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Improvement in Quality of Plasma Sprayed Titanium Dioxide as Thermal Barrier Coating Material

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Abstract: The depletion of fossil fuel resources at a faster rate in the present world generating an essential demand for increase in efficiency of internal combustion engines. The use of coating in the automotive industry has been found to yield a significant effect on the efficiency of engines. Higher the operating temperature more will be the efficiency of the system. However, such higher temperatures demand for enhanced temperature resistant materials in the combustion area of engines. There are various TBC materials under investigation to find the best which give good performance and also affordable to coat in CI as well as SI engines. The main purpose of this paper is to verify weather is there any improvement in wear and other essential qualities of Plasma sprayed Titanium Dioxide as Thermal Barrier Coating (TBC) material.
Keywords: Thermal Barrier Coating, Plasma Spray Process, Titanium Dioxide, Wear, Corrosion

I. INTRODUCTION

Thermal-barrier coatings (TBCs) are refractory-oxide ceramic coatings applied to the surfaces of metallic parts in the hottest part of automobile engine parts, gas-turbine engines which enabling modern engines to operate at significantly higher temperatures than their predecessors. Many engineering design factors influence the overall efficiency of automobile engines, but a major step in increasing engine temperature and engine efficiency was the introduction of TBCs. The first use of Thermal barrier coating (TBC) was for aircraft engines. Then the concept of TBC Coating for diesel engines began in 1980s. Because of petroleum crisis and the subsequent increase in the cost of fuels, the improvement of fuel economy with better performance of the I.C Engines has become a high priority to the researchers. A lots of investigations had modeled and analysed the effects of in-cylinder thermal insulation. Reducing the heat rejection in reciprocating engines is a possible way of reducing the fuel consumption rate. This may be possible by eliminating a part of the cooling system and incorporating high-temperature insulting materials in the combustion chamber to withstand the higher combustion temperature. The advent of high temperature, high performance ceramics has tempted engine researchers to strive for higher operating temperatures with subsequent higher engine thermal efficiency by reducing fuel consumption. Investigations still going on to find out the most suitable Thermal Barrier Coating material which gives better performance and also affordable to use it in both SI and CI engine parts. While selecting a TBC material, Its essential to analyse weather it satisfies the essential property requirements. So my work is an analytical study to check weather Titanium Dioxide is a good TBC material or not.

II. THERMAL BARRIER COATING

Thermal barrier coatings (TBC) are highly advanced material usually applied to metallic surfaces, such as on gas turbine or engine parts, operating at elevated temperatures, as a form of exhaust heat management. TBC materials not only act as heat resisting medium but also prevent the thermal fatigue and shocks. Thus coating a TBC material in combustion engines is essential for long life, higher efficiency and also for reducing the fuel consumption rate.

A. Essential Property Requirement of TBC.

For coating in engine piston, combustion chamber, or in any substrate the following properties are essential.

High Melting Point.
Low Thermal conductivity.

Chemical inertness.
Good wear resistance.
Good corrosion resistance.
Thermal expansion coefficient match with metallic substrate.
Good adhesion to metallic substrate.
Low sintering rate of the porous microstructure.

B. Various TBC Materials

1) Zirconates: The main advantages of zirconates are their low sintering activity, high thermal expansion coefficient, low thermal conductivity and also good thermal cycling resistance. The main problem is the very high thermal expansion coefficient which results in residual stress in the coating, and this can cause crakes and also phase transfer takes place at a temperature above 500°C.

2) Yittria Stabilized Zirconia: 7-8% yittria stabilized zirconia has high thermal expansion coefficient, low thermal conductivity and high thermal shock resistance. Main Disadvantages of yittria stabilized zirconia are its sintering above 1473 K, phase transformation at 1443 K, corrosion and oxygen transparent.

