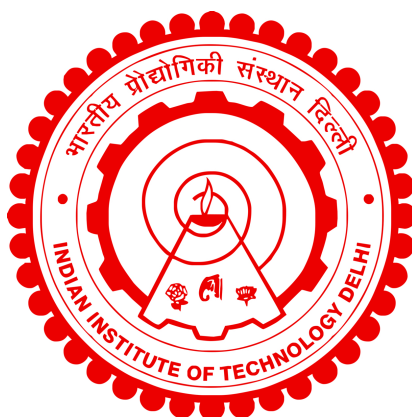


MULTIFUNCTIONAL CERAMIC-BASED COATINGS ON STRUCTURAL STEELS

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CENTRE FOR AUTOMOTIVE RESEARCH AND
TRIBOLOGY (FORMERLY ITMMEC)

INDIAN INSTITUTE OF TECHNOLOGY DELHI

July 2023

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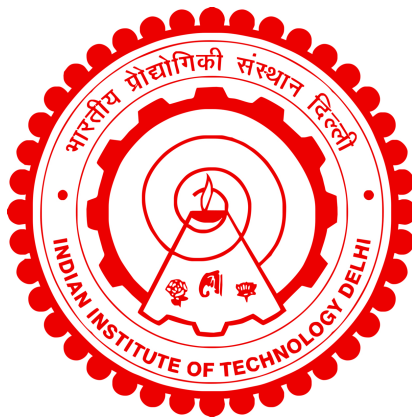
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Centre for Automotive Research and Tribology (formerly ITMMEC)

Submitted

in partial fulfillment of the requirements of the degree of Doctor of Philosophy

to the



**INDIAN INSTITUTE OF TECHNOLOGY
DELHI**

July 2023

Dedicated to my teachers

Certificate

This is to certify that the thesis entitled “**Multifunctional ceramic-based coatings on structural steels**”, submitted by **Avi Gupta** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of the original, bonafide research work carried out by him under my supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations related to the award of the degree.

The results in this thesis have not been submitted in part or in full to any other University or Institute for awarding any degree or diploma to the best of our knowledge.

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Acknowledgements

यस्य सर्वे समारम्भाः काम-सङ्कल्प-वर्जिताः ।

ज्ञानाग्नि-दग्ध-कर्माणं तम् आहुः पण्डितं बुधाः ॥ श्रीमद् भगवद् गीता ४.१९ ॥

One is understood to be in full knowledge whose every endeavour is devoid of desire for sense gratification. He is said by sages to be a worker for whom the reactions of work have been burned up by the fire of perfect knowledge.

(Shrimad Bhagavad Gita, 4.19)

In the journey of seeking the meaning and purpose of life, the idea of attaining perfect knowledge is critical. For what the almighty has bestowed upon me in this academic phase of my life, I have gotten closer to the essence of that perfect knowledge. I feel indebted to my teachers for being the providers of the same.

Prof. Deepak Kumar is a fine embodiment of a teacher. I was inspired and created as a critical thinker, a person of strong character, and a man with a larger perspective not only by his care but also by his tough inquiry. His nurturing attempts to help me become resilient will endure in me forever. Under his supervision, it couldn't be much easier to conduct an academic analysis of such high quality than he made it for me.

I am thankful to Prof. B.K. Panigrahi, Head CART, for providing facilities for the research work. I am sincerely thankful to my SRC members Prof. S. Fatima (SRC Chairman), Prof. R.K. Pandey and Prof. Akhil Garg for their encouragement and timely suggestions.

My heartfelt gratitude goes out to my seniors/mentors, Dr. Sanjeet Kumar, Dr. Harprabhjot Singh, and Dr. Ajay Pratap Singh Lodhi for their brotherly support throughout my research work. They always lent me a hand whenever I needed it.

I express gratitude to my colleagues Mr. Ankit, Mr. Bharat, Mr. Abhijit, Mr. Abhijith, Ms. Bhavyanidhi, Ms. Gazal, Mr. Arun, Dr. Jaya, Ms. Sunali, Mr. Rishmaya, Mr. Jonty, Mr. Nitish, Mr. Priyank and Mr. Akshit for their companionship,

invaluable advice, motivation, support, criticism, and help during this journey.

