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Investigations on Corrosion Behaviour of Cold-Sprayed Titanium on SS316L Steel

Saiful Wali Khan · Gidla Vinay · Avneesh Kumar · Parminder Singh · Harpreet Singh

Indian Institute of Technology Ropar, Rupnagar (Punjab) India.

ABSTRACT

Cold-Spray (CS) is a coating technique in which micron sized particles are propelled with a carrier gas at supersonic velocity hitting the substrate with high kinetic energy. Consequently, plastic deformation and localised melting at particle substrate interface cause the deposition and coating build up. Unlike other thermal spray techniques, CS does not involve heating particles to a high temperature thus this process helps in developing coatings with low oxide content even for thermally sensitive materials. Corrosion of structures is a big global challenge and CS is a promising technique to develop corrosion resistant coatings with higher deposition rates. In this current work, Titanium coating was developed on SS-316L by a high-pressure CS and analysed for its mechanical and corrosion properties. Corrosion resistance of the generated coating was tested in a 3.5% NaCl medium for varying exposure time to understand the corrosion behaviour during long hour exposures.

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Introduction

Corrosion of a material is a natural process in which the deterioration of the material takes place when it reacts with the surrounding environment [1]. It is one of the major challenges which causes damage to structural equipment like bridges, automobiles, drinking water supply systems and buildings resulting in huge loss to life and property. A study on cost of corrosion by U.S. Federal Highway Administration (FHWA) revealed that, in U.S the direct annual cost associated with corrosion of metals is around $ 276 billion which accounts for a 3.1% share of their Gross Domestic Production (GDP) [2]. The harmful effects and loss caused by corrosion can be prevented by various ways such as surface modification, which is a process of altering/modifying the physical, biological, or chemical characteristics of the surface which is exposed to the environment [3].

Surface coating is one such surface modification technique in which a layer of substance with high corrosion resistance is applied on the top of the exposed surface of the component. The most widely used coating methods are electrochemical deposition, sol-gel deposition, vapour deposition, and thermal spray. Among the mentioned processes thermal spray is one of the well accepted coating processes used for such applications [4]. The drawback of using thermal spray processes is the involvement of high temperatures which results in detrimental defects such as porosity, oxidation, and phase change [4, 5]. Cold Spray (CS) is one of the coating techniques which comes under the family of thermal spray processes [6]. Unlike other thermal spray techniques, CS does not involve heating of particle to a high temperature thus this process helps in developing coatings with low oxide content and without any phase change or oxidation even for thermally sensitive materials like titanium and its alloys [6,7]. The deposition process in CS coatings is such that the micron sized particles (usually in the size range of 10 - 50 μm) are propelled by a carrier gas (such as Helium, Nitrogen and Air) in a convergent-divergent nozzle thereby exiting at a supersonic velocity. These high-speed particles bombard on to a targeted substrate with high kinetic energy and deformation at substrate-coating interface causing localised melting, thereby particle adhering to the substrate [6].

Steels are alloys of iron and carbon. The steels containing 10.5 % or more chromium are termed as stainless steels (SS) because of the formation of self-healing oxide film coating, which is responsible for its high corrosion resistance [8]. These stainless steels also offer good mechanical strength, high machinability, and excellent weldability, which makes them promising materials for various engineering applications [9]. However, steels have lower corrosion resistance in the marine environment and are prone to corrosion attack [10]. Titanium and its alloys are known to have good corrosion resistance in such environments and can possibly be used as coating materials for protecting steels in marine applications [11]. The property of titanium to have a high affinity towards oxygen results in information of a passive TiO layer, making it outstanding material against high corrosive environment. When the passive layer breaks, it exposes the titanium beneath the passive layer, the exposed titanium again reacts with the oxygen to re-establish the protective passive layer [12]. Thermal spray processes are generally used to deposit titanium-based coatings, but due to the high reactiveness of titanium, it results in the formation of its oxides making the coating inhomogeneous, porous, and brittle [13]. Thus, CS due to lower deposition temperature becomes a better choice to coat such metals with minimal change in feedstock and its properties. Kawakita et al. [14] produced titanium coatings with different porosity and oxidation levels by modified High-Velocity-Oxy-Fuel