3) Alumina: Advantages are its high hardness and chemical inertness. It has relatively high thermal conductivity and low thermal expansion coefficient compared with yittria stabilized zirconia. Even though alumina alone is not a good thermal barrier coating candidate, Only the addition of small percentage yittria stabilized zirconia can increase the hardness of the coating and improve the oxidation resistance of the substance.

3) Mullite: Mullite is an important ceramic material because of its low density, high thermal stability, stability in severe chemical environments, low thermal conductivity and optimum strength. Compared with yittria stabilized zirconia, mullite has a much lower thermal expansion coefficient and higher thermal conductivity, and is much more oxygen resistant. The low thermal expansion coefficient of mullite is an advantage when compared to yittria stabilized zirconia in high thermal gradients and in thermal shock conditions. But one main disadvantage is its large mismatch in thermal expansion coefficient with metallic substrate which leads to poor adhesion. The other disadvantage of mullite is its possibility of crystallization at approximate 1023-1273K.

*4)Forsterite:*The optimum level thermal expansion coefficient of forsterite permits a good match with the substrate. At thicknesses of some hundred microns, it shows a very good thermal shock resistance. However, its limited availability and high cost is its main drawback to use it as Thermal Barrier Coating.

5)Titanium Dioxide: Main advantages of titanium Dioxide is its high easy availability ,chemical stability and also low cost. Possibility of Crystallization at a temperature above 1500 K is one of the disadvantages.

III. TITANIUM DIOXIDE (TIO_2)

Titanium dioxide is one of the most investigated metal oxide due to its outstanding performance in a wide range of applications, chemical stability and low cost. Among the many metal oxides that can be used as functional coatings for devices, titanium dioxide has drawn considerable attention which is extracted from minerals such as ilmenite (FeTiO3), rutile and anatase (which, together with brookite, are polymorphic crystal structures of TiO2), perovskite (CaTiO3), and titanite (CaTiSiO5), the annual yield of TiO2 grew to above approximately 6 million tons in 2008, and its industrial success is also supported by its lower cost of production compared with other functional metal oxides (Ref 1, 2). Only rutile and anatase play a key role in the applications of TiO2. In both tetragonal structures, a basic building block consists of a titanium atom surrounded by six oxygen atoms in an approximately octahedral arrangement. As can be observed in Fig. 1, the two bonds between oxygen and titanium at the vertices of the octahedron are slightly longer, and in the case of anatase there is a deviation from a 90 bond angle relative to the other four bonds (Ref 3).

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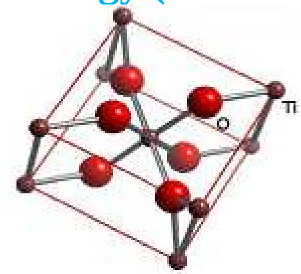

Fig 1 . Structure of Titanium dioxide

Titanium dioxide, also known as Titanium Oxide or Titania, with its molecular formula TiO2 and molecular weight 79.87 g/mol, is a kind of white powder. It is a soft solid powder and melts at 1800 Degrees Celsius. It has special performance, such as insulation, corrosion, flags, etc. It has a wide range of applications, from paint to sunscreen to food colouring. When used as a food colouring and the other most important application areas are paints and varnishes as well as paper and plastics, which account for about 80% of the world's titanium dioxide consumption. Other pigment applications such as printing inks, fibers, rubber, cosmetic products and foodstuffs account for another 8%. It is polymorphous and it exists in three types of crystal structures: (a) rutile, (b)anatase and (c) brookite. Only rutile is used commercially and the structure is shown in the Fig.1.

