A Review on Recent Trends in Surface Coatings

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Abstract: Corrosion of the components is a predominant factor which controls the life of metallic parts. Metals parts of various structures are often subjected to damage due to corrosion driven failures causing loss of functionality and dimensions. In order to reduce corrosion, there are two ways one is introducing new materials and the other is improving the existing materials by adding alloying materials or by surface coating techniques. Surface coatings are a feasible way to enhance the corrosion resistance of metallic materials, thus expanding the life span of the metal components. Aim of this paper is to draw comparison between various coating techniques and analyze which surface coating technique and coating materials improves the corrosion resistance of the materials. Further, in this review paper coat materials on the base material by mostly cold spray and plasma spray techniques. So, these two surface coating modification techniques are discussed in detail.

Keywords: Corrosion, wear, coatings.

1. Introduction:

Corrosion is a natural phenomenon in which gradual degradation of the material takes place by chemical or electrochemical reaction. In general, marine corrosion is classified into 5 types as galvanic corrosion, crevice corrosion, stress corrosion, intergranular corrosion and flow accelerated corrosion.[1].

1.1. Economic impact of corrosion globally:

According to NACE’s(National Association of Corrosion Engineers), IMPACT (International Measures of Prevention, Application and Economics of corrosion Technologies). By 2013, the global cost of corrosion is estimated to be almost US $3trillion which is equal to 34% of global GDP. This indicates picture perfectly the entire scenario of the corrosion impact on world. So there is a need to enhance the corrosion resistance of the material[2].Due to cost constraints new material usage is difficult. So we opted to surface coatings. Out of all surface coatings Thermal spray is an age old process still it is dominant technique because of the emerging new techniques along with the feasibility in the choice of the both substrate and the coating material[3].

2. Discussions:

2.1. Zn alloy coatings on the mild steel:

The Zn-Al and Zn-Sn is coated on the mild steel using plasma spraying technique. The coating materials are mixed in following proportions Zn-Al(75/25), Zn-Al(50/50), Zn-Al(25/75) and Zn-Sn(75/25), Zn-Sn(50/50), Zn-Sn(25/75).Corrosion tests are performed in 3.65% NaCl solution at room temperature. From this the below results are obtained shown in table-1.The relation between the corrosion potential and corrosion densities are shown by potentiodynamic polarization curve known as TAFEL plot.
From the slope of the tafel plot, it is observed that lower current densities and higher polarization resistance provides highest corrosion resistance [4-5]. Among Zn-Sn and Zn-Al alloy compositions the Zn-Sn(50/50) has better corrosion resistance than Zn-Al(25/75) [4,5].

Table 1. Corrosion current densities of Zn-Sn coatings in 3.5wt% NaCl [Ref 4-5]

| Substrate | Coating material | Technique       | Current density $i_{corr}$(A/cm$^2$) | Polarization resistance ($R_p$) |
|-----------|------------------|-----------------|--------------------------------------|---------------------------------|
| Mild steel| Zn-Sn(25/75)     | Plasma spraying | 5.24×10$^{-4}$                       | 43.49                           |
| Mild steel| Zn-Sn(50/50)     | Plasma spraying | 4.44×10$^{-5}$                       | 354.71                          |
| Mild steel| Zn-Sn(75/25)     | Plasma spraying | 9.29×10$^{-4}$                       | 66.288                          |
| Mild steel| Zn-Sn(25/75)     | Plasma spraying | 5.08×10$^{-4}$                       | 144.68                          |
| Mild steel| Zn-Sn(50/50)     | Plasma spraying | 5.66×10$^{-4}$                       | 92.67                           |
| Mild steel| Zn-Sn(75/25)     | Plasma spraying | 6.67×10$^{-4}$                       | 60.482                          |
| Mild steel| uncoated         | -               | 2.39×10$^{-2}$                       | 1.968                           |