Corresponding Author: Harpreet Singh, Tel: +919855709052
Email: harpreetsingh@iitrpr.ac.in

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(HVOF) process over steel substrate. It was found that polished coating with least porosity showed the best corrosion performance in artificial sea water tested for 1 month [14]. Wang et al. [11] studied the corrosion behaviour of titanium coating on 1Cr1SS substrate in sea water. Due to the porous surface of the coating, the sprayed coating resulted in higher negative open circuit potential and greater corrosion current than bulk titanium [11]. Hussain et al. [15] studied the effect of the porosity of cold sprayed titanium and its stand-alone deposits for its corrosion behaviour. It was revealed that for vacuum heat-treated coating with a porosity of about 1.8% showed passive current density identical to bulk titanium [15]. Other studies related to CS titanium are reported for deposition characteristics [16]. Only limited studies are available for their corrosion resistance. In the present work titanium coating is developed on SS316L using a high-pressure cold spray system and a comprehensive study on corrosion behaviour of CSed titanium coatings for long hours exposure in 3.5% NaCl is reported along with the mechanical properties.

Experimental

Feedstock powder and coating deposition

Commercially available irregular-shaped Ti (Nanoresearch Elements, US) powder with 99% purity was used as the feedstock material for coating deposition. The feedstock size was in the range of 10-45 µm as reported by the manufacturer. The titanium coating was deposited by using a commercially available high-pressure CS facility (Plasma Giken, PCS-100, Japan) available at Indian Institute of Technology Ropar, India. The De-Laval (convergent-divergent) nozzle having a circular exit was used as nozzle for spraying the feedstock. The coatings were generated using compressed nitrogen as a process and feedstock carrier gas flowing at 30 bar pressure and 900 °C temperature. The scan speed and the stand-off distance were taken as 0.2m/s and 25 mm, respectively.

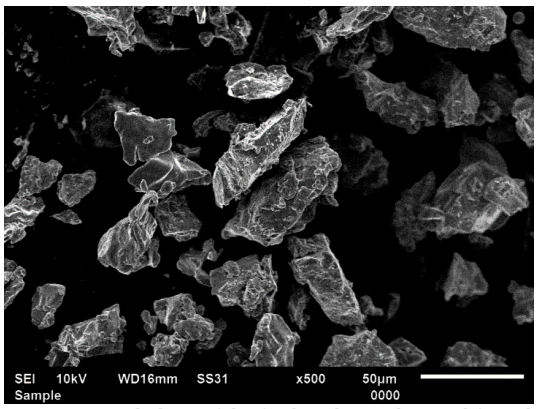


Figure 1: Morphology of the feedstock powder used for cold spraying

Microstructural characterisation

The coated samples were cut with Electrical discharge machining (EDM, ELECTRONICA, SPRINTCUT, INDIA) by following the standard procedures given for thermal sprayed coatings [17]. The specimens were mounted with Bakelite and polished up to 2000 grit size of emery papers. The Scanning-Electron Microscope, SEM (JEOL, JSM-6610 LV, Japan), with Energy-Dispersive Spectroscopy, EDS (JEOL, JSM-6610 LV, Japan) was used for microstructure and cross-sectional analysis of the as-generated and tested coatings. The porosity of the coatings was measured with an Image Analyser (Image-J software). The Vickers microhardness tester (ZWICK/ROELL ZHVl, UK) was used to measure the micro-hardness at 0.05 Kg and 0.3 Kg of load. For every load, at least 10 readings were taken at the cross section and the average value with standard deviation is reported.

