Journal of Materials Science & Surface Engineering, 6(3): 792-796
ISSN (Online): 2348-8956; 10.jmsse/2348-8956/6-3.1

Galvanic Corrosion Behaviour of Zinc Nickel Alloy Plated 15CDV6 Steel Coupled with Zinc Aluminum Flake Coated AISI 4340 Steel

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ABSTRACT
Zinc Nickel alloy electro plating for corrosion protection of high strength steels is a widely studied alternative to Cadmium electro plating. Cadmium is regulated worldwide due to its carcinogenic nature. In this study, galvanic corrosion behaviour of Zinc Nickel alloy plated 15CDV6 steel – Zinc Aluminium flake coated AISI 4340 steel couple was investigated by means of galvanic current, galvanic potential measurements in 3.5% NaCl solution and salt fog tests. For comparative purpose, Zinc Nickel alloy plated 15CDV6 steel-Cadmium plated AISI 4340 steel couple was also studied. Open circuit potential and Polarisation measurements were carried out on the individual coated samples on their respective steel substrates for better understanding of the galvanic corrosion behaviour. Zinc nickel alloy plated 15CDV6 steel – Zinc Aluminium flake coated AISI 4340 steel couple exhibited relatively less galvanic currents, galvanic potentials and lesser white corrosion products in salt fog tests compared to the Cadmium based galvanic couple. The results of these studies indicate better galvanic compatibility and lesser rate of galvanic corrosion for the combination: Zinc Nickel alloy plated 15CDV6 steel and Zinc Aluminium flake coated AISI 4340 steel compared to the other cadmium based galvanic combinations taken up for study.

ARTICLE HISTORY
Received 15-03-2018
Revised 05-04-2018
Accepted 06-04-2018
Published 02-05-2018

KEYWORDS
Galvanic corrosion,
Electroplated Zinc Nickel,
Cadmium coatings,
Zn-Al flake coating,
High strength steel

Introduction

Electrodeposited coatings of Cadmium are extensively used in the aerospace industry for corrosion protection of high strength structural steel hardware and fasteners due to the excellent sacrificial protection offered by these coatings and properties such as lubricity, solderability and electrical conductivity [1]. Cadmium is a proven carcinogen and cadmium electroplating is carried out from hazardous cyanide based chemicals and hexavalent chromate compounds which are carcinogenic in nature are used for the passivation of Cadmium plating. Cadmium coatings leach through rinsing water during electroplating process contaminating ground water. Due to environmental concerns, occupational hazards, and stringent regulations associated with the usage of Cadmium electroplating, the usage of cadmium is restricted worldwide [2-4]. Active application oriented research studies are pursued and reported worldwide for identification of efficient alternatives to Cadmium plating for various applications like corrosion protection of aerospace structural hardware, electrical connectors, fasteners and bolts made of high strength steel [5-9]. The reported alternative coatings include Zinc and Zinc alloy based coatings, Aluminium based coatings and Aluminium-Molybdenum based coatings for various functional applications like corrosion protection, lubricity, solderability, minimal reduction of fatigue strength and elimination of susceptibility to hydrogen embrittlement [10-16]. It is evident from the literature that although several coatings match the corrosion performance of Cadmium plating, there is no one single coating which can be identified to match the above mentioned properties desirable for aerospace applications. 15CDV6 is a low carbon, low alloy, ultra high strength steel with yield strength of 950 to 1000 MPa. Due to its attractive combination of properties of high strength, weldability, formability and toughness, 15CDV6 is an important candidate material for the fabrication of aerospace structural hardware [17-18]. AISI 4340 is a high strength steel with molybdenum, nickel and chromium as major alloying elements and can be heat treated to a range of hardness from 20 to 50 HRc for the best combination of strength, toughness and shock resistance which makes it a widely used material for fabricating different class of fasteners [19]. These steels require a suitable surface protection technique to ensure service life and corrosion protection of the aerospace hardware. Among the alternatives studied for replacement of Cadmium plating, Zinc nickel alloy plating is studied extensively due to the favourable properties such as good corrosion protection offered for steels, excellent formability and welding characteristics [20-23]. The authors earlier studied and reported Cadmium free coating scheme based on Zinc Nickel alloy plating as an alternative to Cadmium plating for the corrosion protection of 15CDV6 structural steel [24]. Zn Ni alloy plating does not possess the required lubricity and torque-tension characteristics for coatings on fasteners apart from corrosion protection. Cadmium is a soft metal and provides the required lubricity for fasteners by acting as a solid lubricant under loads due to the applied torque. Zinc Aluminium flake coating possesses the required torque tension characteristics making it a desirable coating on steel fasteners [25, 26].

