Aluminium Electroplating on Steel from a Fused Bromide Electrolyte

Prabhat K. Tripathy^{a,*}, Laura A. Wurth^b, Eric J. Dufek^c, Toni Y. Gutknecht^d, Natalie J. Gese^a, Paula A. Hahn^e, Steven M. Frank^a, Guy L. Fredrickson^a and J. Stephen Herring^f

^a*Separations Department, Nuclear Science and Technology Directorate, Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415, USA*

^b*ZAF Energy Systems, Inc., Columbia Falls, Montana, MT 59912, USA*

^c*Biological and Chemical Processing Department, Energy and Environment Science and Technology Directorate, Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415, USA*

^d*Chalmers University of Technology, Gothenburg, Sweden*

^e*Chemical and Radiation Measurement Department, Energy and Environment Science and Technology Directorate, Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415, USA*

^f*Nuclear and Science Engineering Department, Nuclear Science and Technology Directorate, Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415, USA*

^{*}*Corresponding Author, Email: Prabhat.Tripathy@inl.gov ; Telephone: +1 208 533 7193, FAX: +1 208 533 7471*

Abstract

A quaternary bromide bath (LiBr-KBr-CsBr-AlBr₃) was used to electro-coat aluminium on steel substrates. The electrolyte was prepared by the addition of AlBr₃ into the eutectic LiBr-KBr-CsBr melt. A smooth, thick, adherent and shiny aluminium coating could be obtained with 80 wt.% AlBr₃ in the ternary melt. The SEM photographs of the coated surfaces suggest the formation of thick and dense coatings with good aluminium coverage. Both salt immersion and open circuit **potential** measurement suggest that the coatings did display good corrosion-resistance behavior. Annealing of the coated surfaces, prior to corrosion tests, suggested the robustness of the metallic aluminium coating in preventing the corrosion of the steel surfaces. Studies also indicated that the quaternary bromide plating bath can potentially provide a better aluminium coating on both ferrous and non-ferrous metals, including complex surfaces/geometries.

Key words: Bromide plating bath, Functional electrolyte, Aluminium electro-coating, Current density and Coating morphology

1. Introduction

Steel, aluminium and its alloys represent bulk of the structural materials industry world over and their use have been quite extensive in many industries that include shipping, aerospace, construction, mining, petroleum and automotive. Besides being less expensive these materials have multiple combinations of useful engineering criteria, required for their successful deployment in key industries. However, these industries have been spending billions of dollars to mitigate the corrosion of these structural components. Corrosion, particularly in highly corrosive environment that contain free chloride ions (for example ground water and underground mining activities), is a major challenge these industries are grappling with. Although steel, aluminium and its alloys provide some degree of resistance, to corrosive attack, in relatively milder corrosive service conditions (stainless steel gets passivated due to the formation of chromium oxide, Cr_2O_3 , on its surface and aluminium very easily forms a tenacious oxide layer, $\gamma\text{-Al}_2\text{O}_3$, on its surface), they fail (sometime catastrophically) in moderate-to-severe corrosive environment. The economic and environmental impact of the corrosion of steel components is quite staggering and its associated cost is approximately \$275 billion, amounting to 3.1% of the GDP, in the U.S. alone [1]. About 25-30% of this cost could be saved if proper corrosion mitigation schemes are adopted [1]. Economic impact of corrosion in other countries has been estimated to be in the range 3-4% of their GDPs. Approximately 40% of U.S steel production is used to replace the corroded metal parts and consumer goods [2]. Thus there is a pressing need for the development of suitable methods and non-chromium/cadmium based materials to mitigate corrosion on various steel components. However, replacement of currently used chromium/cadmium based coatings, by cost-effective materials, has been quite challenging.