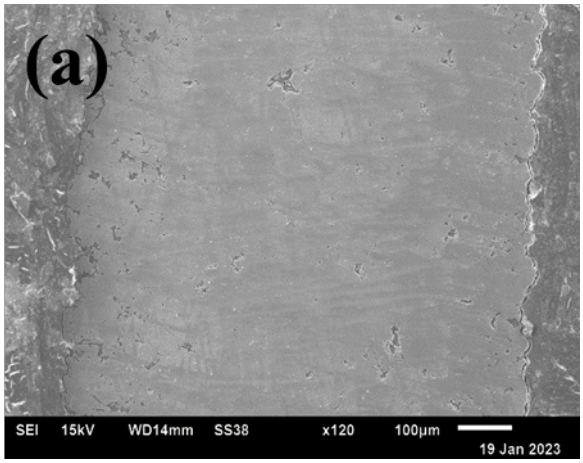
Corrosion behaviour

The developed coatings were evaluated for their corrosion behaviour using electrochemical corrosion by conducting potentiodynamic polarisation tests. For electrochemical analysis, Metro ohm Autolab workstation (Multi Autolab M204, Netherlands) equipped with Nova 2.1 software was used. A three-electrode cell setup where the coating to be tested is connected to the working electrode, platinum wire is used as a counter electrode and Ag/AgCl is used as the reference electrode for the analysis. Samples with an area of 10 mm * 10 mm were tested and the remaining faces of the samples were covered with masking tape. The generated coatings and bulk SS316L were exposed to electrolyte for different durations, namely 24 hr, 48 hr and 72 hr in 3.5 % NaCl solution. Before conducting the potentiodynamic polarisation tests, each sample was tested for their OCP (Open Circuit Potential) for 1800 s or dE/dT < 1E-6 V/s. After the potentiodynamic polarisation tests, corrosion current density, E_{corr}, polarisation resistance, anodic and cathodic slope were calculated from the tafel plots drawn using Nova 2.1 software.

Results and Discussion

Coating generation and microstructure of coatings

The morphology of the feedstock used for the coating generation is shown in Fig 1. The powder is of irregular shape size ranging from 10-45 µm. The substrate was mirror polished before spraying. Several researchers [18,19] have claimed that mirror polishing gives better adhesion, however there are some contradictory results observed by Kumar et al. [20]. A Kumar et al. [21] have used polished substrates for titanium and titanium based composite coatings and observed that polished substrates give better adhesion, so in the present study polished substrates were used. Titanium has a critical velocity of 712 m/s [22] owing to its high strength and HCP structure. In the present study, irregular-shaped particles are used which yield better velocity owing to high drag force compared with spherical-shaped particles. For the coating generation, a tungsten-carbide nozzle



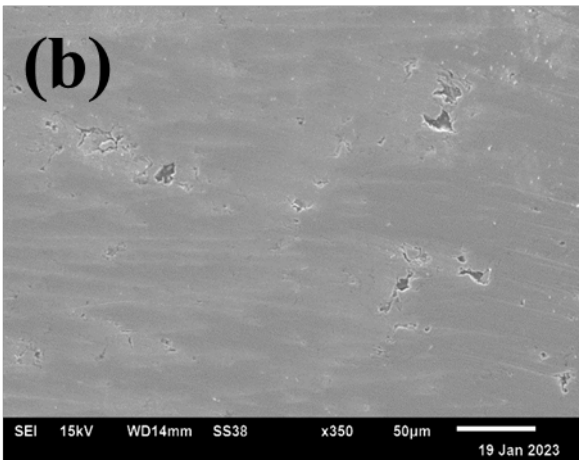
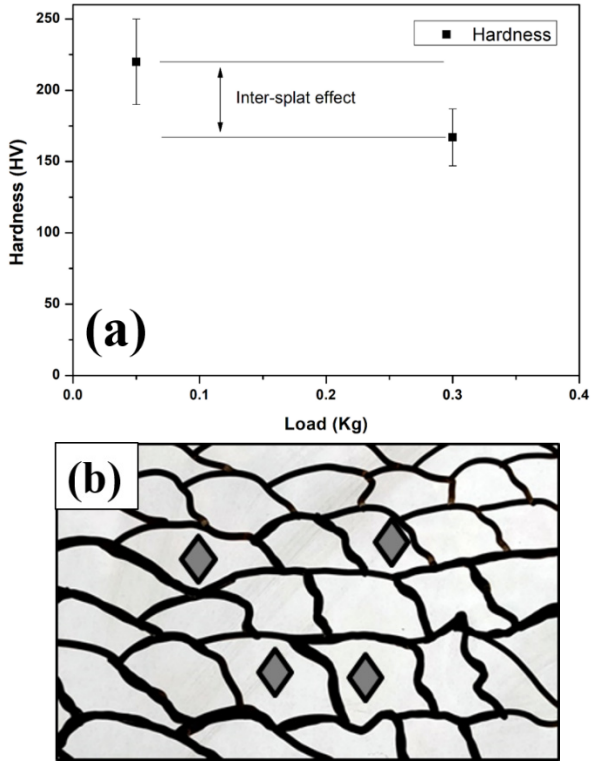


Figure 2: (a) SEM cross section image of the coating, (b) Magnified SEM cross section image of the coating

with a circular exit was used and the nozzle transverse movement was kept at 0.2 m/s. Each coating was sprayed for 8 number of passes. Coating thickness was measured using the cross-section images from SEM (Fig 2a). A total number of ten readings were taken at random places and the average thickness of 850 µm is reported.

