

TiO₂ COATING BY GEL OXIDATION

H. Z. Abdullah^{1*} and C. C. Sorrell²

¹Faculty of Mechanical and Manufacturing Engineering,
Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia

*Email: hasan@uthm.edu.my

Phone: +607-453-7818 ; Fax : +607-453-6080

²School of Materials Science and Engineering,
University of New South Wales,
Kensington, Sydney, NSW 2052, Australia

ABSTRACT

Gel oxidation is a thermochemical method for the production of an oxide film on a metallic substrate, where the metallic substrate is subjected to gelation by immersion in NaOH solution, followed by oxidation. These films are prepared for biomedical implant coating. Continuous and discontinuous gelled and TiO₂ films of submicron thickness were produced on high-purity Ti foil substrates (50 μm thickness) by soaking in NaOH solutions (0.5M, 1.0M, 5.0M, and 10.0M). Gelation involved soaking at 60°C for 24 hours. After drying in air for 24 hours, the samples were heated at 300°C/hour and soaked for 1 hour in air at 400°C, 600°C, and 800°C. The compositions, microstructures, and thicknesses of the films were determined using: glancing-angle X-ray diffraction, Raman microspectroscopy, and field emission scanning electron microscopy (FESEM). Raman microspectroscopy revealed the formation of an amorphous sodium titanate gel layer following chemical treatment. As expected, the thickness of the gel layer increased with increasing NaOH concentration. However, the two highest concentrations (5.0M and 10.0M) resulted in a cracking of the gel layer upon drying in air. TiO₂ did not crystallize during heating at 400°C but rutile formed directly upon heating at 600°C and 800°C. It can be concluded that the concentration of NaOH and the temperature change the thickness and phases of the titania.

Keywords: Titania; thick films; gel oxidation; glancing-angle x-ray diffraction; Raman microspectroscopy

INTRODUCTION

Gel oxidation is a thermochemical method used to prepare bioactive titanium (Ti) surfaces because hydroxyapatite (the mineral component of bone) precipitates from simulated body fluid onto the resultant titania (TiO₂) surfaces (Aznilinda, Herman, Ramly, Raudah, & Rusop, 2013; Kim, Miyaji, Kokubo, & Nakamura, 1996; Kokubo, Miyaji, Kim, & Nakamura, 1996; Mahendran, Lee, Sharma, & Shahrani, 2012). Since Ti implants are coated with a thin layer of residual oxide, gel oxidation can deposit a TiO₂ surface layer of controlled thickness and morphology. The acids HCl and H₂SO₄ are usually used for etching, and NaOH and hydrogen peroxide (H₂O₂) are used for gelation. Heat treatment dehydrates and densifies the gel to form amorphous sodium titanate (<600°C) or a mixture of crystalline sodium titanate and TiO₂ (≥600°C) (Jonasova, Müller, Helebrant, Strnad, & Greil, 2002; Kim et al., 1996). Varying NaOH concentrations and heat treatment temperatures alter the physico-chemical properties of the surface layer.

EXPERIMENTAL PROCEDURE

Sample Preparation

High-purity titanium foils of dimension of 25mm x 10mm x 0.5mm were wet hand-polished using 1200 grit (~1 μ m) abrasive paper, followed by immersion in an ultrasonic bath containing acetone, rinsing with distilled water, and drying with compressed air. The 200mL NaOH solutions for gelation were prepared by dissolving solid NaOH in distilled water. No acids or H₂O₂ were used for etching or gelation, respectively.

Gel Oxidation

The titanium foils were treated as summarized in Table 1. Following soaking in aqueous NaOH solutions of different concentrations at 60°C for 24 hours, they were washed with distilled water, dried in air for 24 hours, heated at 300°C/hour, and oxidized in air for 1 hour at 400°C (sample series B), 600°C (sample series C), and 800°C (sample series D).

Table 1. Gelation treatment conditions for sixteen samples.