Now the Zn and its alloy coating takes place by using an unbalanced magnetron sputtering in presence of Argon gas at the base pressure of 1.4×10$^{-3}$pa and thickness of 2µm. The samples are tested in 3.5 wt% NaCl solution by spraying it on the samples. The pure Zn film has corrosion current density of 3.918×10$^{-2}$ A/cm$^2$ while the 87.8Zn-12.2Mg sample has corrosion current density of 2.586×10$^{-3}$ A/cm$^2$. The preferred composition for obtaining better corrosion resistance is 87.8Zn-12.2 wt% Mg beyond the 15.8% Mg the corrosion resistance falls down[6]. In the preferred composition of the Mg content in the Zn composition coating shows better corrosion resistance than the pure Zn coating [6].

The Zn-5wt%Al is coated on the mild steel substrate by using sputter deposition. Due to the different temperatures employed for the substrates, the thickness is coated on the sample is differed as at low temperature 3µm and at high temperature 30µm, and the microstructure also varies. As at high temperature an open woolen-like microstructure is shown and at lower temperature close and compact microstructure is observed. The samples are tested in 3.5wt% NaCl to check the corrosion resistance. It shows that the corrosion resistance is mainly depends on the number of Zn atoms present on the surface of the substrate [7]. The mild steel is coated with the CrAlSiN by varying the Si content from 0 to 11.5wt%. The CrAl interlayer layer is deposited with a thickness of 100nm in presence of the sputter and reactive gas- Ar and nitrogen with a flow rate of 20 and 10 sccm. The Si is added with varying the composition and deposited with a thickness of 1.2µm. The samples are treated in the 3.5wt% NaCl. The Si content with 8.7wt% possesses high hardness and corrosion resistance. With further increasing the Si content in the coating the hardness and corrosion properties are decreased [8].

2.2. Aluminum alloy coating on the magnesium substrate:

By using thermal spray method the Al/SiC matrix composite is coated on the Mg substrate. The SiC particle distance is average 50µm and standoff distance is 15-20cm. Compared to mono layer multi-layer coatings provides a better corrosion resistance due to low porosity. In this technique sand off distance influence the corrosion resistance of the coating. It was confirmed by 98% improvement in corrosion resistance of the coating in 3.6 wt% NaCl solution. by reducing the standoff distance from 20cm to 15cm[9]. By using the magnetron sputtering coating method the coating materials aluminum, aluminum nitride, diamond-like carbon are coated on Mg alloy. The coating deposited as three layers. The Ar flux maintained at 40 sccm in chamber. At first, the pure aluminum is coated on the Mg substrate at sputter current of 2 A in presence of base pressure of 2.2×10$^{-3}$ Torr and the chamber temperature is 35ºC. This acts like an intermediate layer between the substrate and AlN coating. In the later stage, AlN is deposited on the surface and in the final stage, the Diamond-like carbon(DLC) coating is applied on the
substrate with a sputter current of 0.2 A. Now it was tested in 3.5 wt% NaCl solution by immersing the coated and uncoated samples for 6 hr. The results obtained from the immersion test are for uncoated sample $E_{corr} = -1.57V$ and $i_{corr} = 2.25 \times 10^{-5} A cm^{-2}$ and for coated sample is $E_{corr} = -1.48V$ and $i_{corr} = 1.28 \times 10^{-6} A cm^{-2}$. The multi-layer coated Mg substrate possesses good corrosion resistance [10]. Now the AlN coatings are applied on the Mg alloys like AZ31 and AZ91 by DC magnetron sputtering. The coatings are applied on the substrate with bias voltage of -60 V, pressure 0.4 pa, magnetron current 5 A and standoff distance 90 mm. Al interlayer is used for more adhesion and hard coating, so AlN is applied as an interlayer. The AlN coated AZ91 alloy showed the $i_{corr}=3mA/cm^2$ and $E_{corr}=-725mV$ almost [11]. The thickness of Al layer deposited on the substrate is 250 nm. The $i_{corr}$ values of Al coated AZ31 substrate material is $7.15\mu A/cm^2$. The corrosion formation on the surface is mainly due to the dissolution of the OH- ions in 3.5 wt% NaCl by situating the Cl- ion on the coating surface [12].