Galvanic corrosion is an electrochemical process in which one member of the galvanic couple behaves as anode and corrodes preferentially when it is in electrical contact with another member of the galvanic couple in the presence of an electrolyte [27-29]. The potential difference and current generated due to this process of galvanic corrosion is called the galvanic potential and galvanic current in a particular medium. The greater the galvanic current flowing between the contacting surfaces, greater is the rate of galvanic

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corrosion. Lower galvanic currents and galvanic potentials are preferred for better galvanic compatibility of aerospace hardware [30-31]. Galvanic corrosion is a localized phenomenon and occurs very rapidly and causes serious damage to the structural integrity of the hardware [32].

Aerospace hardware experience severe service conditions like varied levels of humidity, temperature and marine environments. During selection of coatings for aerospace structural hardware, selection of coatings with galvanic compatibility is of immense importance to minimize the effect of galvanic corrosion. In aerospace structural hardware fabricated from 15CDV6 steel and integrated with AISI 4340 fasteners, the effect of galvanic corrosion can be minimized by the selection of suitable coatings with better galvanic compatibility and thus ensuring extended service life of the hardware.

The objective of this work is to study the galvanic corrosion compatibility of Zinc Nickel alloy plated 15CDV6 steel with Zinc Aluminum flake coated AISI 4340 steel. The purpose of this galvanic corrosion studies is to explore the possibility of replacement of widely used Cadmium plating on high strength steel fasteners with Zinc Aluminium flake coating. For comparative purpose, the galvanic corrosion compatibility studies of Zinc Nickel alloy plated 15CDV6 steel with Zinc Aluminium flake coated AISI 4340 steel is carried out. The selected pairs for study will further be referred to as galvanic couples in this article.

Experimental

Coating Details

Zinc Nickel alloy plating

Zinc Nickel alloy layer of 10-12 micron thickness was deposited from an alkaline Zinc Nickel plating bath on 15CDV6 steel substrate with an Ultimate tensile strength of 1100MPa. The coating process was carried out in compliance with the Aerospace Material Specification: AMS 2417G, Zinc Nickel alloy plating. The coating was deposited with an alloy composition of 85% Zinc and 15% Nickel. Hydrogen dembrittlement treatment for the coating for a duration of 8 hours was carried out at 200^{0} C within four hours after electro deposition followed by trivalent chromate passivation of the Zinc Nickel alloy plating.

Cadmium plating

Cadmium coating of 10-12 micron thickness was electrodeposited from an alkaline cyanide based electroplating bath on AISI 4340 steel substrates and M10 fasteners fabricated from AISI 4340 steel with a Ultimate tensile strength of 1300 MPa. The coating process was carried out in compliance with the Aerospace Material Specification: AMS QQP 416E. Hydrogen deembrittlement treatment for the coating for a duration of 12 hours was carried out at 200^{0} C within four hours after electrodeposition followed by hexavalent chromate passivation of the coating

Zinc Aluminum flake coating

Zinc Aluminum flake coating was carried out by spray coating process on AISI 4340 steel substrates and M10 fasteners fabricated from AISI 4340 substrates with an Ultimate tensile strength of 1300 MPa. The coating process was carried out in compliance with the standard ISO 10683: Fasteners, Nonelectrolytically applied Zinc flake coatings. A dispersion of Zinc and Aluminium flakes of 2-3 micron size in a water based thermosetting resin was used for the spray coating process. Curing of the coating was carried out at 330^{0}C for one hour. The ratio of Zinc and Aluminum pigments in the coating was 85% and 15% respectively. The thickness of the sprayed coating was controlled in the range of 10 – 12 microns suitable for application on threaded fasteners with close tolerances.

Evaluation of coatings

Open circuit potential measurements and Polarisation measurements

A simplest electrochemical test used for assessing the corroding nature of the system is the measurement of open circuit potential. The open circuit potential of the freely corroding specimen in 3.5% NaCl is measured using Auto lab PGSTAT 30 electrochemical analyzer. Silver/Silver chloride (3M KCl) was used as reference electrode during open circuit potential measurements. The experimental set up for polarization mesurements consists of a three electrode cell in which the coated specimen forms the working electrode of $1cm^{2}$ area. The measurements were carried out using Autolab PGSTAT 30 electrochemical analyser in 3.5% sodium chloride medium with Platinum as auxiliary electrode and Silver/Silver chloride (3M KCl) as reference electrode.