Sample No.	1A-D	2A-D	3A-D	4A-D
[NaOH] Concentration	0.5 M	1.0 M	5.0 M	10.0 M
Oxidation Temperature	A = None	B = 400°C	C = 600°C	D = 800°C

Characterisation

The mineralogical compositions of the films were determined using (1) glancing angle X-ray diffraction (XRD, Philips X'Pert PRO Materials Research Diffraction System) at 45kV and 40mA and an angle of incidence of 0.8°, (2) Raman microspectroscopy (Renishaw MK1 Raman Microspectrometer) with red laser wavelength of 632.8nm, and (3) field emission scanning electron microscope (FESEM, Hitachi, Model S4500 II) at an accelerating voltage of 20kV.

RESULTS AND DISCUSSION

Gel Oxidation

Figure 1 shows a schematic of the reaction sequence as a function of time, gelation, and oxidation. The surface of the Ti metal was always covered with a thin layer of TiO₂ due to ambient oxidation. During soaking in NaOH, a corrosive attack of the TiO₂ film by the hydroxyl groups in the NaOH solution caused partial dissolution of the TiO₂ to form an amorphous (A) sodium titanate hydrogel (Kim et al., 1996; Liu, Chu, & Ding, 2004). Oxidation resulted in concurrent (1) crystallization of the hydrogel to form crystalline (C) sodium titanate (Na₂O·5TiO₂) and TiO₂ (Abdullah & Sorrell, 2012; Liu et al., 2004), and (2) oxidation of the underlying titanium to form TiO₂ (Kim et al., 1996).

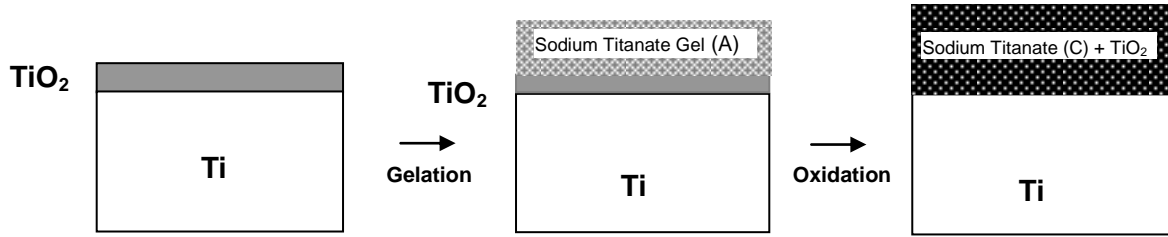


Figure 1. Gelation and oxidation sequence

X-Ray Diffraction

Figure 2 shows XRD patterns of the surfaces of the titanium substrates soaked in (a) 0.5M, (b) 1.0M, (c) 5.0M, and (d) 10.0M NaOH at 60°C for 24 hours and after heat treatment at 600°C for 1 hour (Samples 1A, 2A, 3A, and 4A, respectively). These patterns did not show a hump for amorphous sodium titanate hydrogel at ~48° 2θ probably owing to its low amount (the hump at ~28° 2θ is from the Perspex sample holder). However, the peak at ~48° 2θ for crystalline Na₂O·5TiO₂ resulted when the more concentrated NaOH solution was used. The observation of the crystalline Na₂O·5TiO₂ suggests the presence of the hydrogel (Abdullah, Koshy, & Sorrell, 2013; Kim et al., 1996; Prusi & Arsov, 1992).

