Paper No.
MC13

CORCON
17-20 September 2017
Mumbai, India

From Corrosion to Nanotechnology that Prevents Challenging Global Warming

I.Gurrappa
Defence Metallurgical Research Laboratory
Kanchanbagh PO, Hyderabad- 500 058, India
(igp1@rediffmail.com)

I.V.S.Yashwanth
Department of Metallurgical and Materials Engineering
University of Texas at El Paso, USA

ABSTRACT

The talk covers the significant impact of global warming and various possible ways to prevent it. Then the importance of Nanotechnology starting from the corrosion process through which highly ordered Titania nanotubes, rods, wires and also the powders produced, are explained with recent results. It also demonstrate the recent production of Titania nanotubes, wires, rods of different dimensions using new titanium based substrates and the significance of selecting suitable substrate composition and optimization of process parameters. The talk also demonstrates the importance of corrosion process and its superiority over other techniques in synthesizing nanostructured tubes and powders apart from their characterization, properties and applications. Subsequently, the superiority of prepared nanotubes and the necessity of their use in effectively preventing global warming and modern industries that allow the systems to be used safely at varied environmental conditions, which not only would enhance the efficiency of industrial systems but also their life span and consequently the profitability, are stressed.

Keywords: Corrosion, Titania Nanotubes, Global warming,

INTRODUCTION

Over the years, the atmospheric concentrations of key greenhouse gases have been increased significantly due to human activities. Basic economic developments are the main drivers behind human induced climate change. Increased production of goods and services, changes in the production structure, increased transportation, a higher demand for all kinds of consumer goods, etc., contribute to a higher pressure on the atmosphere thereby increasing the greenhouse gas concentration. The important factor, of course, is the ever increasing demand for energy. At present the world's economy runs on fossil fuels. The combustion of coal, oil, natural gas and derived products provide energy to nearly all economic activities. The emission of Carbon Dioxide (CO_2) is a residual product of burning these fossil fuels. Also changes in land use pattern, deforestation and land clearings are important driving forces leading to a rise in carbon dioxide emissions. The six largest emitting countries according to 2015 data are China (with 29% share in the global total), the United States (14%), the European Union (10%), India (7%), the Russian Federation (5%) and Japan (3.5%) (Fig.1). Regional CO_2 emission trends differed strongly between the countries, in particular, between the top six emitting countries and the European Union, which accounted for two thirds of total global emissions (Fig.2). Figure 3 summarizes the carbon dioxide emissions in selected Indian cities and corresponding sectors. The highest carbon dioxide emission cities in India are Kolkata followed by Visakhapatnam, Ahmedabad and Bangalore (Fig.3). Among the sectors, Industries contribution is highest followed by residential and transportation. Future carbon dioxide emissions will lead to adverse climate changes on both short and long time scales that would be essentially irreversible [1]. Such climate changes will lead to a range of damaging impacts in different regions and sectors, some of which occur promptly in association with warming, while others build up under sustained warming because of the time lags of the processes involved. The strategy should be to halt by using CO_2 emission free energy systems and even reduce the CO_2

concentration in the atmosphere by adopting novel technologies which can convert CO_2 into useful compounds. Such a strategy would mitigate an inevitable, even if slowing, growth of CO_2. By midcentury improved energy efficiency and advanced technologies, perhaps including hydrogen-powered fuel cells, should allow policy options with reduced reliance on fossil fuels and if necessary, CO_2 sequestration. This scenario calls for the mean CO_2 growth rate in the next 50 years to be about the same as in the past two decades. One should note that climate change have impacts not only on cities but also on rural areas through their effects on increased or decreased rainfall which have impacts on agricultural output. Since cities have a high concentration of population density and economic activity, they are vulnerable to climate change. Given the most valued infrastructure is usually located in cities; the economic and social costs of climate change will be much higher in cities. The climate change has already been observed over the globe by either short fall/ heavy rains in different regions, unpredictable weather changes and peak summer reaching the highest temperatures than ever before. It is mainly attributed to global warming.