Galvanic current and galvanic potential measurements

The galvanic currents and galvanic potentials of the coating combinations under study were measured by electrically connecting the galvanic couples immersed in 3.5% sodium chloride solution and measuring the galvanic currents using zero resistance ammeter. The galvanic potentials were measured with respect to silver/silver chloride reference electrode (3M KCl). The measurement of galvanic currents and galvanic potentials were carried out as per the guidelines in the standard ASTM G71-2009, Standard guide for conducting and evaluating galvanic corrosion tests in electrolytes. $10cm^{2}$ area of each substrate in the galvanic couple was used for the galvanic current and galvanic potential measurements. The ratio of area of galvanic couples electrically connected under study was maintained at 1:1.

Salt fog exposure tests

To study the galvanic behaviour in salt fog exposure tests, AISI 4340 steel coated fastener of M10 size was assembled to 15CDV6 plate of size 150mm x 100mm x 5mm coated with Zinc nickel alloy plating. For comparative purpose, Zinc aluminium flake coated fastener of M10 size fabricated from AISI 4340 steel was assembled to 15CDV6 plate coated with Zinc nickel alloy plating. The coated galvanic combinations are exposed to a fine mist of 5% sodium chloride solution generated using a atomizer and the temperature throughout the test duration was maintained at 35 ^{0} C. The salt fog exposure tests were conducted as per the standard ASTM B117. Periodic examinations of the test plates was made for blistering of the film loss of adhesion and appearance of red rust indicating the penetration of corrosive agents to the substrate material initiating corrosion. The tests were conducted in triplicate to confirm the results. The time for occurrence of first failure was noted in the salt fog exposure tests. These test plates with fasteners were subjected to salt fog testing for duration of 21 days.

Results and Discussion

Open circuit potential measurements

The polarisation curves of various coatings under study are presented below in Fig. 1. From the polarisation curves, the corrosion currents and corrosion potentials of various coatings on their respective substrates are calculated [33]. The open circuit potentials, corrosion currents and corrosion potentials of various coatings are provided below in Table 1.

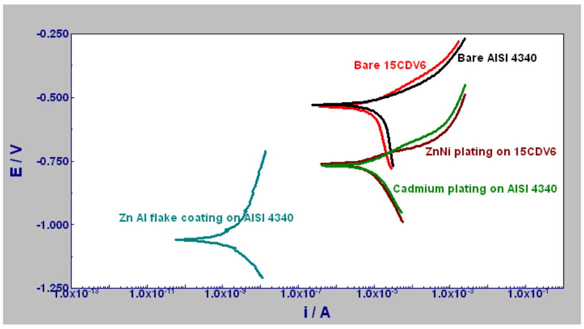

Figure 1: Polarisation curves for various coatings and substrates taken up for study in 3.5% NaCl medium

Table 1: Open circuit potentials, corrosion currents and corrosion potentials of various coatings under study

Sl No	Details of coating	Open circuit potential in mV	Corrosion current in A/cm2	Corrosion potential in mV
1	Zinc Nickel alloy plating on 15CDV6 steel substrate	-0.70	6.20 X10-6	-0.768
2	Zinc Aluminum flake coating on 15CDV6 substrate	-0.96	1.14x10-9	-1.060
3	Cadmium plating on AISI 4340 substrate	-0.74	3.79x10-6	-0.762
4	Bare 15CDV6 steel	-0.52	4.79 x10-6	-0.528
5	Bare AISI 4340 steel	-0.53	3.98 x 10-6	-0.535

From the above values of open circuit potentials and corrosion potentials higher than the steel substrate, it is evident that Zinc Nickel alloy plating provides sacrificial protection to the steel substrate [34]. So, is the case of Cadmium plating as noticed from the open circuit potentials and corrosion potentials higher than that of the steel substrate [35]. In the case of Zinc Aluminum flake coating, the coating provides sacrificial protection indicated by higher negative values of open circuit potentials and barrier protection also as evident from the much lower corrosion current values compared to other coatings taken up for study [36-38].