TABLE I: PROPERTIES OF TITANIUM DIOXIDE

Chemical Formula	TiO_2
Flash Point	Non Flammable
Density (Rutine)	4.23 g/cm3
Melting Point	1,843 °C (3,34 to 9 °F; 2,116 K)
Thermal Conductivity	1.8 to 2.2 w/m k
Molar Mass	79.866 mole

IV. PLASMA SPRAY PROCESS

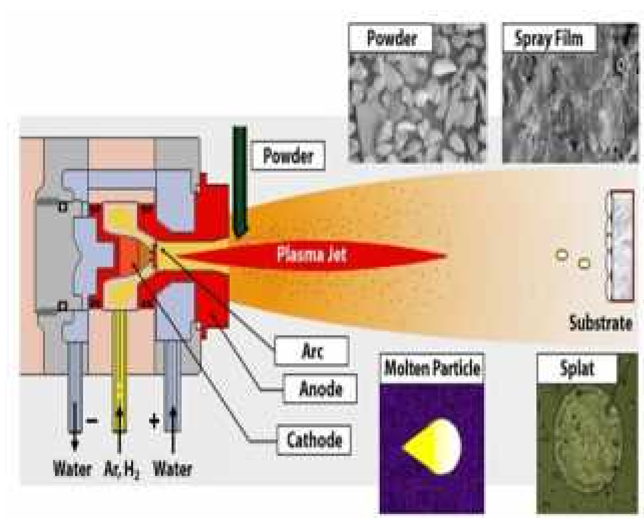

Fig 2 : plasma spray process

In plasma spray device (Fig 2) , an arc is formed in between two electrodes in a plasma forming gas, which usually consists of either argon/hydrogen or argon/helium. As the plasma gas is heated by the arc, it expands and is accelerated through a special shaped nozzle, producing a velocities up to MACH 2. Temperature in the arc zone approaches nearly 20,000°K. Temperatures in the

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plasma jet are still 10,000°K several centimeters form the exit of the nozzle. Nozzle designs and flexibility of powder injection schemes, along with the ability to generate very high process temperatures, enables the plasma spray technique to utilize a wide range of coatings. The range goes from low melting point polymers such as nylon, to very high temperature melting materials such as refractory materials including tungsten, tantalum, ceramic oxides like Titanium Oxide,Stabilized Zirconia etc and other refractory materials

V. EXPERIMENTAL PROCEDURE

A .Coating Preparation

Aluminium (Al), Stainless steel(SS) are the different substrate material as a base of piston and piston ring. Initially a 6 mm diameter and 30mm length substrate is smoothened through blasting process by using Alumina as Abrasive materials. Prior to the spraying of the Titanium Dioxide coatings, an MCrAlY layer was applied as bond coating to enhance adhesion and to reduce thermal expansion mismatch between the substrate and the ceramic coatings .The thickness of the bond coating was around 100 μm on average, and the top Titanium Dioxide coatings. are in the range of 300 to 450μm. Coating is done by plasma spray process with specifications follows

TABLE II: PLASMA SPRAY COATING SPECIFICATIONS.

Coating parameters	Specifications
Plasma Gun	3 MB Plasma spray Gun
Nozzle	GH Type Nozzle
Flow rate of argon gas	80-90 LPM
Pressure of argon gas	100-120 PSI
Flow rate of hydrogen gas	15-18 LPM
Pressure of hydrogen gas	50 PSI
Power feed rate	40-45 g per minute
Spraying distance	3-4 in.

B. Coating Characterization.

The microstructure, porosity and crystalline phase and orientation of the Titanium dioxide coatings were characterized. A scanning electron microscope (SEM) is a type of electron microscope that produces images of samples by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition Wear test has conducted in PIN-ON-DISC TESTRIGModelno.TR-20-M26. Pin-on-Disk wear testing is a method of characterizing the coefficient of friction, frictional.force and rate of wear between two materials. During this tribological test, a stationary disk articulates against a rotating pin while under a constant applied load. . X-ray diffraction (XRD) relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. A primary use of the technique is the identification and characterization of compounds based on their diffraction pattern. The diffraction of X-rays by crystals is described by Bragg’s Law, $2d\sin\theta = n\lambda$. The directions of possible diffractions depend on the size and shape of the unit cell of the material. The intensities of the diffracted waves depend on the kind and arrangement of atoms in the crystal structure

VI. RESULTS AND DISCUSSION

A. Coating Thickness Measurement

Thickness of the coating was measured using Sensor and the measurement has done at SI’TARC (Scientific Industrial Testing and Research Centre), Coimbatore. The data point values expressed in microns are the average of three readings. Plasma sprayed coated thickness of Piston is 135.85 µm.