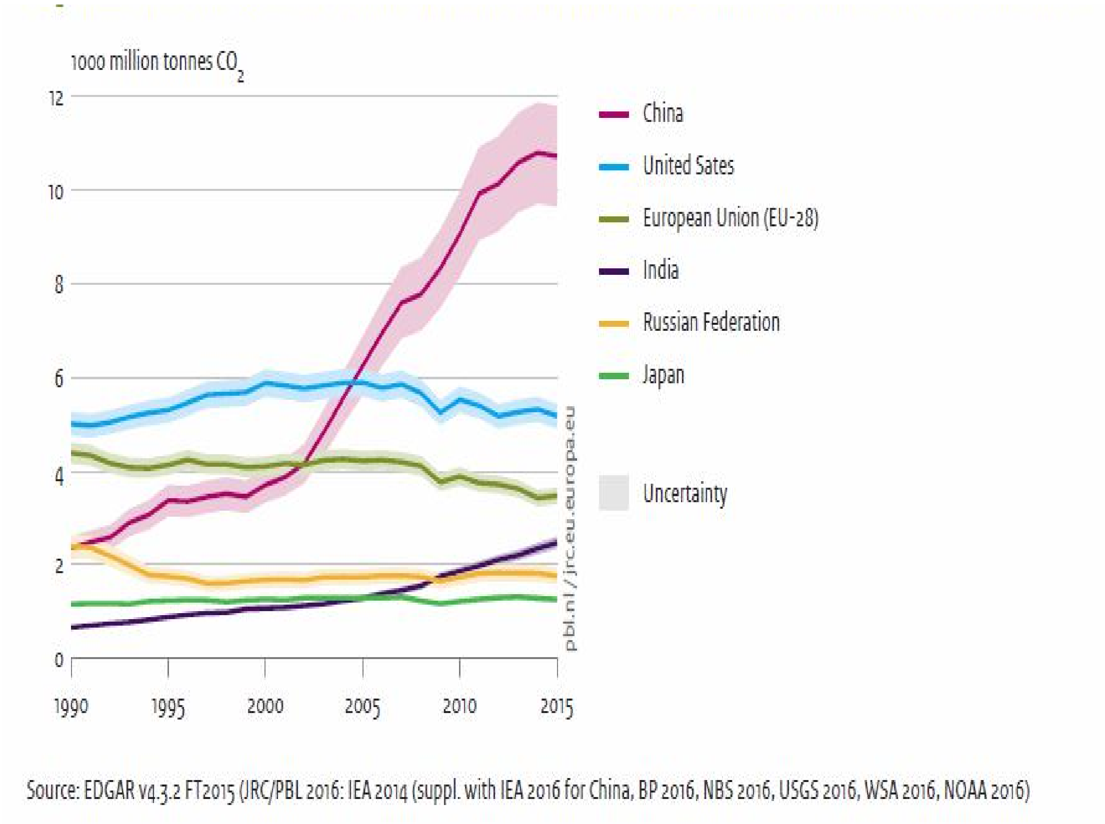
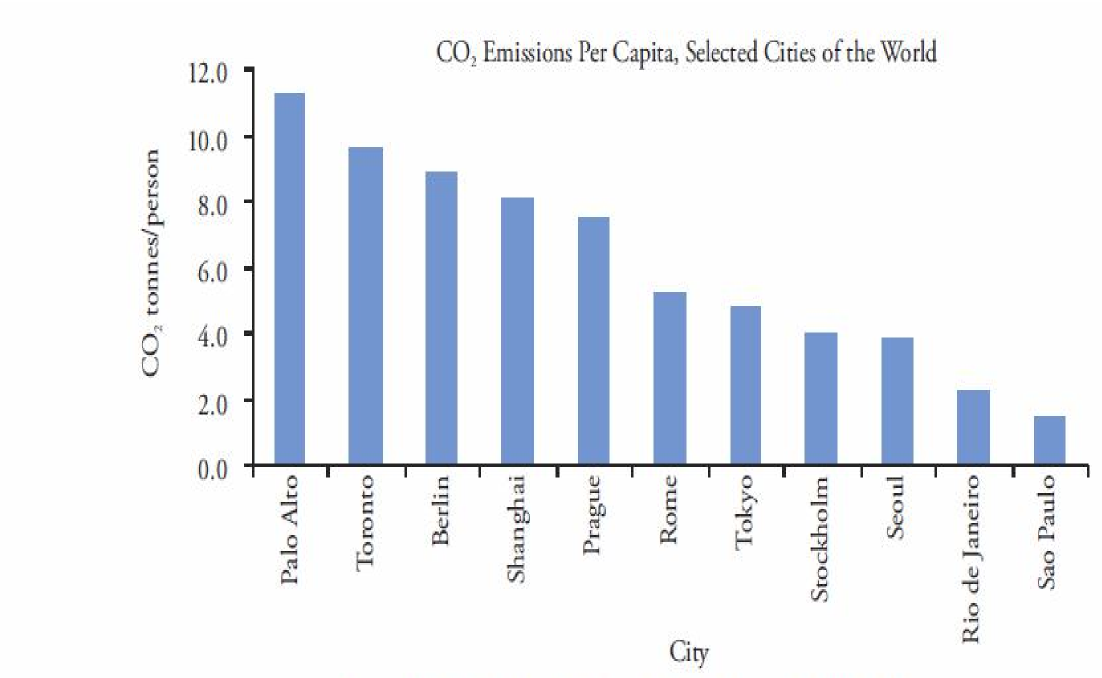


