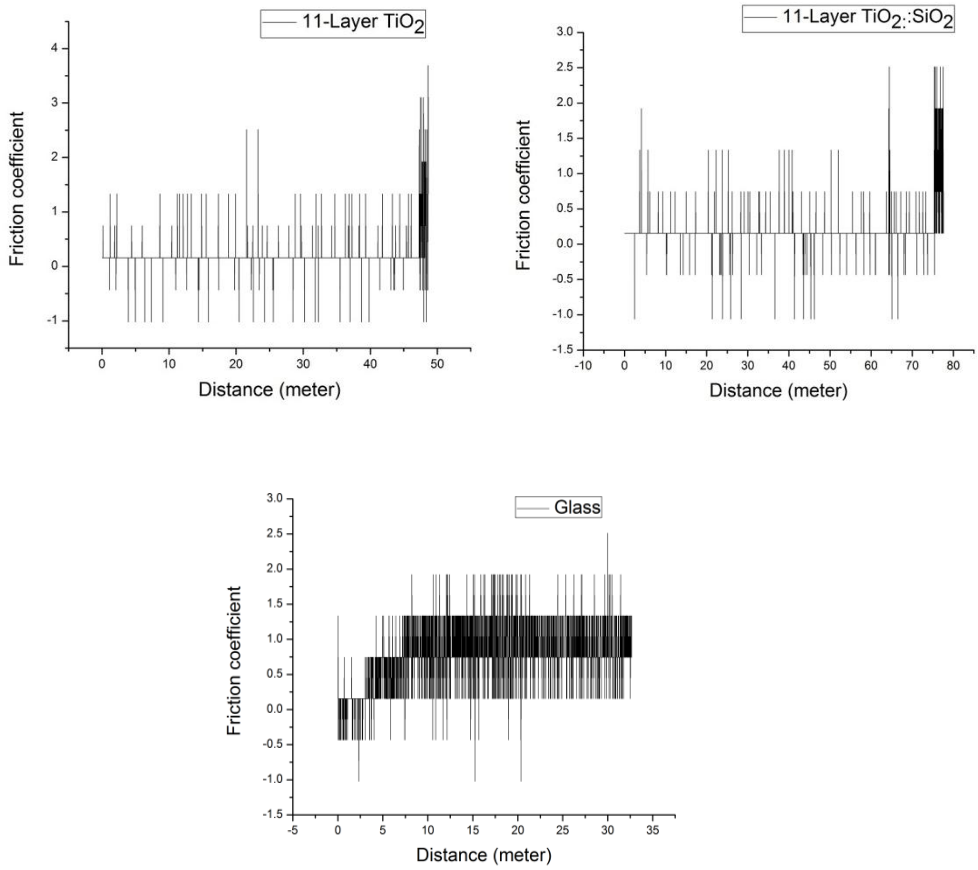

Figure 4. Friction coefficient of the films as a function of distance under 3 N force

Table 2: Average friction coefficient of the films and glass

Films	**Friction coefficient**
Glass	**0.71**
11- layer TiO_2	**0.2**
11-layer TiO_2:SiO_2	**0.17**

Thus, thin films of TiO_2 and TiO_2:SiO_2 inscribe the better friction films greatly enhance the tribological properties of glass substrate. It was observed that multilayer TiO_2:SiO_2 film was superior to multilayer TiO_2 film in wear resistance and lower friction under low loads. Moreover, the presence of SiO_2 can improve the cohesion and mechanical stability of thin film on glass, which are all possibly responsible for the better tribological performances of TiO_2:SiO_2 film [1]. This indicates that the sol–gel TiO_2:SiO_2 film on a glass substrate has relatively long wear life and this can reduce the friction between glass and steel. The TiO_2 coatings appear to be effective in improving wear resistance and reducing friction of glass

substrates. Thus, it is recommended that multi-layer sol–gel TiO_2:SiO_2 films could be used for engineering applications as protection or minimizing the friction of ceramic pairs under dry sliding at relatively low load.
To investigating the friction and wear mechanisms moreover, the worn surfaces of the attained films after destruction sliding against AISI52100 pin were observed by SEM (Figure 5). Figure 5 shows the micrographs of the worn surfaces of 11-layer TiO_2 and 11-layer TiO_2:SiO_2 film sliding against AISI52100 steel pin. Diversely, the surfaces is not very smooth and the sever stick happened, which may lead to pull up the coating and reduce the wear resistance of the films. This is very possibly considering the physical, chemical and mechanical properties of steel. Emblem of plastic deformation also observed under higher magnification in this situation. This can be concluded that the attained sol–gel TiO_2 film registers good plasticity regardless of the sliding counterparts.

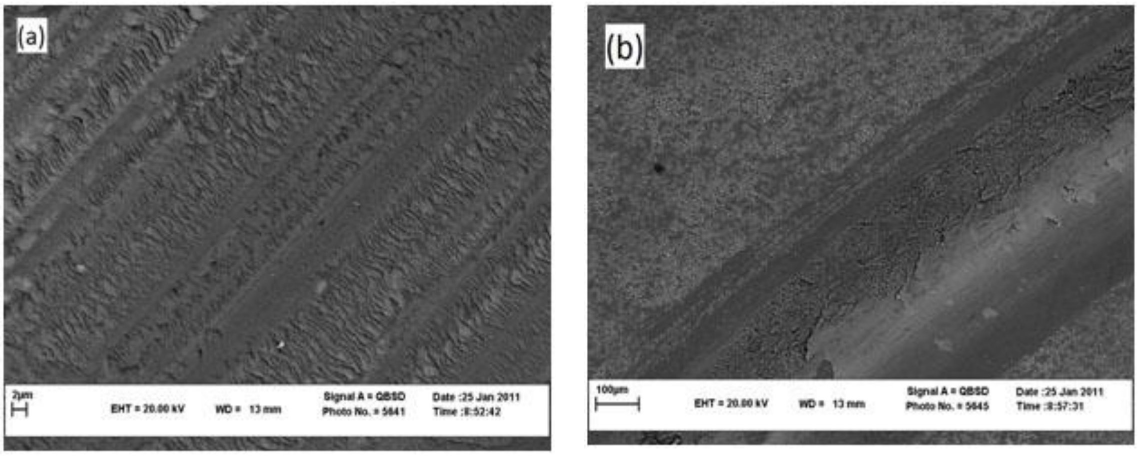

Figure 5. SEM images of worn surfaces of TiO_2:SiO_2 films sliding against AISI52100 steel pin: (a) 11-layer TiO_2:SiO_2, (b) 11-layer TiO_2

4. Conclusion

TiO_2 and TiO_2:SiO_2 thin films are effective in reducing friction and resisting wear compared with the glass substrate. Effect of SiO_2 addition into TiO_2 film on tribological properties was investigated. XRD and EDS investigation evidence that the suitable addition of silica into TiO_2 film can effectively prevent the growth of TiO_2 grains and ensure the durability of TiO_2 due to formation of Si–O–Ti hetero linkages. The finer grain size would greatly improve the resistance of thin film to microfracture. Additionally, as has been reported previously, the presence of SiO_2 can greatly increase the adhesion and mechanical stability of thin film on substrates, which is a key issue in device reliability. All these effects contributed to the excellent antiwear and friction reduction performance of mutually soluble TiO_2:SiO_2 film in sliding against AISI52100 pin under low load. The superior friction reduction and wear resistance of TiO_2 films are attributed to slight plastic deformation as well as good adhesion of the film to the substrate.

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