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Enhancement of Insulation Properties of RAFM Steel Surface by Development of Thin Film Coating of Aluminium Oxide by Laser Technique

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Abstract

Reduced activation Ferritic/Martensitic steel (RAFMS) is a potential candidate material for structural applications specially as coolant channels in the Indian Test Blanket Module System (TBM) for International Thermonuclear Experimental Reactor (ITER). In order to prevent any pressure drop effect during the flow of metallic coolant of Pb-Li liquid through the RAFMS cooling channels due to magneto-hydrodynamic effect (MHD), surface coating with high electrical insulating properties is required prior to use. Hence, in the present study, investigations were carried out to develop coating of alumina (Al_2O_3) on RAFM steel substrate by pulse laser deposition (PLD) technique as alumina has unique properties of high electrical insulation properties. Moreover, by laser technique, it was possible to obtain defect free surface with impervious layer of thin film coating of alumina which is responsible to render high electrical insulation property. Laser pulse transformed the meta-stable Al-O (γ) phase present in the alumina target into thermodynamically stable Al-O (α) phase in the coating. Maximum coating thickness of 2 µm was achieved having uniform and defect free surface. High electrical insulation property in terms of electrical resistivity was achieved (electrical resistivity value: 2.14×10^6 ohm.cm). The alumina coating further showed very high hardness of value of 400 VHN and high adhesive strength of the order of 15 MPa.

Keywords: Laser, Deposition, Alumina, Coating, RAFMS, Characterization

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I. INTRODUCTION

The surface engineering plays an important role for the enhancement/modification of the surface properties of various engineering components to combat against adverse environment in which the parts are subjected. The choice of a surface material with appropriate thermal, electrical and magnetic properties and having adequate resistance to wear, corrosion and degradation is crucial for its functionality. Continuous efforts to enhance the surface properties of various engineering components has resulted in the development of various surface coating techniques such as chemical Vapour Deposition (CVD), Magnetron Sputtering (MS), Pulsed Laser Deposition (PLD) processes etc.. Laser surface modification is an emerging field, wherein lasers are used for imparting superior surface properties on engineering components. In this regard, PLD based excimer laser method is extensively used in microelectronics, biomedical and surface engineering applications to produce functional protective coating films. PLD is a physical vapor deposition (PVD) technique in which a short laser pulse (10 to 30 ns) is focused onto a solid target. The laser rapidly raises the surface temperature of a small portion of the target beyond the vaporization temperature. A plume of evaporated material is ejected from the target is collected and transferred on a nearby substrate to depose high quality coating onto the substrate [1-3].

Alumina (Al_2O_3) on account of its excellent chemical, dielectric, optical, tribological and biomedical properties, alumina films are widely used in biomedical and tribological applications due to higher chemical inertness, excellent wear resistance; hardness and better surface finish. Moreover, aluminum oxide has an excellent chemical compatibility, high electrical resistivity and capability to provide impervious layer of coating against any leakage. Therefore, it has attracted significant attention for a wide range of applications including oxidation and hot corrosion resistance, wear resistance, heat and thermal shock resistance and electrical insulation [4].

Reduced activation Ferritic / Martensitic steel is a potential candidate material for structural applications for Indian Test Blanket Module system for International Thermonuclear Experimental Reactor (ITER) system. However, high electrically insulating coating on RAFM steel is an essential prerequisite prior to use as cooling channels in the blanket system to prevent any pressure drop due to MHD effect during the flow of metallic coolant as well as to form impervious layer of coating to minimize leakage of radioactive tritium [5]. Hence, in the present investigation, attempts were made to develop highly insulating type coating of alumina on RAFM steel substrate by pulse power deposition technique so that dense, defect free and impervious layer of coating is achieved with high electrical insulating properties and adequate adherence. Utility of pulse power lasers was used to transform the meta-stable Al-O (γ) phase present in the target material into thermodynamically stable Al-O (α) phase after deposition on the substrate surface. The microstructural characterization of alumina coated thin film surface was studied with respect to surface morphology, composition, microstructure etc. using SEM-EDS (scanning electron microscopy-energy dispersive spectrum) and optical microscopy. Phase analysis of the coatings was carried out by XRD (X-ray diffraction analysis) and their important properties such as adhesion strength as well as hardness measurement were evaluated to determine their qualities. In order to evaluate the suitability of alumina coating for application as an insulating material; insulation properties of coated as well as uncoated RAFM steel surfaces were determined by measuring their resistivity (ρ) using four probe method. The results of all these studies are discussed in this paper.