2.3. Ti alloy coatings on Al substrate:

Ti-6Al-4V is coated on the 6061-7651 aluminum alloys by using cold spray technique. In this technique De-Laval nozzle (i.e. converging and diverging) type of spray gun is used for impinging Ti-6Al-4V on Al substrate by maintaining the following parameters. Supersonic speeds are achieved by accelerating particles with expansion ratio of 5.6 and standoff distance is 30 mm. The feed rates of the Ti-6Al-4V are 40 g/min through 15 passes and 2 mm thickness coating is achieved. In this method there is 56% reduction in corrosion current density ($i_{corr}$) of the coated sample with uncoated one [13]. Now the Al 7075-T6 disk shaped substrate is coated with TiN by using DC magnetron sputtering. As the Ti is deposited as an intermediate layer for increasing adhesiveness of the coating. The samples are tested by exposing it to 5 wt% NaCl for 72 hr. The $E_{corr}$ for 25 wt% N in TiN is 1.6 V. Bias voltage influence the corrosion resistance of the coating bias voltage value-150 gives the better corrosion resistance of the coating in 3.5% NaCl solution [14]. Al-W is coated on 7075 alloy by using sputter coating technique. Al-W coatings corrosion resistance is depends on W concentration. Darja Kek Merl confirmed that 3.5% of W in Al-W coating proved a better corrosion resistance when compared with 0.6% and 11%. The concentration of W gives better corrosion resistance up to some limit he also confirmed that if W concentration greater than or equal to 11% shows lower corrosion resistance when compared with uncoated sample in 5% NaCl solution it was confirmed by oxide layer formed in corrosion test [15]. The $N_2$ with different compositions (0.035 wt%, 0.13 wt%, 1 wt%) is deposited by magnetron sputtering on AA7075 Al alloy. The Al-0.43 wt% N compositions show good corrosion potential of -0.35 V when compared to bare substrate has -0.75 V [16]. The CrN and Ni/Cr-N is deposited on the AA7075 alloy with Ni concentration greater than or equal to 11% shows lower corrosion resistance when compared with CrN on AA7075 alloy with N flow rate is 9.5 cm$^3$. The thickness of the coating formed is 2.5 μm for CrN and 3 μm for Ni/Cr-N. The samples are tested in 0.1 M NaCl. The corrosion properties on the CrN on AA7075 are not good as the steel coated with CrN. The observed values of the Ni/Cr-N on AA7075 alloy is $E_{corr} = -0.645 V$ and $i_{corr}=0.41 \mu A/cm^2$ and for CrN, the $i_{corr}=0.99 \mu A/cm^2$ and $E_{corr} = -0.679 V$ [17].

2.4. Coatings on the 316L stainless steel:

$TiO_2$ and $Al_2O_3$ are deposited on the 316L stainless steel by arc plasma process method. Corrosion resistance is observed by the bond strength parameter. The bond strength between 316L steel and the $TiO_2$ is 40.607N/mm$^2$ and for $Al_2O_3$ 26.639N/mm$^2$. The bond strength of $TiO_2$ is 1.5 times than that of the $Al_2O_3$ [18,19]. The bond strength $Al_2O_3$ coating reduced due to the steady state crystal transition of α-Al$_2$O$_3$ to the metastable phase of Y-Al$_2$O$_3$ shows erosion with much pores and cracks results lower corrosion resistance of $Al_2O_3$ when compared with $TiO_2$ [19]. By using HVOF (High velocity Oxygen-Fuel) technique 316L stainless steel is coated on ZE41 Mg alloy. Usually the thickness of the coating material is in between the range of 42.418 μm. Spraying distance for the 3 specimens is 1 layer is deposited from 200 mm for SS-1, for SS-2 is 400 mm for 3 layers and 4 layers at 300 mm distance for SS-3 Table-4 Shows corrosion current densities of ZE41 Mg coating on stainless steel substrate [20].
Table 2. Corrosion current densities of ZE41 Mg coating on stainless steel substrate [Ref20]