Metallic coatings provide excellent corrosion resistance and improved physicochemical properties and hence are routinely being used for corrosion mitigation purposes. All the metallic coatings can be broadly divided into two categories, noble (Ag, Cr, Sn, Ni) and sacrificial (Al, Zn, Cd). In steel industry, Zn, Cd and Cr have been extensively used as corrosion-mitigating agents. Although both cadmium and hexavalent chromium coatings provide excellent corrosion resistance characteristics, these metals, in recent years, are being phased out because of their environmental toxicity (cadmium) and carcinogenic effect (chromium). From a corrosion mitigation standpoint, aluminium provides an excellent combination of properties. Besides being cheap, metallic aluminium has been found to be an extremely effective corrosion barrier, particularly for steels. Although aluminium, being more reactive than steel (Table 1), can be used as a sacrificial anode to protect steel in a corrosive environment, for example in submerged marine structures (oil platform, ship hulls etc.), it, owing to its excellent oxide forming ability, can also be used to coat steel to provide the anodic protection. In industry, Al coating is being carried out by a variety of processes that include hot dipping [3-4], thermal spraying [5], sputter deposition [6-7], vapor deposition [8-9] and electrodeposition [10-11] processes. From among these techniques, electrodeposition stands out in terms of several advantages, such as relatively ease of operation, and possibility of obtaining uniform, thick, adherent and smooth coating even on complex objects with adjustable microstructure/morphological features/thickness. However, comparatively larger negative standard electrode **potential** of Al/Al(III) couple (-1.67V vs. SHE) precludes its deposition from the aqueous baths. The literature abounds with the application of various aprotic solvents, such as organic liquids and molten salts for plating aluminium on a variety of substrates. These solvents include aromatic hydrocarbons [12-13], dimethylsulphone [14-15] and ethers [16-17]. Two processes, SIGAL [18] and REA1 [19], based on the organic

solvents are in commercial operation. Although high quality Al coating could be obtained by these two processes, they suffer from a series of disadvantages, such as narrow electrochemical window, lower conductivity, lower solubility of aluminium salts, loss of electrolyte because of the higher volatility and electrolyte flammability. As a consequence, the application of these solvent systems becomes very limited. Since 1980s, room temperature ionic liquids (RTILs) have been proposed for preparing aluminium coatings [20]. Although these solvents offer some excellent characteristics, such as higher electrical conductivity, wider electrochemical potential window, negligible vapor pressure and non-flammability, are expensive and require careful storage, making them unsuitable for larger batch-sized operations. A third category of solvents, also known as high temperature molten salts, have been used to electrodeposit aluminium on a variety of substrates. Alkali chloride salts (NaCl-KCl , $\text{AlCl}_3\text{-NaCl}$, and $\text{AlCl}_3\text{-NaCl-KCl}$) offer several distinct advantages over the RTILs [21-26]. Besides being inexpensive, these solvents (i) offer higher throughput (as these can be operated at elevated temperatures) (ii) have relatively higher electrical conductivities (iii) are extremely stable under a wide range of operating temperatures (iv) are non-flammable (v) can be prepared without traces of moisture (RTILs may contain moisture which will require them to go through a unit operation to remove moisture) and (vii) offer better crystallization, surface diffusion and nucleation characteristics (these properties are better at elevated temperatures). A molten chloride salt (NaCl/NaCl-KCl), containing 70-80 wt. % AlCl_3 , has been successfully used to electroplate aluminium at an operating temperature of 180°C . Use of a binary electrolyte ($\text{AlCl}_3\text{-NaCl}$) has been reported to form a dull, coarsely-grained Al layer with poor anti-corrosion properties [27]. Although several metals (such as tin, lead, zinc, manganese, bismuth, copper, silver, cadmium, gallium, indium and germanium) were added to the binary electrolyte in order to improve the quality of the Al layer, only tin, lead and