II. EXPERIMENTAL

A. *Sample Preparation and Procedure*

As-received RAFM steel was prepared by arc melting technique. The cast ingot was hot forged and hot rolled to 6 mm thick plates. These plates were subsequently subjected to homogenization annealing heat treatment at 700^0C for 2 hrs. The plates were sectioned half by electro-discharge machining technique into 3 mm plates. The roughness/unevenness of the surface of the plates was smoothened by surface grinding using milling process. The plates were subsequently cut into coupons of approximate dimension 20 x 20 x 2 mm for using as substrates to deposit coatings. The RAFM steel used as a substrate has chemical composition containing 9.04% Cr, 0.22% V, 0.06%Ta, 0.55% Mn, 0.12% C, 1.39% W and bal. Fe (wt%) which is as comparable to international standard of composition of European and other varieties of RAFM steels. The samples were metallographically polished by silicon carbide papers in stages and finally by 6 µm diamond paste to produce scratch free mirror finish polished surface. Prior to coating, RAFM steel microstructure was revealed using an etchant composed of 5 ml HNO_3, 1 ml HF, 50 ml distilled water. The disk shaped target used in PLD experiments was prepared by taking high purity (99.9 wt.%) alumina powder of average particle size 30 µm and pressing it into 15 mm diameter disc with 3 mm thickness in an uniaxial hydraulic press applying 200 MPa pressure. The alumina disc was subsequently sintered at $800\text{-}1000^0$C for 2 hours to consolidate and then used as target in PLD system. Fig.1 shows schematic diagram of PLD set-up used in this study. The thin film deposition experiments were carried out inside a stainless steel reaction chamber which was evacuated to residual pressure of 3×10^{-4} Torr (4×10^{-2} Pa) prior to every deposition. The corresponding photo of Pulse power laser deposition system was presented in Fig.2. The UV KrF excimer laser system from Lambda Physik (Model Compex 201), having 248 ns wavelength and 20 ns pulse width was used to ablate the target material. During PLD deposition, laser beam at a fluence of 5.5 J/cm^2 was incident onto rotating alumina target at repetition rate of 10 Hz for duration of 3 and 7 hours. The plume of evaporated material ejected from target deposit thin films onto the substrate kept at 50 mm distance from target which is pre-heated at 600 to 800^oC.