Fig.1: Carbon dioxide emission from fossil fuel use and cement production in the top five emitting countries and European Union



Source: McCaney (2009)

Fig.2: Carbon dioxide emissions in cities around the Globe

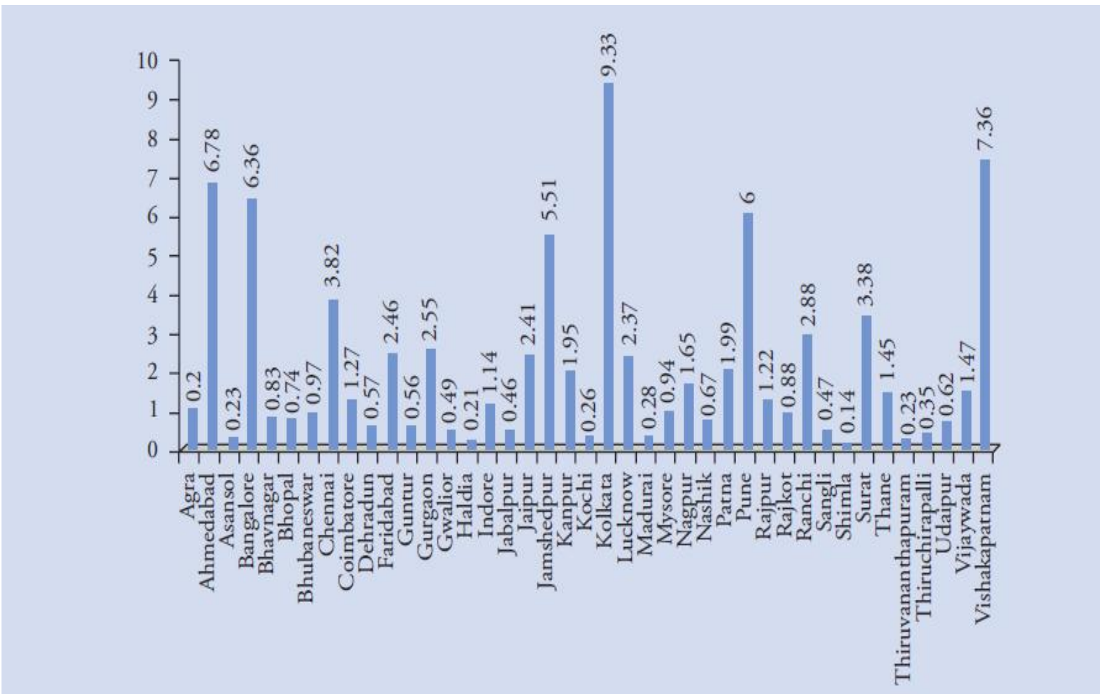


Fig.3: Carbon dioxide emissions in Indian cities (Million Tonnes) [1]