manganese were found to have effectively improved the deposit quality. However, in presence of these metals, the coating invariably was an alloy of aluminium. Despite significant progresses made on the preparation of the Al coating from the chloride melts, one of the unsolved issues has been to develop new electrolyte systems in order to (i) prevent the significant loss of AlCl_3 and (ii) obtain a high quality pure aluminum coating. Although addition of reactive chemicals, such as tetramethyl ammonium chloride (0.5-2.0 wt.%) to the AlCl_3 -NaCl-KCl electrolyte was attempted to bring down the concentration of AlCl_3 to about 50mol%, in order to prevent the loss of AlCl_3 , no data on the vaporization loss of AlCl_3 was reported [28]. Molten alkali bromide salts, as an alternative plating bath, have the potential for solving most of the processing issues, associated with aluminum plating from organic solvents, ionic liquids, and low temperature molten chlorides. The liquidus temperature range for the binary and ternary alkali bromide salts is in the range 226 – 328°C [29]. Such a temperature range permits the formation of aluminum coating on a variety of thermally-sensitive substrates that include precipitation-hardened aluminum, mild steel, stainless steel, copper and brass etc. Moreover, AlBr_3 , being the functional electrolyte, clearly offers distinct advantages in terms of (i) lower operating temperature (MP of AlBr_3 is lower than that of AlCl_3) and (ii) less volatility loss (BP of AlBr_3 is higher than that of AlCl_3) (Table 2). Like most molten salts, alkali bromides are non-flammable and have ionic conductivities similar to or exceeding those of the ionic liquids and/or organic plating baths. That is why, these melts have been used for metal deposition/coating studies. White et al [30] could obtain coherent chromium coatings from the LiBr-KBr-CsBr-CrBr₂ melt in the temperature range 300-450°C. They have observed that unlike in a NaCl-KCl melt (where the chromium reduction was found to be reversible, requiring both lower chromium content in the bath, 2-5 mol%, and cathode current density, 0.025-0.05 Acm⁻²), due to the lower diffusion rate of the

chromium in the ternary bromide melt it became easier to obtain smooth and coherent chromium coatings on copper, nickel and steel substrates. They further observed that the coating structure, formed in the temperature range 275-350°C, to be encouraging in view of the unknown relationship between the structure of the deposit and the plating parameters. Inazawa et al [31] have reported the successful deposition of chromium on a nickel cathode from the LiBr-KBr-CsBr-CrCl₂(2.78 mol%) melt at a temperature of 250°C. No data on the coating/deposition of aluminium from the ternary LiBr-KBr-CsBr melt is available in open literature. The present study was therefore undertaken to prepare the metallic aluminium coating, on mild and stainless steel substrates, from the eutectic LiBr-KBr-CsBr melt containing different amounts of AlBr₃. The coatings were subsequently characterized and evaluated by powder XRD and SEM-EDX techniques. The preliminary corrosion resistance characteristics of the coatings were evaluated by salt immersion and open circuit potential measurements.

2. Experimental

2.1. Materials

Ultra-dry (sealed in glass ampoules under high purity argon) and high purity (99.999% pure, -10 mesh beads) LiBr, KBr, CsBr were procured from *Aldrich-APL LLC*. Anhydrous, ultra-dry (sealed in glass ampoules under dry argon) and high purity (99.999% pure, 5-10 mm lumps) AlBr₃, procured from Alfa Aesar, was used as the functional electrolyte. Rectangular mild/stainless steel plates (~1.4 cm wide, 2.5 cm long and 0.1 cm thick), tool-steel drill bit and SS screws were used as the substrates for plating. Aluminium rod (~95% pure, 0.4 cm dia.) and glassy carbon rod (10 cm long and 0.3 cm. dia.) were used as the anode and quasi-reference electrodes respectively. A cylindrical and high density alumina crucible (9 cm long and 5.5 cm o.d., *CoorsTek*, 99.8% pure) was used to contain the molten electrolyte.

2.2. Equipment

Coating experiments were carried out inside a small, custom-fabricated, stainless steel, argon atmosphere controlled glove box (Fig. 1). The glove box was continuously purged with the laboratory-grade argon (*Air Liquide*) which could maintain very low levels of moisture and oxygen contents (< 0.1 ppm each). Most of the measurements were carried out under < 0.1 ppm moisture and < 1.2 ppm oxygen. Such an atmosphere was needed to protect the anhydrous nature of the bromide salts during the electrochemical measurements. The furnace was externally heated by a resistance heater. The “O” ring (that acted as the seal between the glove box and the furnace) provided the necessary cooling by a glycol-based chiller, plumbed on to the furnace. The electrodes and thermocouple were held in position by an aluminum plug, placed on the furnace cover and hung through a series of thin metal (copper) heat shields into the alumina crucible. The temperature of the bath was monitored by a calibrated, stainless steel-sheathed, chromel-alumel thermocouple (*Omega Engineering*) immersed directly into the molten electrolyte. A Biologic SAS potentiostat/galvanostat (*model VSP*) together with the EC-Lab software (ver. 10.18) was used to record the electrochemical measurements.