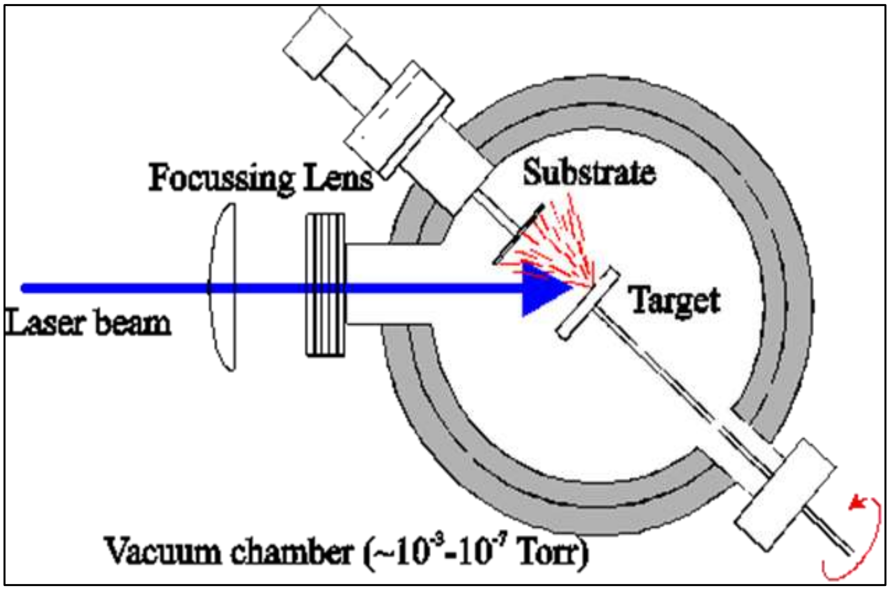

Fig. 1: Schematic diagram of a pulse power laser deposition system

Fig. 2: Photograph of pulse laser deposition system

B. *Characterization and Property Evaluation*

The optical microscopic examination of etched specimen of RAFM steel substrate was carried out at various magnifications to reveal its micro-structural details. The deposited thin film of alumina coatings were subjected to examination by scanning electron microscopy (SEM) to measure the coating film thickness and to study the surface morphology of the coated surface. Further, evaluation of elemental composition of substrate as well as coating was carried out by energy dispersive spectrometry (EDS) and X-ray diffraction (XRD) analysis to evaluate the phases of the coating formed. The coating phases were confirmed by x-ray diffraction analysis. The hardness profiles of the coated and uncoated surfaces were measured using Vickers micro-hardness tester.

The adhesive strength between the coating and substrate was measured using Posi-Test AT Pull-off adhesive tester. In this respect, 10 mm dia. aluminium dolly was glued on to the surface of the coating and force was applied by hydraulic pressure to pull-off the dolly which was measured to find out the adhesive strength.

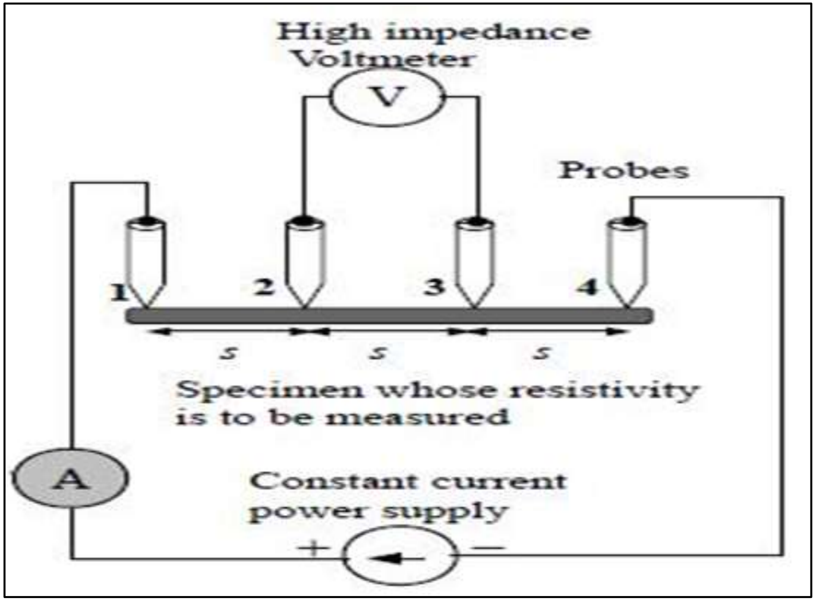

Fig. 3: Sketch diagram showing measurement of resistivity by four probe method

The surface resistivity of the coated and uncoated RAFM steel substrate surfaces was measured by four probe method at various temperatures (RT to 200^{0}C).The sketch of an experimental set-up used for measurement of resistivity by four probe method is shown in Fig.3. The high impedance current source is used to supply current through outer two probes; a voltmeter measures the voltage across the inner two probes to determine resistivity. As per the Ohm's law, the resistance R of a material is proportional to its length L, and cross-sectional area A, which can be stated by the formula, $R= \rho\ (L/A)$ where ρ is the resistivity. Assuming that the size of the metal tip of the probe is infinitesimal and sample thickness is greater than the distance between the probes, the resistivity value can be deduced using the formulae,

$$\rho_0 = \frac{V}{I} \times 2\pi S$$

Where ‘V’ is the potential difference between inner probes in volts, ‘I’ is current through the outer pair of probes in ampere and ‘S’ denotes spacing between the probes in meter [6].