Galvanic current and galvanic potential measurements

The galvanic potentials and galvanic currents measured as a function of time for the galvanic couples under study is presented below in Fig. 2 and Fig. 3 respectively. It is noticed from the above plots in figure 1 that the galvanic potentials of Zinc Nickel alloy plated 15CDV6 steel and Zinc Aluminum flake coated AISI 4340 steel is in the range of 0.28 volts to 0.2 volts during first four days of immersion. At this phase, Zinc aluminium flake coating is expected to protect the steel sacrificially due to the higher open circuit potential and corrosion potential exhibited by the coating compared to Zinc Nickel alloy plating. After four days of immersion, the galvanic potential decreases drastically and is maintained in the range of 0.05V to 0.02 V after 10days of immersion. The galvanic currents for this couple are in the range of 10^{-6} A/cm^2 initially for 4 days and subsequently declining to lower values and are maintained in the range of 10^{-8} A/cm^2 after 6 days of immersion. In the case of Zinc Aluminium flake coating, it is reported earlier that after three days of exposure to sodium chloride solution, the sacrificial nature of Zinc Aluminium flake coating shifts to barrier protection on steel substrate [36-38]. This behaviour of reduction in galvanic potential and galvanic current for the Zinc Nickel alloy plated 15CDV6 steel and Zinc Aluminium flake coated AISI 4340 steel galvanic couple is attributed to the shift in mechanism of protection from sacrificial protection to barrier protection after few days of immersion in sodium chloride solution.

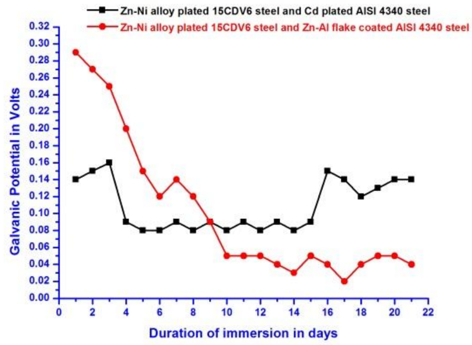

Figure 2: Galvanic potentials of the galvanic couples under study measured as a function of time

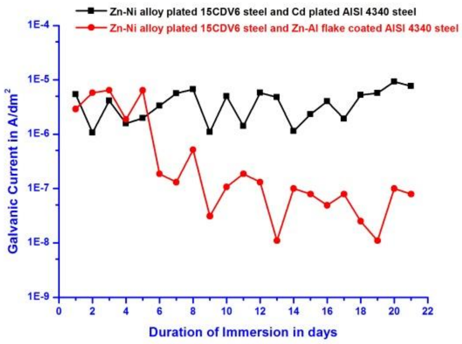

Figure 3: Galvanic currents of the galvanic couples under study measured as a function of time

With regards to the galvanic couple, Zinc Nickel alloy plated 15CDV6 steel and Cadmium plated AISI 4340 steel, Cadmium plating is expected to provide continuous sacrificial protection [16]. Although, Zinc Nickel plating is sacrificial in nature with comparable open circuit potentials and corrosion potentials to that of Cadmium plating, the protection offered by Zinc Nickel plating tends to become noble with increase in immersion time due to the dissolution of zinc rich phases leaving behind a noble Nickel rich phase [39]. Hence, Cadmium is expected to corrode sacrificially in preference to Zinc Nickel alloy plated contacting surface. Due to this continuous sacrificial protection offered by the Cadmium plating, this galvanic couple exhibits higher corrosion currents of the order of 10^{-6} A/cm^2 and relatively higher galvanic potentials all through the duration of study than the other galvanic couple taken for study. The relatively lower galvanic currents for the Zinc nickel alloy plated 15CDV6 steel and Zinc Aluminum flake coated AISI 4340 steel imply a lower rate of galvanic corrosion for this galvanic couple when compared to Zinc nickel alloy plated 15CDV6 steel and Zinc Aluminum flake coated AISI 4340 galvanic couple [30,31].

Salt fog exposure tests

The photographs of test plates with fasteners coated with various coatings under study before and after exposure to salt fog tests are provided in Fig. 4 (a-d) respectively. It is observed from the salt fog tests that the plates coated with Zinc nickel alloy plating on 15CDV6 steel in contact with Cadmium plated AISI 4340 fastener show relatively greater extent of corrosion with large amount of white corrosion products of oxides of cadmium on the fastener due to the continuos sacrificial protection offered by the Cadmium plating during the period of exposure to salt fog test [35]. These results are also supported by relatively higher galvanic currents and potentials for this galvanic couple compared to the other galvanic couple taken up for study . The extent of corrosion on Zinc Aluminum flake coated fastener is relatively less with lesser amount of corrosion products as seen in Fig. 4 which may be explained due to the barrier protection offered by Zinc Aluminum flake coating apart from its sacrificial nature [36-38].