The SEM images of the generated coatings depict that the particles are well intact with each other. The porosity of the as-sprayed coating was measured from the cross-sectional SEM images. The porosity of the present coating was less than 1.5 %. Generally, high porosity is observed in CS titanium coatings due to the high critical velocity and HCP structure of titanium which results in poor deposition [22]. High porosity is desirable in bio medical applications which helps in growth of cells through the pores [21]. Here, owing to the process parameters a dense coating has been obtained which is desirable in corrosion applications [4,5].



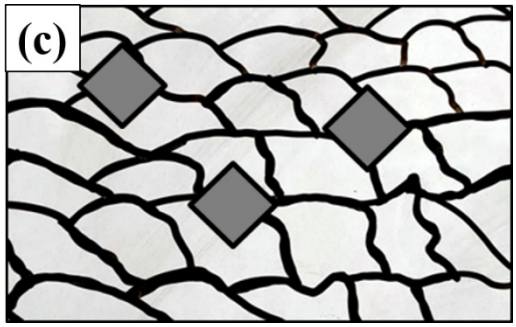
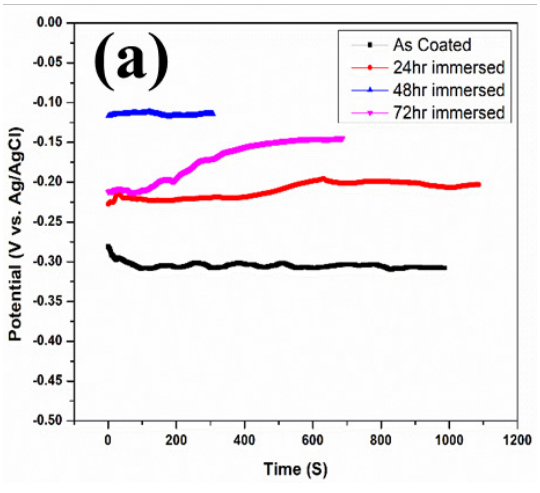


Figure 3: (a)Hardness of the coatings at various loads; Schematic representation of impression of indent size on the coating (b)0.05 Kg load (c)0.3 Kg

The micro-hardness of coating was measured using the Vickers microhardness tester on the cross-section of the samples for two loads that is, 0.05 kg and 0.3 kg. For each load at least ten indents were taken, and the average value is reported. For 0.05 kg load, the micro-hardness achieved is 220±30 HV, while for 0.3 kg it is 167±20 HV. The high hardness is attributed to the cold work done due to the plastic deformation of the particle. A decrease in hardness of around 50 HV is observed with increase in load (Fig.3a). The Vickers micro-hardness technique is load independent, still, a drop in micro-hardness is observed. It is because the impression of the indenter with 0.05 kg load is 19*20 µm^2 while the indenter impression with 0.3 kg load is more than 55*50 µm^2. The indent with 0.05 kg load covers a smaller number of splats / can be inside a splat only (Fig.3b). In contrast to it, the number of splats covered in 0.3 kg load will at least contain three to four deformed particles/splats (Fig.3c). Hence, this decrease in hardness can be attributed to the inter-splat bonding.

Corrosion analysis

The OCP results for the as-deposited and long hour immersed coatings are shown in Fig 4. The OCP was done for 1800s or dE/dT <1E-6 V/s. From Fig. 4a, 4c, it is observed that with the increase in immersion time OCP has shifted towards noble end that is, the positive side [23,24]. OCP in positive side means that it is difficult to initiate corrosion, here, the shift towards the positive side indicates the formation of oxide layers with increase in immersion time.