III. RESULTS AND DISCUSSION

Prior to coating, metallographic characterization was performed on the surface of uncoated RAFM steel to evaluate its suitability as a substrate for forming alumina coating. The optical microstructure of the RAFM steel surface was depicted in Fig.4. The microstructure of RAFM steel substrate surface demonstrated a dual phased microstructure containing both ferritic and martensitic phases decorated with carbides of $M_{23}C_6$ types. The grains are mostly equiaxed but also mingled with partially elongated grains. However, overall microstructure is uniform and devoid of presence of any cracks, cavity or porosity. This microstructural stability of RAFM steel was found conducive for using as substrate for developing alumina coatings. The SEM images of surface morphology of coatings deposited while the substrtaes were kept at temperatures of 600^0C and 800^0C are presented in Fig.5 and Fig.6 respectively. Fig.5 shows uniform and dense formation of alumina coating all over the substrate surface. Coating particles were partially melted on the pre-heated RAFMS substrate (600^0C) and formed a dense impervious layer of coating without any presence of porosity. Fig.6. exhibits that coating particles transformed into a coagulated mass layer which spreads stepwise uniformly all over the substrate ensuring a firm bonding with the substrate. This can be contributed to the preheating of the substrate to further temperature of 800^0C. The cross-sectional SEM study was carried out to distinguish the interface and coating layers from the substrate and also to determine the coating thickness. The corresponding SEM image was presented in Fig.7. The coatings as well as the interfacial layers were clearly depicted in the SEM image which indicate that coating layer was uniformly formed all along the substrate surface without having any crack or cavity and the coating thickness varied from 500 nm to 2 μm for the duration of 3 and 7 hours respectively during the laser deposition process.

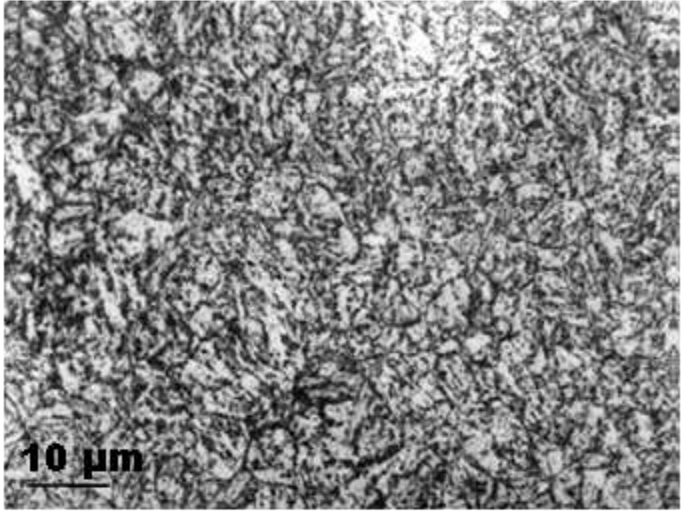

Fig. 4: Optical microstructure of RAFM Steel Substrate

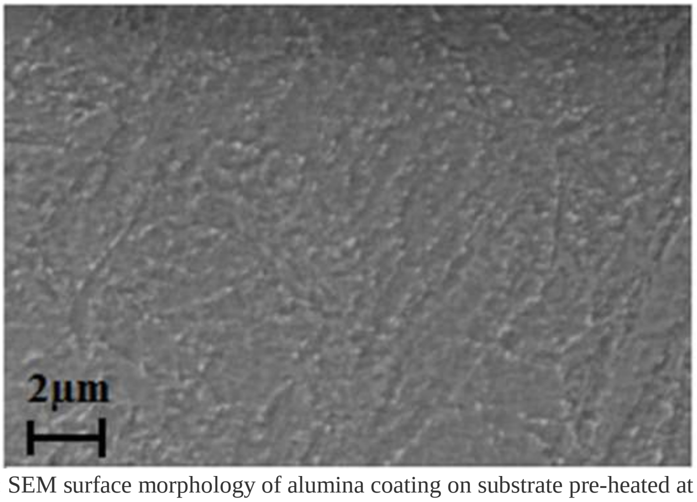

Fig. 5: SEM surface morphology of alumina coating on substrate pre-heated at 600^0C

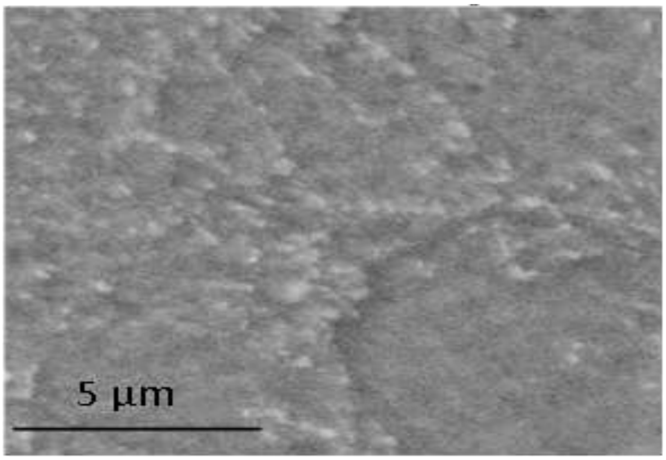

Fig. 6: SEM surface morphology of alumina coating on RAFMS substrate pre-heated at 800^0C