I am thankful to the staff of the Centre for automotive research and tribology – CART (formerly ITMMEC), the Department of material science and engineering (DMSE), the nanoscale research facility (NRF), IIT Delhi, and the Central research facility (CRF) IIT Delhi, for experimental support.

I am also thankful to the department of atomic energy, board of research in nuclear sciences (DAE, BRNS, India (Sanction no. 34/14/01/2018-BRNS)) for providing financial support for the HVOF coating unit, and the Indian navy for providing DMR 249A steel as the substrate material for the studies.

I sincerely thank the Board for sports activities (BSA) IIT Delhi and its staff for associating me with the honour of being a part of the institute's hockey team. I maintained a healthy working atmosphere for myself because of BSA IIT Delhi.

Without the pillars of my life, my family, I couldn't have been standing where I am today. I seek enlightenment from them to grow as a better person and try to bring contentment to all the lives associated with me.

Avi Gupta

Synopsis

Steels are susceptible to surface- and sub-surface-related degradations (e.g., corrosion and wear) depending upon the working environment; however, desired properties can resolve these issues. Low alloy steels like ASME SA 387 Gr22 Cl2 are used for structural applications exposed to extreme environmental conditions such as high-temperature corrosive and erosive environments in the petrochemical industry, turbomachinery, chemical reactors, and nuclear industry. These extreme environmental conditions severely affect the performance of critical components. To mitigate the impacts of erosion and corrosion, a novel bilayer coating system comprising of alumina (Al_2O_3)-based coating (the primary layer), and silica-zinc oxide (SiO_2 — ZnO) nano core-shell incorporated PU-based coatings (secondary topmost layer) were also developed for DMR 249A steel. The high-velocity oxygen-fuel (HVOF) technique was used to fabricate the alumina-based coatings, whereas the hand lay-up process was used to develop polyurethane (PU) based coatings. The coating material chosen comprises ceria (CeO_2) and hexagonal boron nitride (hBN) as the reinforcements. The physical characteristics of the coatings are recorded in terms of density measurement, thermogravimetric analysis (TGA), and surface wettability analysis. The hardness and elastic modulus of the coatings are estimated at room temperature using nanoindentation and microhardness at high temperature (400°C) using Vickers hardness tests. Metallurgical characterization and eroded surface analysis are done using Scanning electron microscopy (SEM), Field emission scanning electron microscopy (FESEM), Transmission electron microscopy (TEM), Energy dispersive

X-ray spectroscopy (EDS), Raman spectroscopy, and X-ray diffraction (XRD). High temperature (400°C) erosion performance of the coatings is recorded using a solid particle Air-jet erosion tester. The Corrosion performance of the coatings is analyzed using the potentiodynamic polarization technique and electrical impedance spectroscopy (EIS). Improvements in the mechanical properties and erosive wear resistance of the hybrid coating are attributed to microstructural changes and the generation of new phases. The values of $\frac{H}{E}$, $\frac{H}{E^2}$, and $\frac{H^3}{E^2}$ are used to develop the mechanistic understanding of coatings' erosion behavior. Significant improvement in hot erosion performance (Erosion reduction $\approx 96\%$ at 30° and $\approx 63\%$ at 90°) and corrosion resistance ($\approx 92\%$ reduction in corrosion rate) is recorded for the coating reinforced with 0.8 wt.% ceria (CeO_2) and 3 wt.% hexagonal boron nitride hBN as compared to the bare steel. A detailed investigation is also carried out starting with analyzing the corrosion initially, followed by the slurry erosion process. The C-A8C6h coating exhibited the least current density ($5.96 \times 10^{-6} \text{ A.cm}^{-2}$) and highest potential value (-0.71 V), and C-A showed the highest current density ($9.74 \times 10^{-5} \text{ A.cm}^{-2}$) and the corresponding potential of -0.83 V. Erosion decrements of $\approx 90\%$ at 30° impact angle and $\approx 76\%$ at 90° impact angles were observed for C-A8C3h coating when compared to the substrate in the saline environments. The improved erosive and corrosive characteristics of the coatings are attributed to the refined microstructural aspects, in-situ generation of hard second phases, and induction of hydrophobicity in the composite structure. Compared to bare steel, the PU coating doped with 4 wt.% $\text{SiO}_2\text{-ZnO}$ nano core-shell particles exhibited a

tremendous increase in erosion performance (Erosion reduction $\approx 100\%$ at 30° and $\approx 99\%$ at 90°) and corrosion resistance ($\approx 92\%$ reduction in corrosion rate). Bilayer coating configuration with enhanced microstructural characteristics and induction of hydrophobicity in the coatings is attributed to the increased erosion and corrosion resistance of the coatings.