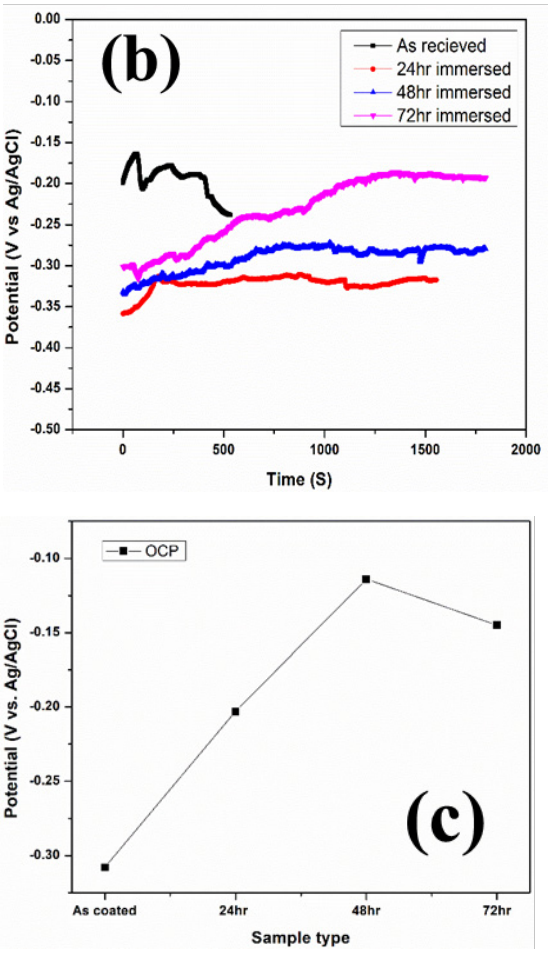


Figure 4: (a)OCP for different conditions of the CSed-Ti coatings, (b)OCP for different conditions of substrate SS316L, (c)OCP variation in the coating tested with different conditions

Among all the samples, the 48hr immersed sample has shown steady OCP with noblest side. Contrary to this, the OCP of 72hr immersed sample is not found stable when compared with other three samples which means that oxide layer formed on sample is not stable. Moreover, a drop in OCP is observed for 72hr immersion sample when compared with 48hr immersion sample. Fig 4b. shows the OCP of SS316L substrate with different immersion time and it is observed that the OCP has shifted towards negative side with immersion times, however it moved towards the positive side with increase in immersion time.

Fig 5a shows the potentiodynamic plots of as-coated and long hour immersed samples. It is observed that E_{corr} has shifted towards the positive side with the increase in immersion time. E_{corr} is a measurement for corrosion initiation. Corrosion current density is a measurement of corrosion resistance, which is calculated by drawing tafel plot i.e, drawing slopes at anodic and cathodic transition. Table.1 shows the E_{corr}, corrosion current density, anodic slope, cathodic slope, and polarisation resistance. It is observed that undipped/as coated sample showed current density of 3.65 E-6 A/cm^2. 48hr immersed sample showed corrosion current density of 1.2E-6, which indicates that it is having high corrosion resistance. The lower the current density the higher the corrosion resistance. A passive layer has been formed in all the cases as illustrated in Fig 5a. Passivation layer means the formation of a stable oxide layer, which further stops the corrosion process. This can be observed by a constant increase in voltage with no change in current density. For as-coated samples the passivation layer occurs much later when compared with the immersed samples. This tells that with immersion, oxide layer is formed in the window of immersion time. For 24hr and 72hr immersed samples, disruptions are observed in the anodic regions, this could be attributed to the breakage of formed oxide layer where again there will be corrosion reaction or active dissolution of corrosion medium into the coating. The SS316L substrate potentiodynamic plots are shown in Fig. 5b. From the tafel plots, it is understood that all the samples showed higher corrosion current density (Table.2) when compared with the CSed-Ti coatings. The corrosion current density for similar exposure times is almost double.