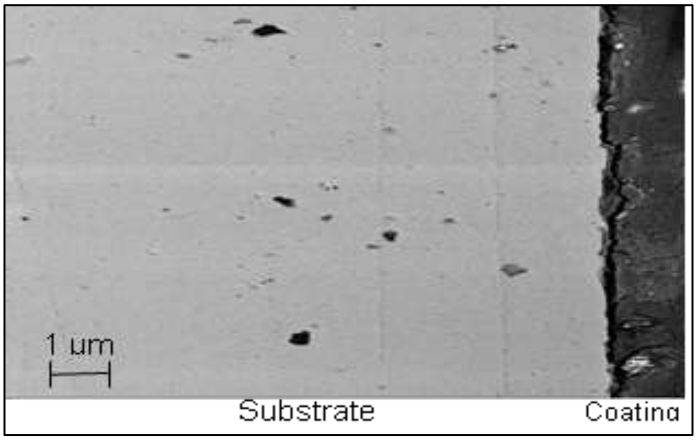

Fig. 7: Cross sectional SEM image of coating formed on RAFMS substrate

The results of EDS analysis of the composition of coating and underlying substrate was presented in Fig.8. The peak ratio of Al and O resembles to alumina (Al_2O_3) coating phase whereas other elemental peaks correspond to the composition of RAFM steel substrate. During the period of deposition of alumina coating by laser beam, pre-heating of the substrate at 700-800^0C helped in the formation of coating as well as major transformation of metastable γ alumina phase into α-Al_2O_3 as the as received target material originally was γ phase . The combined effect of high preheating temperature of the target and the additional heat provided by laser power to convert alumina into vapor phase facilitated the formation of metastable γ alumina into desirable α phase on the substrate surface. There are several factors which can influence the sequence of phase transformation of alumina such as particle size, heating rate, impurities, and atmosphere due to the effect on the kinetics of transformation. The final coating phase was subsequently confirmed by XRD analysis as depicted in Fig.9. Which showed peaks corresponding to alpha alumina phase. Alumina is a polymorphous material and can exist in the form several meta-stable polymorphs such as α, γ, δ, θ, etc. However, α-Al_2O_3 is thermodynamically most stable and ductile phase which is desirable properties for coating formation. All other alumina phases are meta-stable. In the present case, α- Al_2O_3 was formed as substantiated by XRD analysis [7-9].