B. Surface Roughness Measurement

The average height of the bumps on a surface, measured in micro meters is termed as average roughness (Ra).Coated Piston : 9.85 µm

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Normal Piston: 10.889 µm

The measurements has done at SI'TARC (Scientific Industrial Testing and Research Centre), Coimbatore

.The average height of the bumps on a surface of Plasma Sprayed Titanium Dioxide coated substrate is less when compared to Normal substrate. So it indicates there is less roughness of the coated substrate and thus may be wear also less for the coated substrate.

C. Micro Structure

The following figures shows SEM images of Titanium Dioxide powder

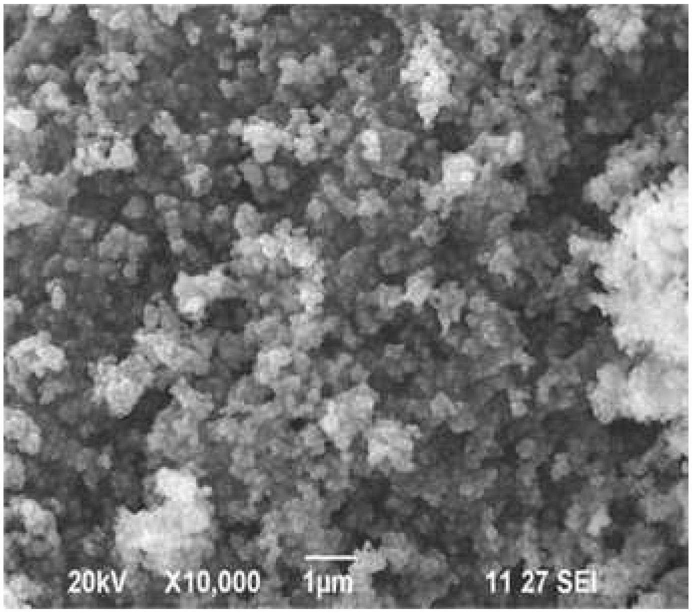

Fig. 3 : SEM image of TiO2 powder with magnification (x 10,000)

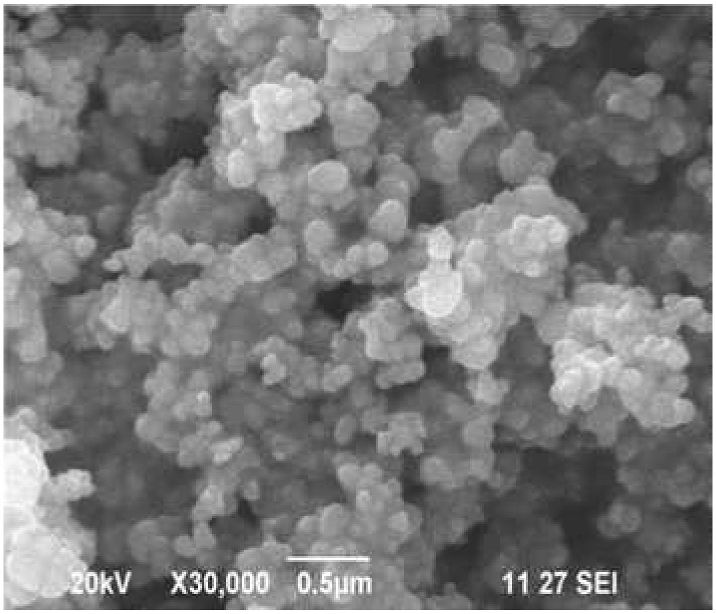

Fig. 4: SEM image of TiO2 powder with magnification (x 30,000)