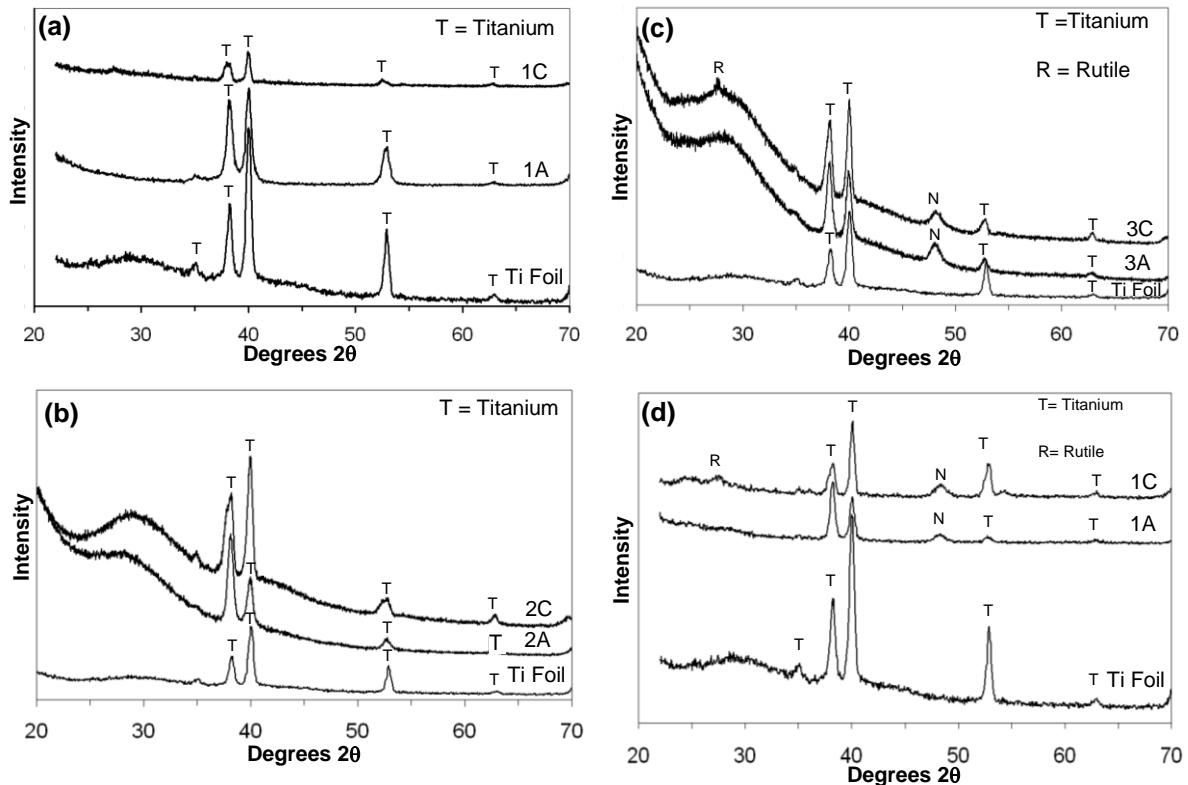


Figure 2. XRD patterns of the surfaces of titanium substrates (Ti foil) treated with: (a) 0.5M, (b) 1.0M, (c) 5.0M, and (d) 10.0M NaOH at 60°C for 24h and heated at 600°C for 1h, corresponding to Samples 1C, 2C, 3C, and 4C, respectively.

Raman Microspectroscopy

Figure 3 shows mineralogical analyses for the samples from the Raman microspectroscopy data. These patterns are similar to those for XRD, where the peak height indicates amount of phase and the peak sharpness indicates degree of crystallinity. The data is given in terms of the NaOH gelation concentration and the oxidation temperature: the numbers 1, 2, 3, and 4 correspond to NaOH concentrations of 0.1, 1.0, 5.0, and 10.0 M; the letters A, B, C, and D correspond to oxidation conditions of nil (no oxidation), 400°, 600°, and 800°C for 1 hour. Thus, the samples series for which data is given are (a) 1A-D, (b) 2A-D, (c) 3A-D, and (d) 4A-D, respectively.