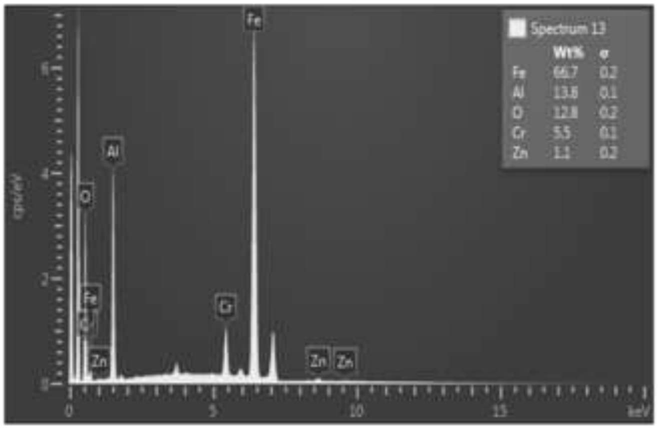

Fig. 8: EDS analysis of composition of coating formed on the surface

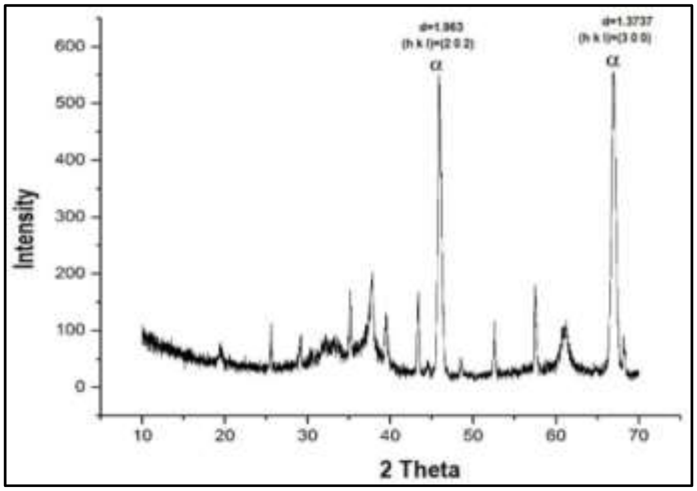

Fig. 9: XRD pattern of coating deposited on RAFMS

During measurement of the resistivity by four probe method, the average value of V/I was determined for each temperature and the resistivity was calculated using formula,

$$\rho = (V/I)_{avg} \times 2\pi S$$

Where S= 0.2 cm in this case. The variation of resistivity values of RAFM steel surface at various temperatures are described in Table-1. The corresponding Fig.10 shows the variation of resistivity of RAFM steel with temperature; it was found that the resistivity of RAFM steel increases from $3.29 \times 10^{-7}$to 6.29×10^{-7}ohm.m as the temperature increases from 30 to 200^0C. Table-2 shows the variation of resistivity of alumina coated surface with temperature. The resistivity of alumina coatings was found varying from 1.33×10^4 to 2.14×10^4ohm.m or 2.14×10^6 ohm.cm as temperature varies from 30 to 200 ^{0}C (Fig.11). This value resistivity value satisfies the requirement for minimum resistivity value as essential for fusion reactor coating material [9]. The alumina coating showed much higher resistivity than that of the RAFM steel surface; which demonstrates that using PLD technique highly insulating type coating of alumina could be deposited on the RAFM steel substrate.

Table – 1:
Resistivity values of uncoated RAFM steel at various temperatures

Temperature	*Average V/I (ohm)*	*Resistivity (ρ) ohm.m*
RT	2.62×10^{-5}	3.29×10^{-7}
50	3.41×10^{-5}	4.29×10^{-7}
100	4.62×10^{-5}	5.81×10^{-7}
150	4.83×10^{-5}	6.07×10^{-7}
200	5.02×10^{-5}	6.29×10^{-7}

Table – 2:
Resistivity values of alumina coated RAFM surface at various temperatures

Temperature	*Average V/I (ohm)*	*Resistivity (ρ) ohm-m*
RT	1.06×10^{6}	1.33×10^{4}
50	1.18×10^{6}	1.43×10^{4}
100	1.55×10^{6}	1.95×10^{4}
150	1.67×10^{6}	2.10×10^{4}
200	1.70×10^{6}	2.14×10^{4}