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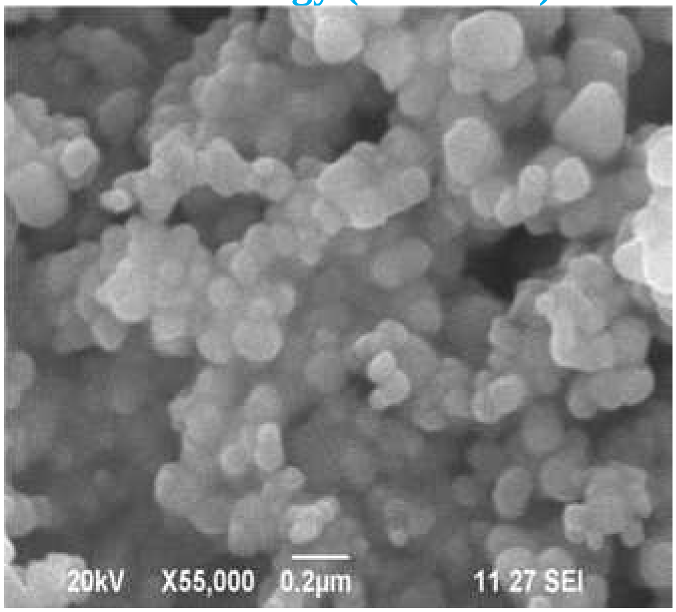

Fig. 5: SEM image of TiO2 powder with magnification (x 55,000)

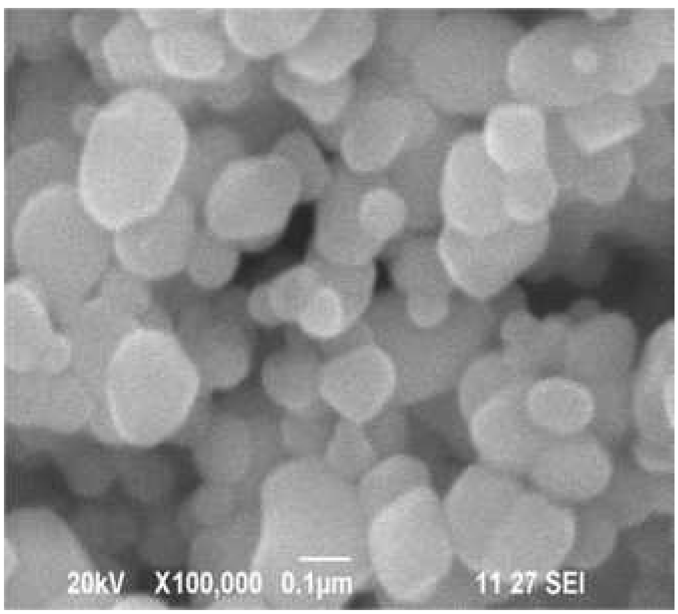

Fig. 6: SEM image of TiO2 powder with magnification (x100,000)From Figure 3 to Figure 6 shows various magnifications of powder Titanium Dioxide with magnification (x 10,000) , (x 30,000) , (x55,000) , (x 100,000) . It can be seen that the particles are equi-axed type and distributed homogeneously. SEM test of Titanium Dioxide sample powder has been conducted from Nano Technology Department of KARUNYA UNIVERSITY, Karunya Nagar, Coimbatore.

D. Wear Test

Wear test has conducted in PIN-ON-DISC WEAR TEST RIG Model no. TR-20-M26. The disc diameter is around 0.12m. The testing is conducted under constant load of 20N and constant speed of 3 m/s i.e. 600 rpm and by varying the Sliding distance in meters as 500, 1000 and 1500 respectively. The Sliding time of the concerned distance is 3, 6 and 8.5 min. Conducted the wear test from PSG technology, Coimbatore.