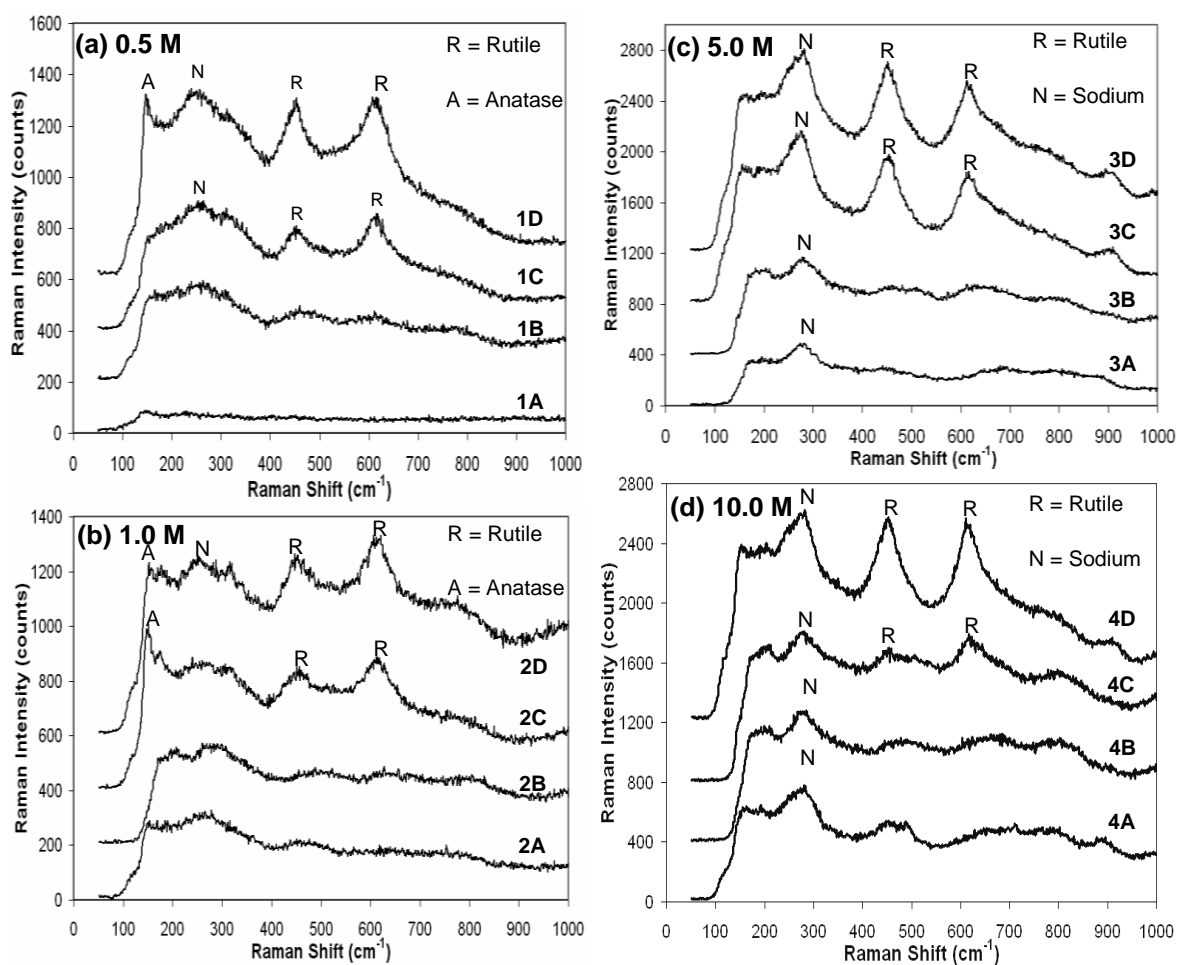


Figure 3. Raman microspectroscopy patterns of the surfaces of samples (a) 1A-D, (b) 2A-D, (c) 3A-D, and (d) 4A-D

Confirmation of the presence of the sodium titanate gel derives from the Raman microspectroscopy data shown in Figure 3; the assignment of peaks is based on literature documented as shown in Table 2. It can be seen that sodium titanate was observed in all conditions. Prior to oxidation (sample series A) and following low-temperature oxidation at 400°C (sample series B), it was amorphous or poorly crystallized. At the higher oxidation temperatures (sample series C and D), the crystal structure was better developed.