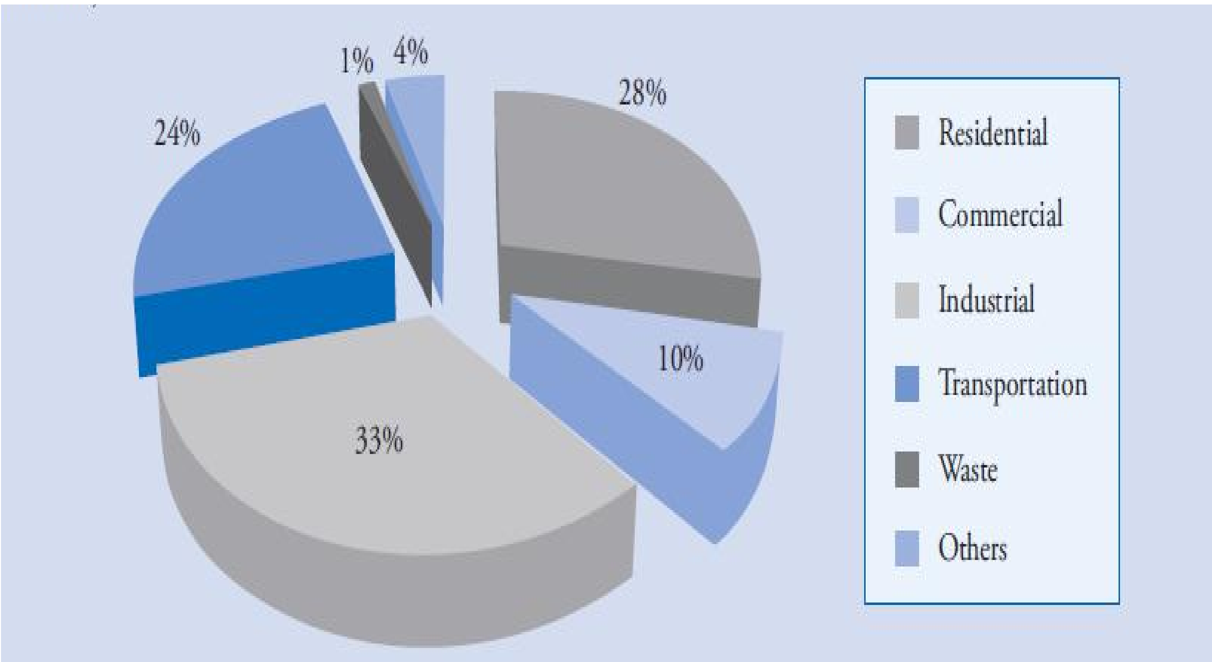


Fig.4: Sector wise CO_2 emissions in the selected Indian cities [1]

Global warming has emerged as an important policy issue for the all the countries to formulate one unanimous international policy and must be adhered to in order to minimize dangerous consequences across the globe. The published results have strongly suggested that nanotechnology have great potential for use in a variety of applications. CORROSION is known as a destructive activity due to which several structures fail thus losing trillion dollars. The same technique is helpful to produce NANOSTRUCTURED TUBES which prevent a challenging global warming as well as have tremendous potential industrial applications. Though some research has been going on in this direction, a considerable focus with application oriented research is essentially needed. The efforts in developing models to predict the climate change have been going on: however, the serious attempts to prevent global warming by removal of atmospheric carbon dioxide utilizing novel and economically viable technologies are essentially needed as mentioned earlier. One such attempt is to use nanotechnology in particular Titania nanotubes. The Titania nanotubes gravely help to prevent air pollution by converting CO_2 or CO present in the air to useful or harmless organic compounds. They are also quite useful as excellent filters during water purification process.

SOLAR ENERGY

Cost and efficiency are the most important factors in the success of any solar-based technology aiming to produce electricity from the Sun's irradiation. To become widely adopted, photovoltaic (PV) solar cells must generate electricity at a lower cost than what is now spent on fossil fuels. In fact, a number of new PV technologies are emerging to replace traditional cells based on costly silicon. Among these, dye-sensitized solar cells (DSC) are ideally suited for off-the-grid applications in developing countries and for building integrated photovoltaic's (BIPV). Current DSC based modules in fact have 5% energy conversion efficiency with good performance under any atmospheric condition and low irradiance. Low price is due to inexpensive materials (glass, Titania, dye, electrolyte and carbon powders) used to manufacture the cells rather than by costly vacuum systems. Further lowering costs, the raw materials do not need the extreme purity of silicon employed in conventional PV cells. DSCs were first described in 1977 but the first breakthrough 7% efficiency was reached in 1991 only when scientists used a nanoscopic TiO_2 particle layer and a polypyridyl ruthenium complex as a light absorber [2]. The dye is adsorbed throughout the whole TiO_2 surface at the interface of TiO_2 and a hole-transport material and the TiO_2 nanostructure enhances the area that is used for collecting photons by a factor 100–1000 which is the reason for their improved efficiency (Fig.5). Being the first developed and best known material for DSCs, nanocrystalline Titania is currently employed in the manufacture of real modules by companies like Dyesol in Australia or the consortium Color Sol in Germany. The optimal configuration uses a ~12 mm thick layer of mesoporous crystalline Titania nanoparticles (10–20 nm diameter) covered by a ~4 mm thick film of much larger (~400 nm diameter) particles that scatters photons back into the transparent film (Fig.6) [3-8]