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TABLE III: WEAR LOSS OF TIO2 COATED MATERIAL

Material	Sliding Distance (M)	Initial Weight (G)	Final Weight(G)	Weight Loss (G)
Aluminium	500	11.0635	11.0633	0.0002
	1000	11.0633	11.0630	0.0003
	1500	11.0630	11.0624	0.0006
Steel	500	17.2650	17.2649	0.0001
	1000	17.2649	17.2648	0.0001
	1500	17.2647	17.2643	0.0004

TABLE IV: WEAR LOSS OF NORMAL MATERIAL

Material	Sliding Distance (M)	Initial Weight (G)	Final Weight (G)	Weight Loss (G)
Aluminium	500	3.4763	3.4746	0.0017
	1000	3.4745	3.4722	0.0023
	1500	3.4722	3.4693	0.0029
Steel	500	26.4920	26.4910	0.0010
	1000	26.4910	26.4896	0.0014
	1500	26.4896	26.4878	0.0018

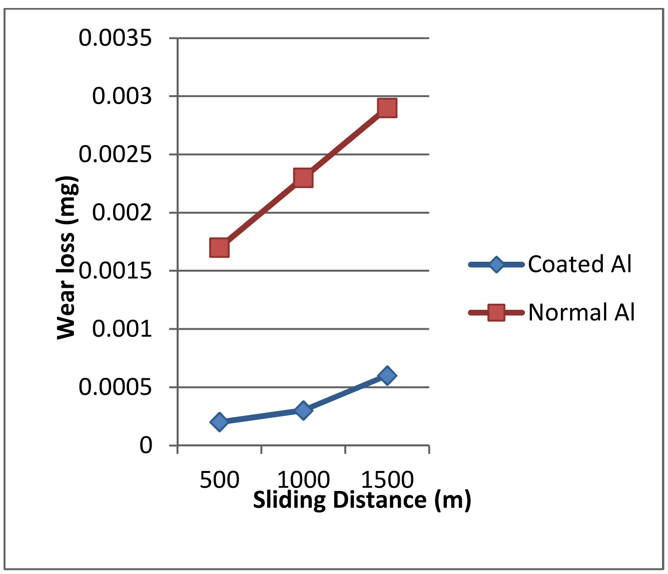

Fig. 10 : Comparison of wear loss between TiO2 coated Al substrate and Normal Aluminium substrate

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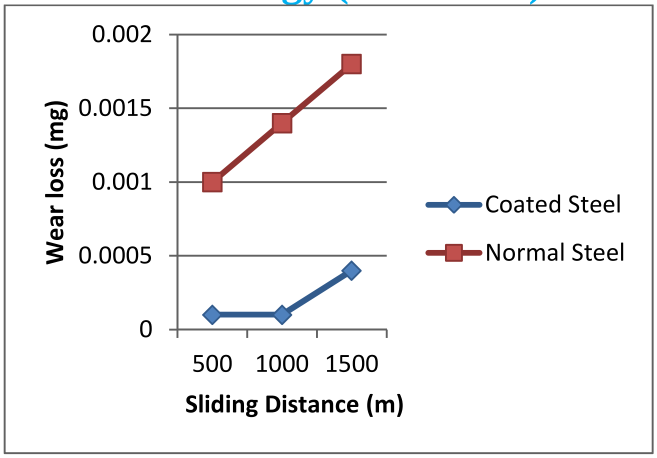

Fig. 11: comparison of wear loss between tio_2 coated steel substrate and normal steel substrate

E. X-Ray Diffraction

The following data and corresponding figure shows the XRD result of coating material Titanium Dioxide powder tested from KARUNYA University , Coimbatore.