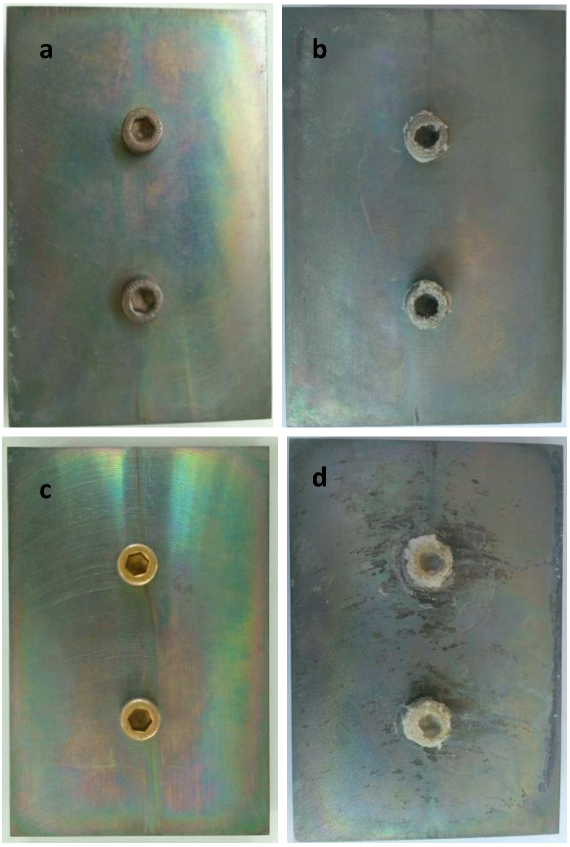

Figure 4: Zinc Nickel coating on 15CDV6 test plate in contact with Zinc Aluminum flake coated AISI 4340 fastener (a) before salt fog test, (b) after salt fog test; Zinc Nickel coating on 15CDV6 test plate in contact with Cadmium plated AISI 4340 fastener (c) before salt fog test, (d) after salt fog

In both the cases, Zinc Nickel alloy plated 15CDV6 test plate shows the presence of white corrosion products of oxides of Zinc due to the initial sacrificial protection offered by Zinc Nickel alloy plating to the steel substrate [34]. Zinc nickel alloy plating and Cadmium plating if subjected to salt fog when coated individually on a steel substrate in the absence of any galvanic contact, need to protect the substrate for a minimum period of 500 hours without the appearance of red rust in salt fog tests conducted in accordance with ASTM B 117 as per the relevant aerospace standards for these coatings [40, 41]. From the results of salt fog tests, it is significant to note that both the galvanic combinations taken up for study viz Zinc Nickel alloy plated 15CDV6 steel in contact with Zinc aluminum flake coated AISI 4340 steel as well as Zinc Nickel alloy plated 15CDV6 steel in contact with Cadmium plated AISI 4340 steel did not show appearance of red rust in salt fog tests upto 21 days exceeding 500 hours indicating the efficient protection offered by these galvanic combinations against galvanic corrosion. Also the test plates with fasteners did not show any signs of failure such as blistering of the coating and loss of adhesion. These results also confirm the galvanic compatibility of these coating combinations taken up for study.

Conclusions

The galvanic corrosion behaviour of Zinc Nickel alloy plated 15CDV6 steel coupled with Zinc aluminum flake coated AISI 4340 steel was compared with Zinc Nickel alloy plated 15CDV6 steel coupled with Cadmium plated AISI 4340 steel. The Zinc Nickel alloy plated 15CDV6 steel and Zinc Aluminum flake coated AISI 4340 steel galvanic couple exhibit relatively lower galvanic currents, lower galvanic potentials in long term galvanic corrosion tests and lesser corrosion products in salt fog tests indicating relatively lower rate of galvanic corrosion and better galvanic compatibility than the cadmium based galvanic combination taken up for study. The relatively lower galvanic currents and galvanic potentials of Zinc Nickel alloy plated 15CDV6 steel coupled with Zinc aluminum flake coated AISI 4340 steel is due to the barrier protection offered by Zinc Aluminum flake coatings unlike the sacrificial protection offered by cadmium plating. Hence Cadmium based galvanic couple taken up for study exhibits relatively higher galvanic potentials and galvanic currents in long term experiments. These results indicate that Zinc Aluminium flake coating is a promising alternative to Cadmium plating for minimizing galvanic corrosion of fasteners that are in galvanic contact with Zinc Nickel alloy plated high strength steel.

Acknowledgements

The authors express their sincere thanks to Shri.MSR Prasad, Director, Defence Research and Development Laboratory, Hyderabad for his continued encouragement and support. The financial support from Defence Research and Development Organisation for pursuing this work is greatly acknowledged

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