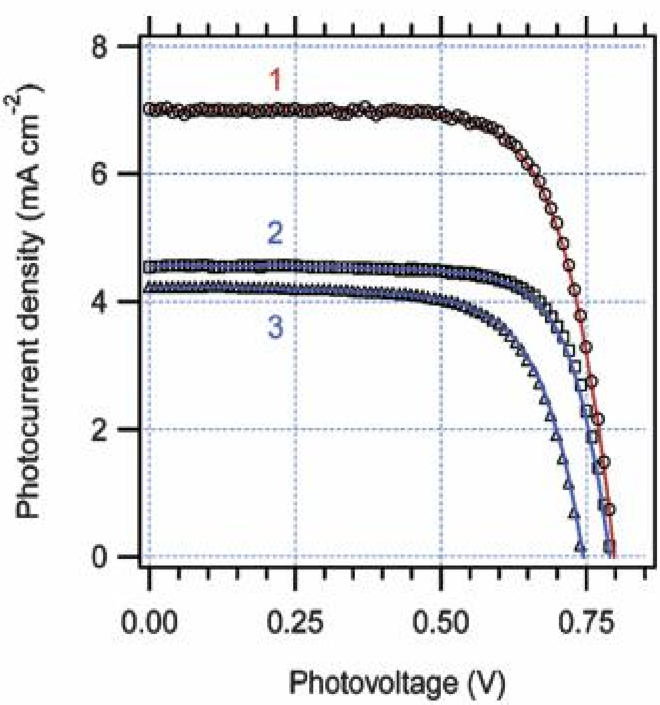


Fig.5: The characteristics of a solar cell made of Nano TiO_2 films sensitized by N945 [4]

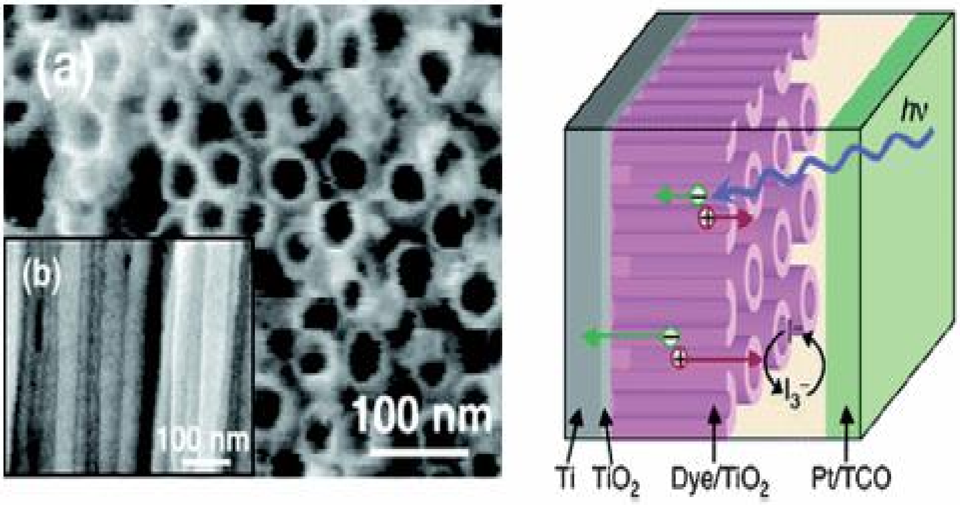


Fig.6: Typical arrangement of Titania nanotubes for enhanced efficiency of dye sensitized solar cells [5]

CORROSION PROCESS

Self-organized oxide tube arrays can be obtained by corroding a suitable material under appropriate conditions. When metals are exposed to a sufficiently anodic voltage in an electrochemical configuration, an oxidation reaction $M = M^{n+} + n\ e^-$ will be initiated. Depending mainly on the medium and the particular conditions, essentially three reactions takes place: i) The Mn^+ ions are solvatized in the medium i.e. the metal is continuously corroded ii) the formed Mn^+ ions react with O^{2-} (provided by H_2O in the medium) to form a compact oxide (MO) layer iii) under some electrochemical conditions, competition between solvatization and oxide formation is established (leading to porous MO). Under even more specific experimental conditions, a situation is established where self-organization during the growth of porous oxide takes place; furthermore, under some specific conditions, disorganized rapid growth of TiO_2 nanotube bundles or formation of thick self-organized nanotubes, meso-porous layers, rods or wires can be formed. In essence, destructive corrosion process is useful for constructive nanotechnology, which is the recent and having a unique characteristics and useful for a variety of applications [9-11].