2.3. Procedure

Prior to carrying out the coating experiments, the melting point of the ternary electrolytes, containing calculated amounts of AlBr_3 (5-90 wt.%), was determined in a Netzsch DSC set up (*model STA 449 F3*). The salt samples were prepared in the argon atmosphere glove box and sealed in a gold-coated steel crucibles by applying a torque in the range 2.4-2.8Nm. The thermograms were analyzed with the *Proteus Thermal Analysis* software. About 80-100g of salt mixture was melted in the alumina crucible. The electrodes, with adjusted heights, were lowered into the melt and the coating experiments were carried out by varying the operating

temperature (325-400⁰C), electrolysis time (5-180 min.), current density (0.1-1.5Acm⁻²) and AlBr₃ content (10-80 wt.%). Fundamental electrochemical measurement (with transient techniques) preceded the applied (coating) measurements. Phase analysis of the solidified electrolyte (LiBr-KBr-CsBr-AlBr₃), prior to coating experiments, was carried out by the powder XRD technique (*PANalytical Empyrean X-Ray Diffractometer*) at room temperature.

The samples for powder XRD measurements were prepared in a small box furnace, placed inside an argon atmosphere controlled glove box where the moisture and oxygen levels were <0.1 ppm and 1.2 ppm respectively. Such a measure was adopted to prevent any type of contamination of the salt mixture by the atmospheric air/moisture given the extreme hygroscopic nature of these salts. The solidified salt samples were homogenized in the glove box, mounted on a sample holder and covered with a Mylar film before being exposed to the X-ray beam for recording the diffractograms. Such a procedure proved to be quite effective in preventing the solidified electrolyte from getting exposed to the atmospheric air/moisture.

Coating morphologies were examined under a scanning electron microscope (*JEOL JSM7600* equipped with an *Oxford X-Max 20 mm² EDS detector*). Subsequently, performance characteristics of the coatings were tested by (i) immersing the coated surfaces in simulated salt solutions (5% NaCl solution) and (ii) open circuit potential measurement.

3. Results and Discussion

3.1. Determination of the melting point of eutectic LiBr-KBr-CsBr melt

One of the early works carried out by White et al [30] determined the eutectic melting point of the LiBr-KBr-CsBr salt to be 236⁰C. However, they have not reported details of the measurement procedure. Years later Kasajima et al [32] determined the melting point, by DTA, to be 225⁰C. In order to understand the inconsistencies, it was decided to determine the melting

point of the ternary eutectic melt. Kasajima et al determined the eutectic composition to be (mol%) 56.1 LiBr-18.9 KBr-25 CsBr. In the present study, a few of the compositions (Table 3), used by Kasajima et al, were also used to compare the melting points with the reported values. Both the measurements used same heating rate (5Kmin^{-1}) to record the thermograms. The only difference between Kasajima's study and present measurements was that the former group used Differential Thermal Analyzer (DTA) while in the present work a Differential Scanning Calorimeter (DSC) was used instead. In the present studies, the melting point was determined to be 238.6°C . In order to validate the DSC data, 10g of the salt sample, was melted in an alumina crucible in a box furnace, placed in the argon atmosphere glove box, and a viscous mass, indicating the onset of the melting of the salt sample, was obtained at $\sim 239^{\circ}\text{C}$. Thus the present experimental value was more close to the value reported by White et al.

The possible explanation for the observed discrepancy between the present study and the result reported by White et al and Kasajima et al might be because of the difference in the technique and/or preparation of the salt samples (both White et al and Kasajima et al have not mentioned the details of the chemical purity of the salt samples and their preparatory procedures, it is not clear if the salt samples were mixed and homogenized strictly in an inert atmosphere environment).

3.2.Determination of the melting point of LiBr-KBr-CsBr-AlBr₃ melt

The DSC thermograms of eutectic LiBr-KBr-CsBr salts, containing 10-90 wt.% AlBr₃, suggested a decreasing trend in the melting temperatures with each incremental addition of AlBr₃ (Table 4). For each sample, three heating and cooling cycles were run and the average of the three values (obtained from the heating curves) was recorded as the melting temperature.