Table 2. Published Raman microspectroscopy data

Phase	Sodium Titanate (Balachandran & Eror, 1982)	Rutile (Karunagaran et al., 2003; Ohsaka, Izumi, & Fujiki, 1978)	Anatase (Chu, Chung, Zhou, Pu, & Lin, 2005; Kim, Miyaji, Kokubo, Nishiguchi, & Nakamura, 1999)
Spectral Peaks (cm ⁻¹)	220 – 280 447 ± 10	143 447 612 826	144 195 369 513 637

TiO₂ in the form of rutile is clearly visible following oxidation at 600°C and 800°C (sample series C and D, respectively). A lower level of anatase is also visible, although it is difficult to identify at the lower NaOH concentrations (sample series A and B) owing to the concurrent locations of the termination of baseline, the lower resolution limit of the instrument, and the location of the main anatase peak. Amorphous TiO₂ is visible at low levels both in the absence of oxidation (sample series A) and following low-temperature oxidation at 400°C (sample series B). XRD of the surfaces of unpolished Ti foils confirmed the presence of anatase. Thus, the observation of the peak for anatase following oxidation of samples gelled with the lower NaOH concentrations supports the conclusion that the passive oxidation layer dissolved in the NaOH solution.

Thickness

Figure 4 shows the thicknesses of the oxidized films determined from the cross-sections using the FESEM. The following conclusions can be made: 1) the thickness increased with increasing NaOH concentration and thus degree of gelation; 2) the largest effect on the thickness was obtained with the use of 10 M NaOH and the effects of the lower concentrations were not as highly differentiated; 3) the thickness increased approximately linearly with oxidation temperature and thus the amount of recrystallized material; 4) the thickness was <2µm in all conditions.

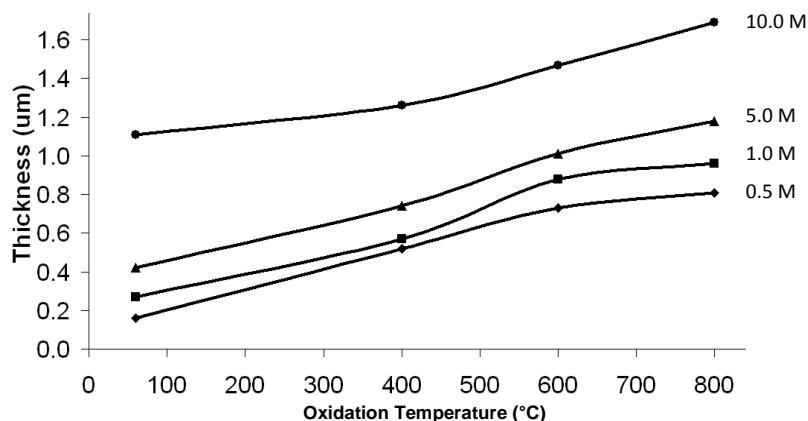


Figure 4. Thicknesses of all titanium substrates as a function of NaOH concentration and oxidation temperature

Scanning Electron Microscopy

Figure 5 shows FESEM images of the coatings formed on the Ti substrates as a function of NaOH concentration and oxidation temperature. The treatment conditions of these samples are summarized in Table 3. Examination of the FESEM images in terms of the NaOH concentration (within a four-image box) and the oxidation temperature (between four-image boxes) reveals that the NaOH concentration plays the more substantial role in the microstructural development while the oxidation temperature plays a less important role.