सार

स्टील सतह और उप-सतह से संबंधित क्षरण (उदाहरण के लिए, जंग और घिसाव) के प्रति संवेदनशील होते हैं और काम के माहौल पर निर्भर करता है; हालाँकि, वांछित गुण इन मुद्दों को हल कर सकते हैं। एसएमई एसए 387 श्रेणी 22 वर्ग 2 जैसे कम मिश्र धातु वाले स्टील का उपयोग किया जाता है। उच्च तापमान जैसी अत्यधिक पर्यावरणीय परिस्थितियों के संपर्क में आने वाले संरचनात्मक अनुप्रयोग पेट्रोकेमिकल उद्योग, टर्बोमशीनरी में संक्षारक और क्षरणकारी वातावरण, रासायनिक रिएक्टर, और परमाणु उद्योग, ये अत्यधिक पर्यावरण स्थितियाँ महत्वपूर्ण घटकों के प्रदर्शन को गंभीर रूप से प्रभावित करती हैं। क्षरण और संक्षारण के प्रभाव को कम करने के लिए, एल्यूमिना से युक्त एक नवीन बाइलेयर कोटिंग प्रणाली (Al_2O_3)-आधारित कोटिंग (प्राथमिक परत), और सिलिका-जिंक ऑक्साइड (SiO_2-ZnO) नैनो कोर-शेल में पीयू-आधारित कोटिंग्स (द्वितीयक सबसे ऊपरी परत) को DMR 249A स्टील के लिए विकसित किया गया। उच्च-वेग ऑक्सीजन-ईंधन (HVOF) तकनीक एल्यूमिना-आधारित कोटिंग्स बनाने के लिए उपयोग किया गया था, जबकि हाथ से ले-अप प्रक्रिया का उपयोग किया गया था। इसका उपयोग पॉलीयूरेथेन (पीयू) आधारित कोटिंग्स विकसित करने के लिए किया गया था। कोटिंग सामग्री का चयन किया गया, सुदृढीकरण के रूप में सेरिया (CeO_2) और हेक्सागोनल बोरान नाइट्राइड (hBN) शामिल हैं। कोटिंग्स की भौतिक विशेषताओं को घनत्व माप के संदर्भ में दर्ज किया जाता है, थर्मोग्रैविमेट्रिक विश्लेषण (टीजीए), और सतह वेटेबिलिटी विश्लेषण से। कोटिंग्स की कठोरता और लोचदार मापांक का अनुमान कमरे के तापमान पर लगाया जाता है विकर्स का उपयोग करके उच्च तापमान (400 डिग्री सेल्सियस) पर नैनोइंडेंटेशन और माइक्रोहार्डनेस का उपयोग करना कठोरता परीक्षण, धातुकर्म लक्षण वर्णन और क्षीण सतह विश्लेषण हैं: स्कैनिंग इलेक्ट्रॉन