TITANIA NANOTUBES

Titania nanotubes, rods, wires and carbon nanotubes exhibit remarkably enhanced characteristics over conventional materials which are extremely useful in a variety of applications like global warming, solar energy, hydrogen production & storage, biomedical, gas sensors and photo catalysis. The efforts have been made to produce Titania nanotubes by corrosion technique on different titanium based alloys and emphasized the importance of suitable titanium alloy composition in the production of Titania nanotubes. Table 1 presents the chemical composition of selected titanium based alloys for production of Titania nanotubes.

Table 1: Chemical composition of pure titanium and its alloys (wt%)

Alloy	Al	Sn	Zr	Mo	Nb	V	Si	C	Ti
Pure Titanium	-	-	-	-	-	-	-	-	Pure Titanium
Ti 64	6.0	-	-	-	-	4.0	-	-	Balance
IMI 834	5.8	4.06	3.61	0.54	0.7	-	0.32	0.5	Balance

The results suggest that the Titania nanotube formation is strongly dependent on the titanium alloy composition which is used for the corrosion process. The nanotubes are not produced on either pure titanium or titanium alloy Ti 64 (Fig.7). They could not be grown probably because the medium is less corrosive to them or the process duration is short. But highly ordered Titania nanotubes are formed on the titanium alloy IMI 834 in HF and phosphoric acid medium on the entire surface of the titanium alloy (Fig.8). The XRD results confirmed the formation of crystalline Titania on the titanium alloy (Fig.9). It clearly demonstrates that the titanium alloy composition plays a significant role in producing Titatia nanotubes. The difference between Ti 64 and IMI 834 is the addition of 4% tin, 3.6% zirconium, small amounts of niobium (0.7%) silicon (0.32%), molybdenum (0.54%) and carbon (0.5%) in IMI 834. Aluminium content is almost same in both the alloys. However, good amount of vanadium (4%) is present in Ti 64 along with aluminium and considered as beta titanium alloy. This composition changes made IMI 834, a near alpha titanium alloy having good structural properties and it is highly suitable for fabrication of Titania nanotubes on IMI 834. The combination of elements in the alloy promoted Titania nanotubes formation. It is further evidenced by not growing the Titania nanotubes either on pure titanium or titanium alloy Ti 64 in the same conditions as that of IMI 834. Further, highly ordered Titania nanotubes were formed on another aerospace alloy 6242 and the results are patented. Hence, the present results established that titanium alloy composition is an important deciding factor apart from the applied voltage, time, electrolyte and temperature in producing Titania nanotubes [9-10]. The results also revealed that titanium alloy IMI 834 is a highly suitable material in producing Titania nanotubes by an economically viable corrosion technique in 0.5%wt HF and 1M H_3PO_4 medium. Highly ordered Titania nano rods have synthesized for the first time on IMI 834 alloy by corrosion technique under optimized conditions and the results are patented. Titania nanotube powders are also synthesized successfully in environmentally friendly environment from different titanium based as well as titanium aluminides [12]. As mentioned earlier, these Titania nanotubes can be successfully used in preventing global warming which is a major threat to the entire world. They can also be used in solarisation of a variety of systems starting from household to transportation, power plants and to the space vehicles including aero planes, photo catalysis, sensors and biomedical applications.