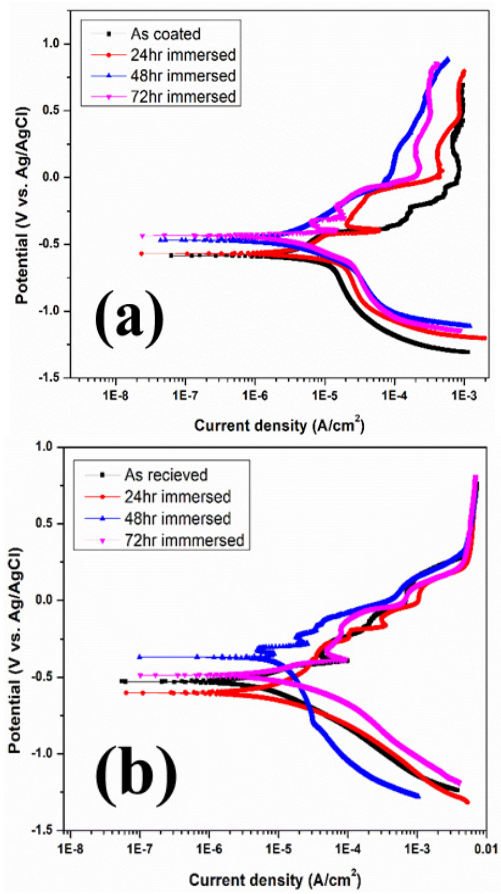


Figure 5: (a)Potentiodynamic plots for CS Ti coating with different immersion time (b) Potentiodynamic plots for substrate SS316L with different immersion time

Polarisation resistance refers to the resistivity offered by the electrolyte surrounding the electrode or an insulation effect offered by the products formed by the electrode, which is an indication of corrosion resistance. The higher the polarisation resistance, the higher the corrosion resistance. From Table.1, it is observed that 48hr immersed CSed-Ti sample showed highest polarisation resistance while 72hr immersed sample show least polarisation resistance due to its anodic slope (b_a). The substrate material SS316L show least polarisation resistance when compared with similar condition of the CSed-Ti coatings.

EDS results of the corroded samples shows the similar trend, where it is observed high oxygen percentage in 72hr

Table 1: Polarisation results of CS Ti coatings with different immersion time

	E_{corr} (V)	I_{corr} (A/cm²)	OCP (V)	Polarization resistance	b_a	b_c
As coated sample	-0.549	3.65E-06	-0.308	14010	0.24395	0.22807
24hr immersion	-0.55172	3.80E-06	-0.203	10910	0.25485	0.15235
48hr immersion	-0.47024	1.20E-06	-0.114	21694	0.25269	0.16185
72hr immersion	-0.42838	2.42E-06	-0.145	6617	0.04463	0.20983

Table 2: Polarisation results of SS316L substrate with different immersion time

	E_{corr} (V)	I_{corr}(_A/cm²)	OCP(V)	Polarization resistance	b_a	b_c
SS316L substrate	-0.5283	2.41E-06	-0.238	9945	0.0937	0.13507
24hr immersion	-0.59478	4.06E-06	-0.317	7443	0.14546	0.13353
48hr immersion	-0.373	6.21E-06	-0.28	6780	0.18262	0.2064
72hr immersion	-0.4743	5.99E-06	-0.193	4801	0.1207	0.14694