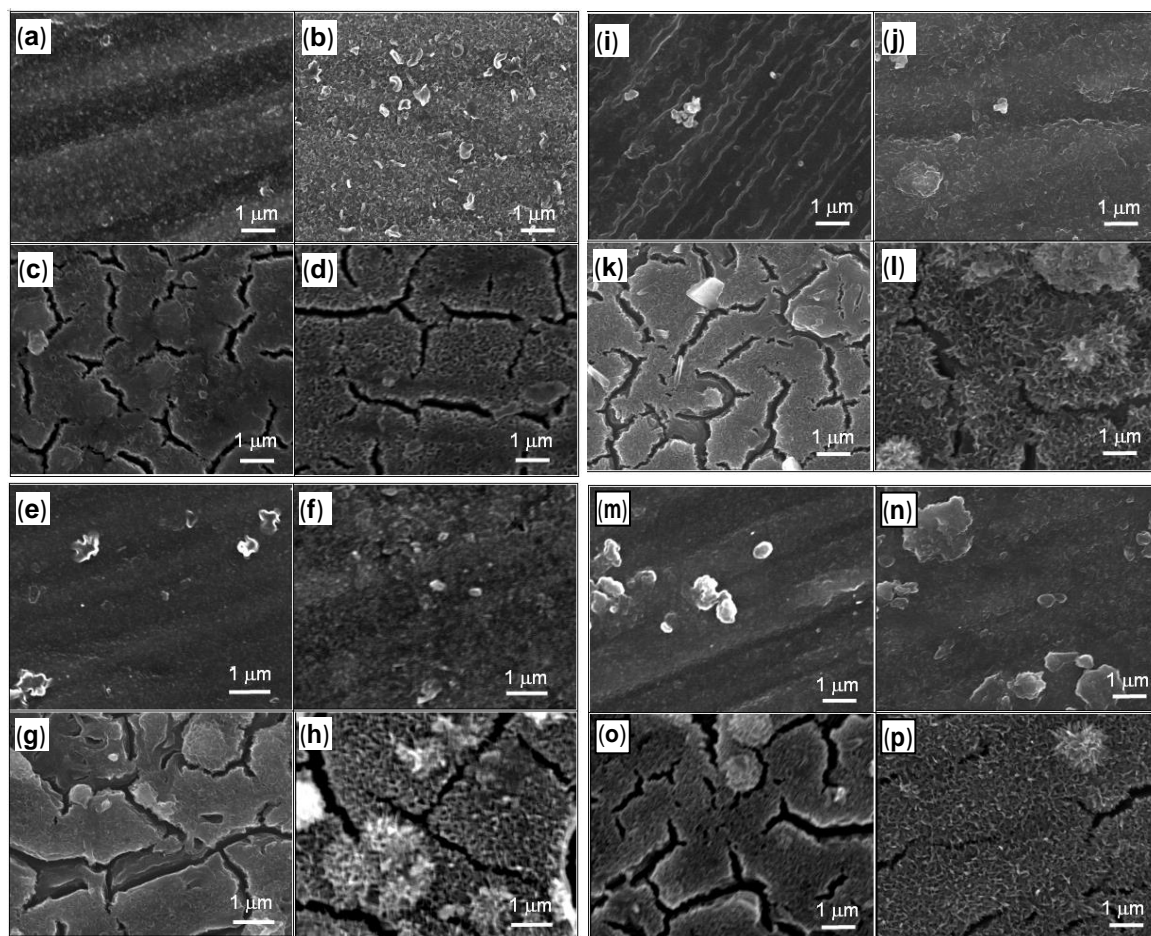


Figure 5. FESEM images of the surfaces of titanium substrates for all treatment conditions (summarized in Table 3)

The features that can be seen are summarized as follows. 1) Continuous Coatings: These relatively featureless surfaces can be seen at the two lowest NaOH concentrations, where the thickness was least and thus the most flexible. 2) Loosely Attached Particles: These can also be seen at the two lowest NaOH concentrations. They probably resulted from flaking of the soft gel. 3) Drying Cracks: These are present at the two higher NaOH concentrations. These probably resulted from the greater shrinkage of the two thicker gel layers. 4) Texture Development: This can be seen at the two higher NaOH concentrations. It probably resulted from recrystallization of Na₂O·5TiO₂ and TiO₂.

Table 3. Samples and Treatment Conditions

Figure	Sample Number	[NaOH] (M)	Oxidation (°C)
5(a)	1A	0.5	Nil
5(b)	2A	1.0	Nil
5(c)	3A	5.0	Nil
5(d)	4A	10.0	Nil
5(e)	1B	0.5	400
5(f)	2B	1.0	400
5(g)	3B	5.0	400
5(h)	4B	10.0	400
5(i)	1C	0.5	600
5(j)	2C	1.0	600
5(k)	3C	5.0	600
5(l)	4C	10.0	600
5(m)	1D	0.5	800
5(n)	2D	1.0	800
5(o)	3D	5.0	800
5(p)	4D	10.0	800

CONCLUSION

Gelation on the surfaces of Ti foils resulted in: (1) dissolution of residual anatase on the foil surface, and (2) initial formation of an amorphous or poorly crystalline layer of sodium titanate. The thickness of the coating was a function of the NaOH concentration (for fixed immersion time). When the coatings were subjected to 5.0M or 10.0M NaOH, drying shrinkage cracks developed. Oxidation of the gels resulted in the formation of well-adhered coatings on Ti. Heating at 600°C and 800°C was necessary to result in large-scale recrystallization of $\text{Na}_2\text{O} \cdot 5\text{TiO}_2$ and TiO_2 . The thickness of the oxidized layer increased linearly with temperature but the NaOH concentration had a more significant effect.