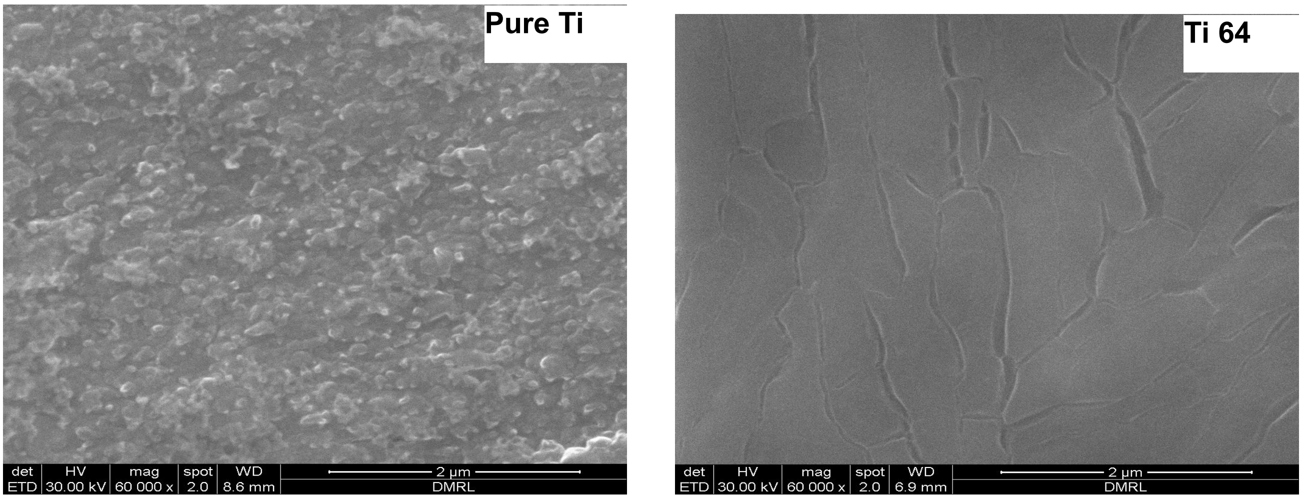


Fig.7: The surface morphology of anodized pure Ti and Ti 64 in 1M H_3PO_4 and 0.5 wt% HF electrolyte

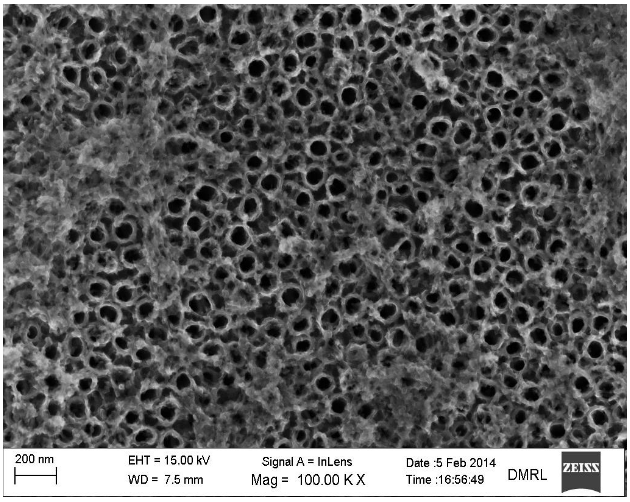
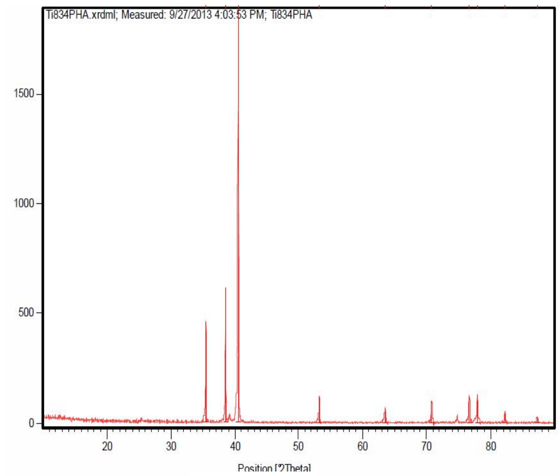


Fig.8: Field Emission Scanning Electron Micrograph of nanotubes grown on IMI 834 in 0.5%wt HF and 1M H_3PO_4 electrolyte



Ti 64

Fig..9: XRD pattern of nanotubes

It is important to mention here that Ti-6Al-2Sn-4Zr-2Mo (Ti 6242) and Ti-6Al-4V (Ti 64) are the most commonly used alloys in aero engines where the temperature reaches up to 300-450°C. New titanium alloys developed by changing alloy chemistry have made it possible to increase the aero engine temperature up to 600°C. The near alpha titanium alloy, IMI 834 belong to this category [13]. The mechanical properties of IMI 834 and other titanium alloys are dependent on variables such as alloy chemistry, manufacturing methods and environmental conditions during the service. Since, these variables greatly influence the microstructure, which inherently affects their properties. Extensive research on the titanium alloy IMI 834 was carried out under simulated aero engine conditions by Gurrappa [14-15] and developed high performance and smart coatings to increase its life during service [16]. Good amount of research work has been carried out on pure titanium and their alloys like Ti 64, TiNb, and TiAl etc. But no work has been reported on titanium alloy IMI 834 related to Titania nanotubes to the best of authors knowledge. Based on the results obtained, the suitable titanium alloys to obtain highly ordered nanotubes for a variety applications have been identified as 6242 and IMI 834. In essence, the investigation has established that the titanium alloys IMI 834 and 6242 are not only useful for fabrication of components used in aerospace applications but also ideal materials to produce Titania nanotubes which are having tremendous potential applications in a variety of applications.