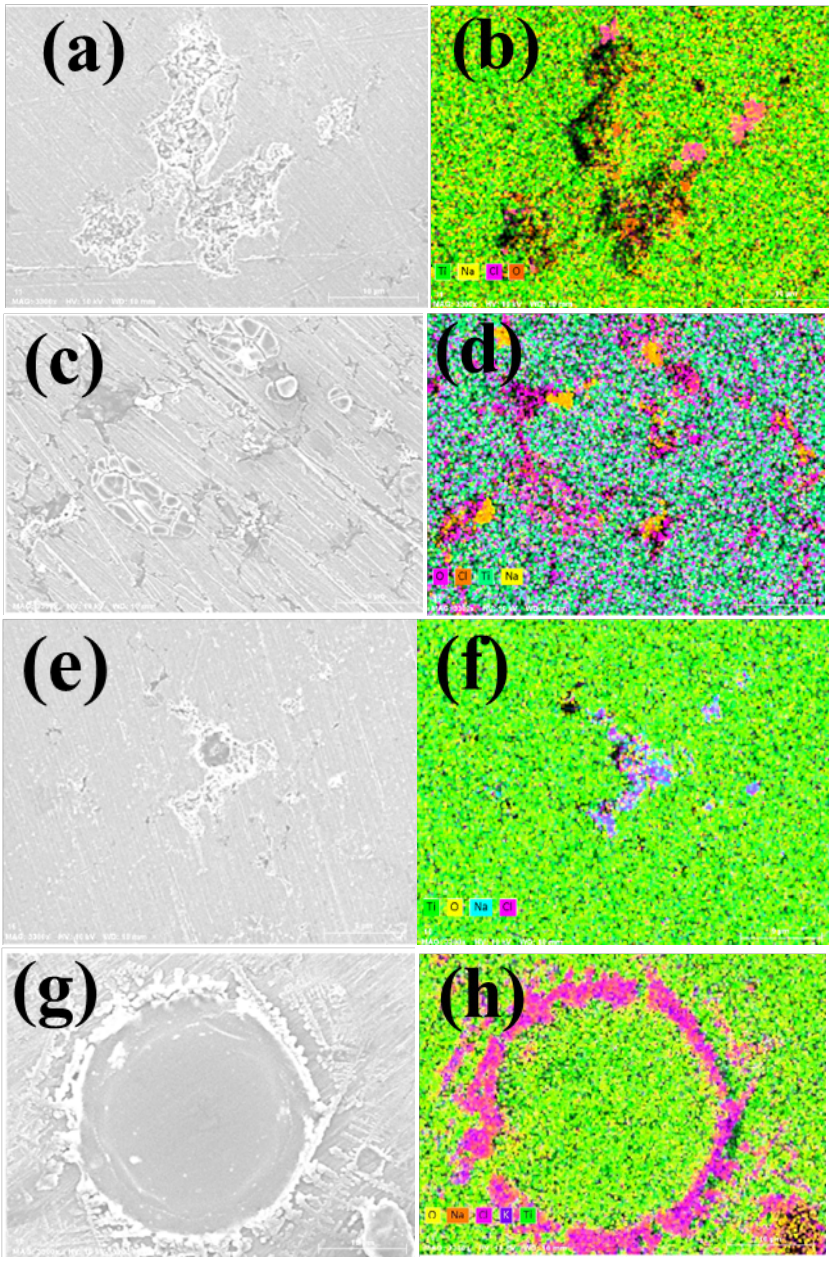


Figure 6: SEM and EDS images of corroded samples; (a, b) as-coated samples; (c, d) 24hr immersion; (e, f) 48hr immersion; (g, h) 72hr immersion.

immersed coating, while the least is observed in 48hr immersed samples (Fig 6). The surface roughness of the corroded samples was analysed to understand the surface changes occurred on the samples after the long hour immersion. The initial surface roughness before corrosion shows an Ra value of 0.25 µm. The sample immersed for 24 hr showed an Ra value of 0.782 µm, which is observed to decrease to 0.164 µm for 48hr immersed sample and increase to 0.96 µm for 72hr sample. The increase of surface roughness in 72hr sample could be an indication of the breakage of oxide layer, which might have exposed new surface due to which there is increase an in-surface roughness.

Conclusions

Irregular shaped titanium powder is deposited on SS316L substrate using a high-pressure cold spray system and the coating generated is 850 µm thick. The generated coating is dense in microstructure and splats are intact with each other. Hardness is used as an indirect method to show the contribution of cold work and the inter-splat bonding effect. The developed coatings were tested for their electrochemical properties after exposed to 3.5% NaCl for different exposure time and it was revealed from the potentiodynamic plots that CSed-Ti coating formed passive layer with immersion time therefore increasing the corrosion resistance. The investigated coatings exhibited a better corrosion resistance when compared with the SS316L substrate. As a future scope, oxide layer stability can be examined by Electrochemical Impedance Spectroscopy (EIS) analysis and heat treatment of the coatings could be done to improve the inter-splat bonding.