Basic Data Process

Group : out –XRD- 1098

Data : Titanium Dioxide

Strongest 3 Peaks

TABLE V : STRONGEST 3 PEAKS

No:	Peak no:	2Theta(deg)	d (A)	I/ I 1	FWHM	Intensity (Counts)	Integrated Intensity (Counts)
1	1	25.6215	3.47404	100	0.40890	2450	10829
2	5	48.3621	1.88052	30	0.42170	757	3498
3	3	38.1280	2.35837	22	0.39710	547	2159

TABLE VI: PEAK DATAS

Peak no:	2Theta(deg)	d (A)	I/ I 1	FWHM	Intensity (Counts)	Integrated Intensity (Counts)
1	25.6214	3.47404	100	0.40890	2450	10829
5	37.3143	2.40791	6	0.41870	154	696
3	38.1280	2.35837	22	0.39710	547	2159
4	38.8756	2.31472	8	0.40290	189	820
5	48.3621	1.88052	30	0.42170	747	3498
6	54.2214	1.69033	20	0.41570	491	2087
7	55.3833	1.65758	19	0.39010	474	2006
8	63.0232	1.47378	16	0.43780	388	2164
9	69.0646	1.35886	6	0.42550	159	890
10	70.6143	1.33279	6	0.53870	141	807
11	70.3710	1.26005	10	0.40320	245	1227
12	83.0073	1.16242	7	0.36950	161	852

Group : Out- XRD- 1098

Data : Titanium Dioxide

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Date and Time : 10-12-2015 14:24:05

Measurement condition

X-ray tube

Target : Cu
Voltage : 40.0 (kV)
Current : 30.0 (mA)

Slits

Auto Slits : not used
Divergence slit : 1.00000 (deg)
Scatter slit : 1.00000 (deg)
Receiving Slit : 0.30000

Scanning

Drive axis : Theta – 2Theta
Scan range : 10.0000 – 90.0000 (deg)
Scan mode : Continuous Scan
Scan speed : 10.0000 (deg/min)
Sampling pitch : 0.1000 (deg)
Preset time : 0.60 (sec)

Data Process condition

Smoothing : Auto
Smoothing point : 5
B.G. Substruction : Auto
Sampling Points : 5
Repeat times : 30
Ka1-a2 Separate : [Manual]
Ka1 a2 ratio : 50 (%)
Peak Search : Auto
Differential points : 5
FWHM threshold : 0.050 (deg)
Intensity threshold : 30 (par mil)
FWHM ratio (n-1)/ n : 2
System error Correction: No
Precise Peak Correction: No

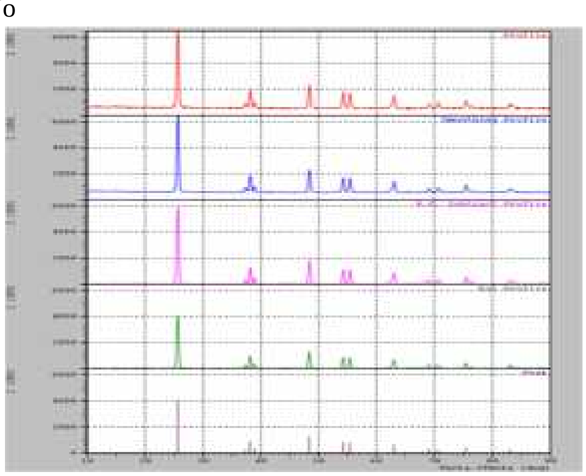

Fig 12: XRD Paterns of the Titanium Dioxide powder

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VII. CONCLUSION

Various tests are carried out on Plasma sprayed coated Titania on Aluminium and steel sample. This study helps to understand the possibility of using Titanium Dioxide in Piston parts of Internal combustion engines for its better thermal efficiency and less fuel consumption. The SEM images shows that the particles are equi-axed type and distributed homogeneously. Although some porosity is observed. Unmelted particles are not observed in the coatings due to complete melting during spraying. In the powder, various phases has identified. Besides the tetragonal and cubic phases, there are some monoclinic phase in the titanium dioxide powder. There are no reaction products at the coating-substrate interfaces, which indicates good bonding between them. The test results conclude that it is possible to use Titanium Dioxide as Thermal Barrier Coating(TBC) Material and there is a good future scope for it in Automobiles and industries for enhancing the efficiency with less fuel consumption rate.