ACKNOWLEDGEMENTS

The authors would like to thank Universiti Tun Hussein Onn Malaysia (Short Term Grant; Vot 1078) and the Ministry of Higher Education, Malaysia, for financial support for this work.

REFERENCES

- Abdullah, H., Koshy, P., & Sorrell, C. (2013). Gel oxidation of titanium for biomedical application. *Advanced Materials Research*, 620, 122-126.
- Abdullah, H. Z., & Sorrell, C. (2012). Gel oxidation of titanium and effect of uv irradiation on precipitation of hydroxyapatite from simulated body fluid. *Advanced Materials Research*, 488, 1229-1237.
- Aznilinda, Z., Herman, S. H., Ramly, M. M., Raudah, A. B., & Rusop, M. (2013). Memristive behavior of plasma treated TiO_2 thin films. *International Journal of Automotive and Mechanical Engineering*, 8, 1339-1347.

- Balachandran, U., & Eror, N. (1982). Raman spectra of titanium dioxide. *Journal of Solid State Chemistry*, 42(3), 276-282.
- Chu, C., Chung, C., Zhou, J., Pu, Y., & Lin, P. (2005). Fabrication and characteristics of bioactive sodium titanate/titania graded film on niti shape memory alloy. *Journal of Biomedical Materials Research Part A*, 75(3), 595-602.
- Jonasova, L., Müller, F. A., Helebrant, A., Strnad, J., & Greil, P. (2002). Hydroxyapatite formation on alkali-treated titanium with different content of na+ in the surface layer. *Biomaterials*, 23(15), 3095-3101.
- Karunagaran, B., Rajendra Kumar, R., Senthil Kumar, V., Mangalaraj, D., Narayandass, S. K., & Mohan Rao, G. (2003). Structural characterization of dc magnetron-sputtered tio2 thin films using xrd and raman scattering studies. *Materials Science in Semiconductor Processing*, 6(5), 547-550.
- Kim, H. M., Miyaji, F., Kokubo, T., & Nakamura, T. (1996). Preparation of bioactive ti and its alloys via simple chemical surface treatment. *Journal of biomedical materials research*, 32(3), 409-417.
- Kim, H. M., Miyaji, F., Kokubo, T., Nishiguchi, S., & Nakamura, T. (1999). Graded surface structure of bioactive titanium prepared by chemical treatment. *Journal of biomedical materials research*, 45(2), 100-107.
- Kokubo, T., Miyaji, F., Kim, H. M., & Nakamura, T. (1996). Spontaneous formation of bonelike apatite layer on chemically treated titanium metals. *Journal of the American Ceramic Society*, 79(4), 1127-1129.
- Liu, X., Chu, P. K., & Ding, C. (2004). Surface modification of titanium, titanium alloys, and related materials for biomedical applications. *Materials Science and Engineering: R: Reports*, 47(3), 49-121.
- Mahendran, M., Lee, G. C., Sharma, K. V., & Shahrani, A. (2012). Performance of evacuated tube solar collector using water-based titanium oxide nanofluid. *Journal of Mechanical Engineering and Sciences*, 3, 301-310.
- Ohsaka, T., Izumi, F., & Fujiki, Y. (1978). Raman spectrum of anatase, tio2. *Journal of Raman Spectroscopy*, 7(6), 321-324.
- Prusi, A., & Arsov, L. D. (1992). The growth kinetics and optical properties of films formed under open circuit conditions on a titanium surface in potassium hydroxide solutions. *Corrosion science*, 33(1), 153-164.