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References

1. Schweitzer, P. A. (2003). Fundamentals of corrosion: mechanisms, causes, and preventative methods (No. 10589). CRC press.
2. http://impact.nace.org (accessed on 12/12/2022)
3. Davis, J. R. (Ed.). (2001). Surface engineering for corrosion and wear resistance. ASM international.
4. Vinay, G., Chavan, N. M., Kumar, S., Jyothirmayi, A., & Bodapati, B. R. (2022). Improved microstructure and properties of cold sprayed zinc coatings in the as sprayed condition. Surface and Coatings Technology, 438, 128392.
5. Stoltenhoff, T., Kreye, H., & Richter, H. J. (2002). An analysis of the cold spray process and its coatings. Journal of Thermal spray technology, 11, 542-550.
6. Papyrin, A., Kosarev, V., Klinkov, S., Alkhimov, A., & Fomin, V. M. (2006). Cold spray technology. Elsevier.
7. Lima, R. S., Karthikeyan, J., Kay, C. M., Lindemann, J., & Berndt, C. C. (2002). Microstructural characteristics of cold-sprayed nanostructured WC–Co coatings. Thin solid films, 416(1-2), 129-135.
8. Trethewey, K. R., & Chamberlain, J. (1995). Corrosion for science and engineering.
9. Davis, J. R. (2000). Stainless steels. Materials Park: ASM International.
10. Melchers, R. E. (2008). Development of new applied models for steel corrosion in marine applications including shipping. Ships and Offshore Structures, 3(2), 135-144.
11. Wang, H. R., Li, W. Y., Ma, L., Wang, J., & Wang, Q. (2007). Corrosion behavior of cold sprayed titanium protective coating on 1Cr13 substrate in seawater. Surface and Coatings Technology, 201(9-11), 5203-5206.
12. Maeusli, P. (1985). Surface characterisation of titanium and titanium-alloys. Biological and biomechanical performance of biomaterials, 57-62.
13. Kinos, T., Chen, S. L., Siitonen, P., & Kettunen, P. (1995). Corrosion properties of shrouded plasma sprayed titanium coatings. In Proc. 14th Int. Thermal Spray Conf., 22.-26.6. 1995, Kobe, Japan (pp. 573-576).
14. Kawakita, J., Kuroda, S., Fukushima, T., Katanoda, H., Matsuo, K., & Fukanuma, H. (2006). Dense titanium coatings by modified HVOF spraying. Surface and Coatings Technology, 201(3-4), 1250-1255.
15. Hussain, T., McCartney, D. G., Shipway, P. H., & Marrocco, T. (2011). Corrosion behavior of cold sprayed titanium coatings and free-standing deposits. Journal of Thermal Spray Technology, 20, 260-274.
16. Kumar, A., Singh, H., & Kant, R. (2022). Influence of Substrate Roughness and Ceramic Content on Deposition Characteristics of Cold-Sprayed Ti/TiO2 Deposits. Metals and Materials International, 1-15.
17. International, Standard Guide for Preparation of Metallographic Specimens Standard Guide for Preparation of Metallographic Specimens 1, ASTM Int., 2012.
18. Hussain, T., McCartney, D. G., Shipway, P. H., & Zhang, D. (2009). Bonding mechanisms in cold spraying: the contributions of metallurgical and mechanical components. Journal of Thermal Spray Technology, 18, 364-379.
19. Singh, S., Singh, H., & Buddu, R. K. (2020). Microstructural investigations on bonding mechanisms of cold-sprayed copper with SS316L steel. Surface Engineering, 36(10), 1067-1080.
20. Kumar, S., Bae, G., & Lee, C. (2016). Influence of substrate roughness on bonding mechanism in cold spray. Surface and Coatings Technology, 304, 592-605.
21. Kumar, A., Singh, H., Kant, R., & Rasool, N. (2021). Development of cold sprayed titanium/baghdadite composite coating for bio-implant applications. Journal of Thermal Spray Technology, 30(8), 2099-2116.
22. Assadi, H., Kreye, H., Gärtner, F., & Klassen, T. (2016). Cold spraying–A materials perspective. Acta Materialia, 116, 382-407.
23. Wei, Y. K., Li, Y. J., Zhang, Y., Luo, X. T., & Li, C. J. (2018). Corrosion resistant nickel coating with strong adhesion on AZ31B magnesium alloy prepared by an in-situ shot-peening-assisted cold spray. Corrosion Science, 138, 105-115.
24. Xie, C., Li, H., Zhou, X., & Sun, C. (2019). Corrosion behavior of cold sprayed pure zinc coating on magnesium. Surface and Coatings Technology, 374, 797-806.