REFERENCES

1. K.S. Sridhar, Carbon emissions, climate change and impact in Indian's cities, India Infrastructure Report, pp 345-354, 2010

2. B.O. Regan and M.Greatzel, A low cost, high efficiency solar cell based on dye-sensitized collodial TiO_2 films, Nature, Vol. 353, pp 737-740, 1991

3. T.W. Hamann, R.A. Jensen, B.F. Martinson, H.Van Ryswyk and J T. Hupp, Advancing beyond current generation dye-sensitisation solar cells, Energy Environ. Sci., Vol.1, pp 66-78, 2008

4. A. Burke, S.Ito, H. Snaith, Bach, U.J. Kwiatkowski and M. Greatzel, The function of TiO_2 compact layer in dye-sensitized solar cells incorporating planar organic dyes, Nano Lett., Vol. 8, pp 977-981, 2008

5. K. Zhu, N.R. Neale, A. Miedaner and A. J. Frank, Enhanced charge collection efficiencies and light scattering in dye-sensitized solar cells using oriented TiO_2 nanotube arrays, Nano Lett., Vol.7, pp 69-74, 2007

6. S. Lee, I.K.J. Park, D.H. Kim, W.M. Seong, D.W. Kim, G.S. Han, J.Y. Kim, H. S. Jung, K.S. Hong, Crytallographically preferred oriented TiO2 nanotube arrays for efficient photovoltaic energy conversion. Energy Environ. Sci., Vol.22, pp 3548-3552, .2012

7. J. Qiu, F.Zhuge, X. Li, X. Gao, X.Gan, L. Li, B.Weng, Z. Shi, Y.H. Hwan,. Coaxial multi-shelled TiO2 nanotube arrays for dye sensitized solar cells. J. Mater. Chem., Vol. 22, pp 3549-3554, 2012

8. W.H. Ryu, D.H. Nam, Y.S. Ko, R.H. Kim, H.S. Kwon, Electrochemical performance of a smooth and highly ordered TiO2 nanotube electrode for Li-ion batteries. Electrochim. Acta., Vol. 61, pp 19-24, 2012

9. I. Gurrappa and L.Binder, Electrodeposition of nanostructured coatings and their characterization- a review, Science Technol. Adv. Mater., Vol.9, 025007, 2008

10. I.Gurrappa and I.V.S.Yashwanth, The Significance of Electrochemical Techniques in Nanocoatings Technology, "Comprehensive Guide for Nanocoatings Technology", ISBN: 978-1-63482-447-7, Nova Publishers 2015, USA , pp 389-426

11. I.V.S.Yashwanth and I.Gurrappa, Synthesis and characterization of self-organized titania nanotube arrays by electrochemical anodization of titanium metal and Ti–6Al–4V alloy, Adv. Sci. Eng. Med., Vol. 6, 608, 2014

12. I.Gurrappa, V.Vaibhav and Ch. Saiteja, synthesis and characterization of titania nano tubes in flouride free electrolytes- A report 2015

13. I. Gurrappa and A.K. Gogia, Oxidation Behaviour of Titanium Alloy, IMI 834 at Elevated Temperatures, in proceedings of 5th National Convention on Corrosion, New Delhi, India, Vol. 1, pp 210-219, 1999

14. I.Gurrappa, An Oxidation Model for Predicting the Life of Titanium Alloy Components in Gas Turbine Engines J. Alloys. Comp., Vol. 389, pp 190-197, 2005

15. I.Gurrappa and A.K.Gogia, Development of Oxidation Resistant Coatings for Titanium Alloy, IMI 834, Mater. Sci. Tech., Vol. 17, pp 581-587, 2001

16. I.Gurrappa, I.V.S.Yashwanth and A.K.Gogia, Design and Development of Smart Coatings for Titanium Alloys in Gas Turbines, in "Gas Turbines: Technology, Efficiency and Performance" ISBN: 978-1-61122-842-7, D.J. Ciafone (Editor), Nova Publishers, USA, 2011, pp 59-69.