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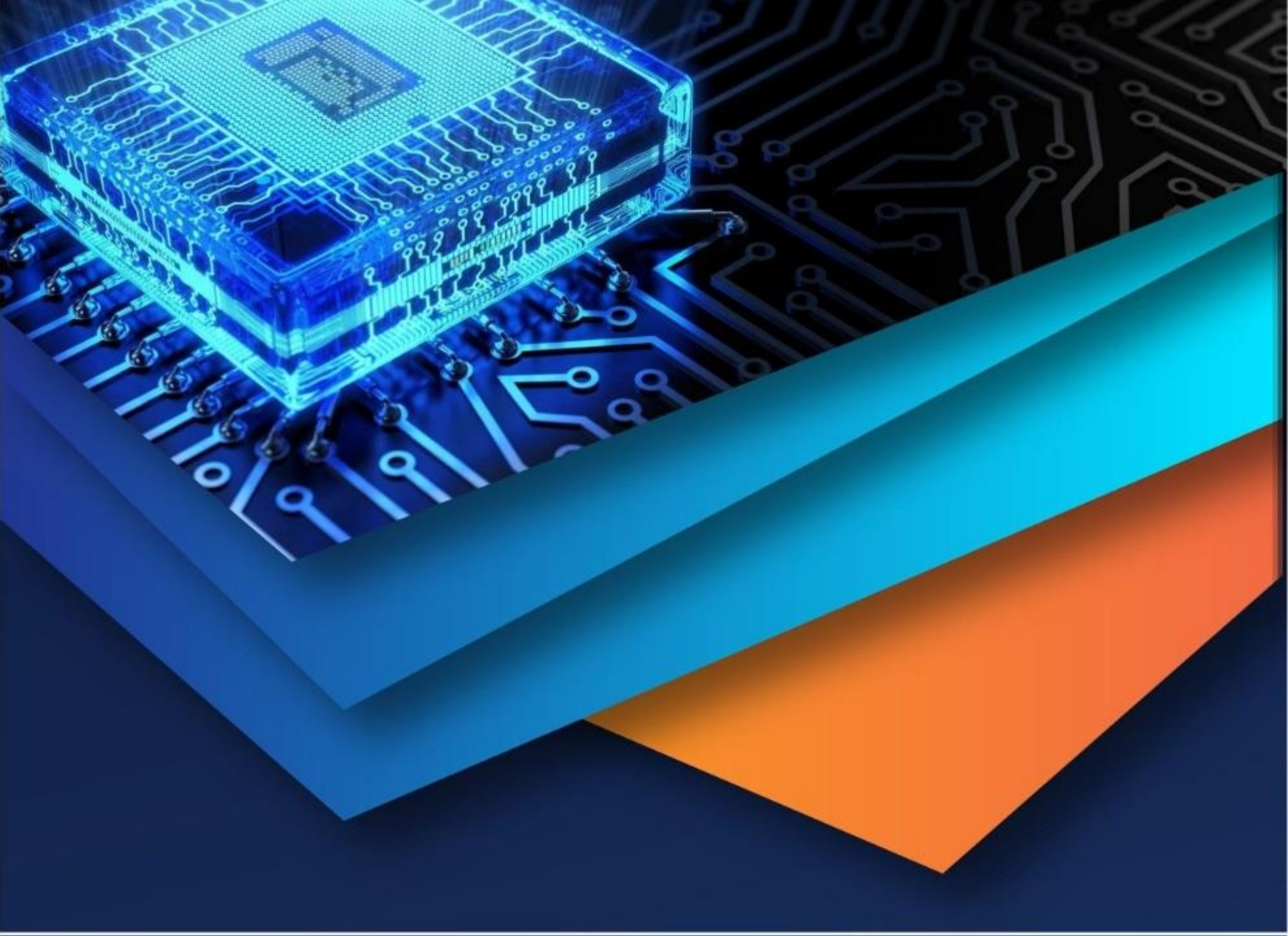

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