| Substrate          | Coating material | \(i_{corr}(\mu A/cm^2)\) |
|--------------------|------------------|---------------------------|
| ZE41 Mg alloy      | Uncoated         | 17.9                      |
| ZE41 Mg alloy      | SS-1             | 2368.8                    |
| ZE41 Mg alloy      | SS-2             | 3.19                      |
| ZE41 Mg alloy      | SS-3             | 4.62                      |

316L stainless steel is coated with Ti by using the sputtering method with vacuum pressure of \(5\times10^{-5}\) mbar by maintaining the thermal time plasma oxidation of 15.45,75min. The working gas is \(O_2\) as 25% and \(H_2\) of 75% with a pressure of 2.6mbar used after coating; the samples are cooled in nitrogen atmosphere. Coating formed at 45 minutes of oxidation time gives better wear resistance under load 1N 100rpm speed. Corrosion and hardness of the TiO\(_2\) coating depends on nitrating range of 7.9 ≤ \(N\) ≤ 32. High hardness and corrosion resistance obtained at 28%-30%\(N\) and 23%. At 1N load TiO\(_2\) showed a wear rate of 0.024×10\(^{-3}\)mm\(^3\)/Nm [21].

The CrSiN coatings are deposited on the 316L stainless steel by using magnetron sputtering. The thickness of the deposited Cr interlayer is 0.4\(\mu\)m and for CrSiCN is 2\(\mu\)m. The corrosion tested are conducted in 3.5wt% NaCl solution, wear on ball-on-disk. With the Si content of 25-30wt% have better corrosion resistance than the CrN, because the Si settles over the cracks and pores formed on the surface of coating [22]. The 25wt% CrSiCN coating posses \(E_{corr} = -0.19V\) & \(i_{corr} = 5.2 \times 10^{-9}Acm^{-2}\) [22].

2.5. Other coating techniques:

Deposition of TiN and TiAlN on the 316L stainless steel by PEALD (Plasma Enhanced Atomic Layer Deposition) reveals that the corrosion resistance of bare substrate is low followed by the TiN when compared TiAlN because of the high corrosion current density. The corrosion current density for bare sample is 1.5\(\mu\)Acm\(^{-2}\), for Tin coated is 1.35\(\mu\)Acm\(^{-2}\), and for TiAlN coated sample is 0.12\(\mu\)Acm\(^{-2}\) [23]. Ni coated at different temperature on low carbon steel by using HVAF technique. Ni coated at 1520ºC reduces the \(i_{corr}\) value by 33% when coated at 1490ºC. It is concluded that high in-flight particle temperature leads to better corrosion. By using this technique we can develop \(Cr_2C_3\)-NiCr and Ni/\(Cr_2C_3\)-NiCr coatings on low carbon steel when compare the two coating second one give the better corrosion resistance this was confirmed by 77% reduction of \(i_{corr}\) value. These two coatings also provide better corrosion resistance when compared with Ni coating. The corrosion resistance of the samples are shown as Substrate <Ni(2) < Ni(1) <\(Cr_2C_3\)-NiCr< Ni/\(Cr_2C_3\)-NiCr resistance [24].

3. Conclusions:

From the above study, the conclusions drawn are as follows:

- As the number of layers of the coating material increased, porosity decreases which leads to better corrosion resistance.
- Variation in the weight percentage of the composition determines the corrosion current densities and polarization resistance.
- Inflight temperature is another vital parameter that governs the corrosion resistance of the material.
• Stand-off distance also decides the thickness of the coating material which ultimately leads to the enhancement of the corrosion resistance. Decrease in the standoff (i.e spraying distance) increases corrosion potential.

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