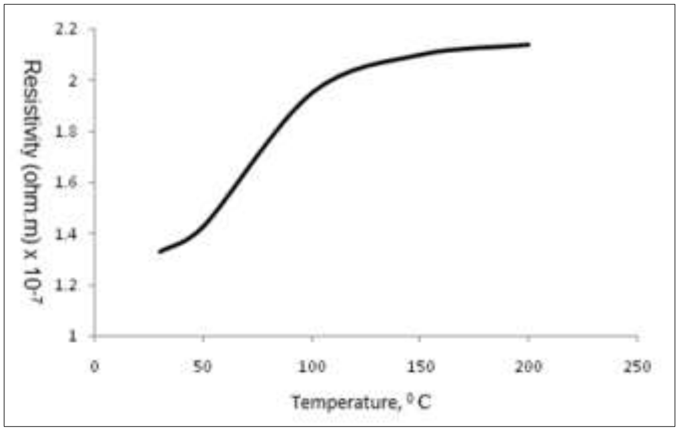

Fig. 10: Variation of resistivity (ρ) of pure RAFM steel with temperature

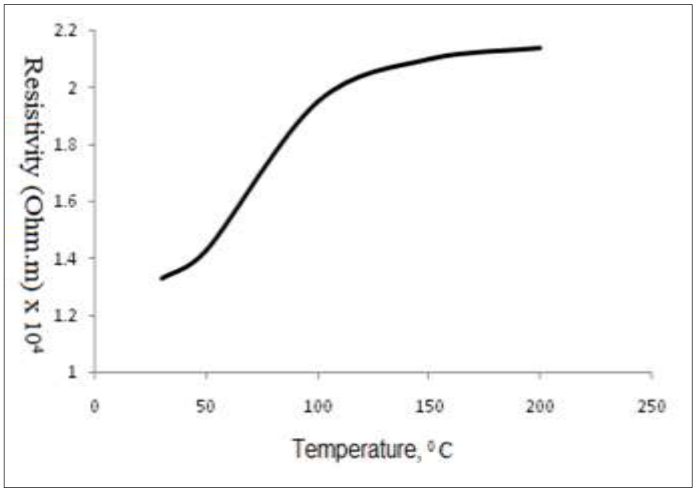

Fig. 11: Variation of resistivity (ρ) of alumina coated RAFM steel surface with temperature

The adhesive strength measured on the alumina coating surface was presented in Fig.12. The adhesive strength between coating and substrate was found to be high in the order of 15 MPa. Fig.13 shows hardness profile measured across the alumina coating surface. The coating was found to be adequately hard against any wear and tear effect indicating average hardness value of 400 VHN as compared to 270 VHN of the substrate.

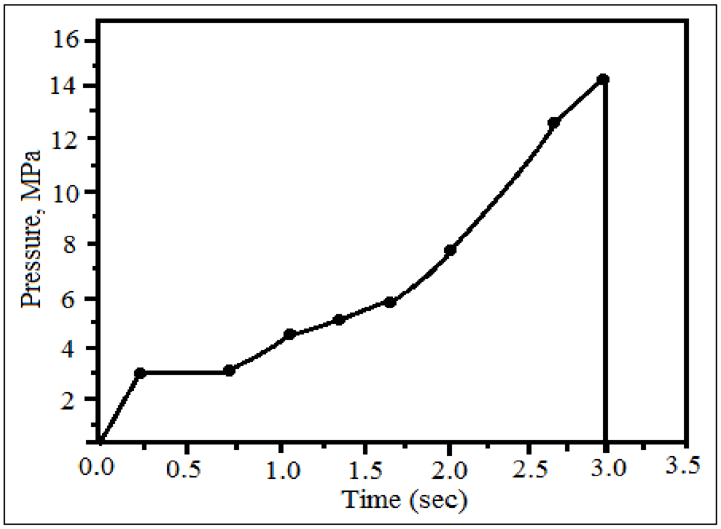

Fig. 12: A typical plot showing high adhesive strength of the coating

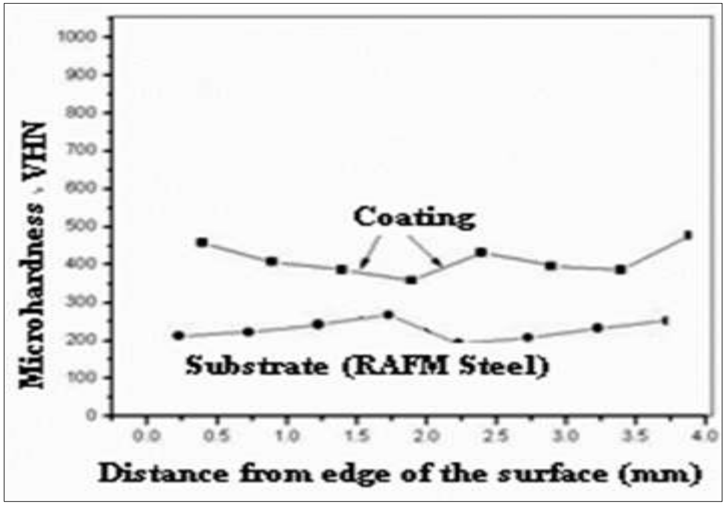

Fig. 13: Hardness profile of alumina coating and RAFMS substrate

IV. CONCLUSIONS

The present work demonstrates the feasibility of developing protective coating of alpha alumina by pulse power laser deposition (PLD) technique over ferritic mertensitic steel of RAFM variety. The uniform coating was found all over the surface of substrate and average coating thickness in the range of 500 nm to 2 µm was noticed. The deposited coating films found much harder than underlined substrate and shows stable desirable α- Al_2O_3 phase. The resulted coating is strong, adequately hard, dense, adherent to the substrate and showed higher resistivity than that of the RAFM steel surface. Further studies on development of alumina coatings by varying substrate temperature, laser power and chamber pressure are being carried out to enchance the coating thickness and improve coating morphology.

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