माइक्रोस्कोपी (एसईएम), फील्ड उत्सर्जन स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (एफईएसईएम), ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोपी (टीईएम), ऊर्जा फैलाव एक्स-रे स्पेक्ट्रोस्कोपी (ईडीएस), रमन स्पेक्ट्रोस्कोपी, और एक्स-रे विवर्तन (एक्सआरडी)। उच्च कोटिंग्स का तापमान (400°C) क्षरण प्रदर्शन एक ठोस का उपयोग करके दर्ज किया जाता है: कण एयर-जेट क्षरण परीक्षक। कोटिंग्स के संक्षारण प्रदर्शन का विश्लेषण किया जाता है: पोटेंशियोडायनामिक ध्रुवीकरण तकनीक और विद्युत प्रतिबाधा का उपयोग करना स्पेक्ट्रोस्कोपी (ईआईएस)। यांत्रिक गुणों और क्षरणकारी घिसाव में सुधार हाइब्रिड कोटिंग के प्रतिरोध को सूक्ष्म संरचनात्मक परिवर्तनों के लिए जिम्मेदार ठहराया जाता है। नए चरणों का निर्माण H/E , H/E^2 , और H^3/E^2 का उपयोग विकसित करने के लिए किया जाता है, कोटिंग्स के क्षरण व्यवहार की यंत्रवत समझ। बड़ा सुधार गर्म कटाव प्रदर्शन में (क्षरण में कमी $\approx 96\%$ 30° पर और $\approx 63\%$ 90° पर) और संक्षारण प्रतिरोध ($\approx$ संक्षारण दर में 92% की कमी) दर्ज किया गया है। कोटिंग को 0.8 wt.% सेरिया (CeO_2) और 3 wt.% हेक्सागोनल बोरान नाइट्राइड के साथ प्रबलित किया गया नंगे स्टील की तुलना में एचबीएन विस्तृत जांच भी की जाती है। प्रारंभ में संक्षारण का विश्लेषण करने के साथ शुरुआत करें, उसके बाद घोल क्षरण प्रक्रिया का विश्लेषण करें। C-A8C6h कोटिंग ने सबसे कम वर्तमान घनत्व प्रदर्शित किया ($5.96 \times 10^{-6} A.cm^{-2}$) और उच्चतम संभावित मान (-0.71 V), और C-A ने उच्चतम वर्तमान घनत्व दिखाया ($9.74 \times 10^{-5} A.cm^{-2}$) और -0.83 वी की संगत क्षमता। कटाव में कमी 30° प्रभाव कोण पर $\approx 90\%$ और 90° प्रभाव कोण पर $\approx 76\%$ देखा गया खारे वातावरण में सब्सट्रेट की तुलना में C-A8C3h कोटिंग के लिए। कोटिंग्स की बेहतर क्षरणकारी और संक्षारक विशेषताओं को जिम्मेदार ठहराया जाता है: परिष्कृत माइक्रोस्ट्रक्चरल पहलू, कठिन दूसरे चरणों की इन-सीटू पीढ़ी, और समग्र संरचना में हाइड्रोफोबिसिटी का प्रेरण। नंगे स्टील की तुलना में, पीयू कोटिंग को 4 wt.% SiO_2-ZnO नैनो कोर-शेल कणों के साथ डोप किया गया कटाव प्रदर्शन में जबरदस्त वृद्धि (क्षरण में कमी $\approx 30^\circ$ पर 100% और $\approx 99\%$ 90° पर) और संक्षारण प्रतिरोध ($\approx 92\%$ संक्षारण दर में

कमी) । दोहरी परत उन्नत माइक्रोस्ट्रक्चरल विशेषताओं और प्रेरण के साथ कोटिंग कॉन्फ़िगरेशन कोटिंग्स में हाइड्रोफोबिसिटी को बढ़ते क्षरण और संक्षारण के लिए जिम्मेदार ठहराया गया है।

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Acknowledgements

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Abbreviations

HVOF	H igh - V elocity O xygen - F uel
TBC	T hermal B arrier C oating
SCC	S tress C orrosion C racking
SEM	S canning E lectron M icroscopy
XRD	X - R ay D iffraction
FESEM	F ield E mission S canning E lectron M icroscopy
EDS	E nergy - D ispersive X - R ay S pectroscopy
YSZ	Y tria - S tabilized Z irconia
hBN	hexagonal B oron N itride
PU	P olyurethane
EIS	E lectrochemical I mpedance S pectroscopy
EDM	E lectrical D ischarge M achining
TGA	T hermal G ravimetric A nalysis
OD	O ptical D ensity
LPG	L iquefied P etroleum G as
PDMS	P olydimethylsiloxane
APTES	3 - A minopropyltriethoxysilane
DBTDL	D ibutyltin D ilaurate

Symbols

ρ	Density
α	Alpha
β	Beta
γ	Gamma
Ω	Ohm
χ	Chi
$^{\circ}$	Degree
h	Hour
s	Second
m	Meter
μ	Micro
C	Celcius
F	Farad
i_{corr}	Corrosion current
V_{corr}	Corrosion potential
$\%$	Percentage