The DSC measurements of the multi-component system showed some interesting observations. Samples containing 10-70 wt.% AlBr_3 showed both eutectic and liquidus temperatures whereas 80 and 90 wt.% AlBr_3 compositions showed just the liquidus temperature (Fig. 2a and b respectively). Absence of the eutectic temperature in these two compositions suggested that the melting process formed a more homogeneous melt which perhaps can function as a better plating composition.

Several authors have reported that the melting temperatures of the chloride salts containing 80 wt.% AlCl_3 was as low as 160°C [27-28]. Contrary to the expectation, the melting temperature of the eutectic bromide salt, containing 80 wt.% AlBr_3 , was observed to be $>300^\circ\text{C}$. Such a scenario might have arisen because of the formation of higher melting complex species (single or multiple).

3.3. Powder XRD analysis of the solidified melt

In order to examine the possible phase formation in the quaternary melt, two representative salt samples (containing 20 and 80 wt.% AlBr_3 respectively) were examined by powder XRD technique (Fig. 3). All the peaks in the XRD profile of $\text{LiBr-KBr-CsBr-10wt.\%AlBr}_3$ could not be identified as the JCPDF data did not match with all the possible existing phases in the Li-K-Cs-Al-Br system. Some of the phases that could be identified in the pattern included LiBr, KBr, CsBr and to lesser extent $\text{Cs(AlBr}_4\text{)}$. Such an observation was found to be in line with Berg's observation who has reported the formation of CsAlBr_4 phase in 1:1 (CsBr-AlBr_3) composition [33]. Also, KAlBr_4 may be present as a very minor phase. No peak for AlBr_3 was found. This may be because of the chemical reaction of AlBr_3 with alkali bromide salts resulting in the

formation of complex species of the general formula, $MA\text{Br}_4$ ($M=\text{Li}/\text{Na}/\text{K}/\text{Cs}$). Although formation of Al complexes in chloride melts, containing higher amounts of AlCl_3 (> 60 wt.%), have been reported in literature [32], no such information on the formation of Al-complexes, in the melts containing relatively lower amounts of AlCl_3 , is available in open literature. It has been reported that an equimolar AlCl_3 - NaCl melt contains NaAlCl_4 phase and no free AlCl_3 [34]. In the present study, formation of traces of $\text{Cs}(\text{AlBr}_4)$ was observed in the ternary melt containing as low as 10 wt.% AlBr_3 . The XRD profiles of $\text{LiBr-KBr-CsBr-80wt.\% AlBr}_3$ (Fig. 3) revealed the presence of LiBr , KBr , CsBr and $\text{Cs}(\text{AlBr}_4)$ without any LiAlBr_4 phase. Like in the case of 10 wt.% AlBr_3 , no AlBr_3 phase was found. These results are in consistent with the literature data that shows that both AlCl_3 and AlBr_3 do not exist in free state in the binary/ternary melt and they usually combine with the alkali chlorides or bromides to form ternary complexes with a general formula ($MA\text{IX}_4$, where $M=\text{Na}/\text{K}/\text{Cs}$ and $X=\text{Cl}^-/\text{Br}^-$).

3.4. Fundamental electrochemical measurements

Transient electrochemical techniques (cyclic and square wave voltammetry) were employed to study the mechanism of deposition and dissolution characteristics of the Al^{3+} in the eutectic LiBr-KBr-CsBr melt. Fig. 4 shows the cyclic voltammogram of Al^{3+} in the eutectic melt at 275°C . Unlike in the case of chloride melts (such as 52:48 NaCl-AlCl_3 melt), the absence of a second peak, in the potential range of interest, suggested that the deposition and dissolution of Al^{3+} took place in just one step. Such an observation was evident from the appearance of a single pair of cathodic ($\text{Al}^{3+} + 3\text{e} = \text{Al}$) and anodic ($\text{Al} = \text{Al}^{3+} + 3\text{e}$) current peak, representing the deposition and dissolution of aluminium (respectively) on the tungsten electrode. As a contrast, the appearance of two peaks in the CV of Al(III) , in the NaCl-AlCl_3 melt, at 200°C suggested that the deposition and dissolution process took place in two steps, viz. (i) $4\text{Al}_2\text{Cl}_7 + 3\text{e}^- = \text{Al} +$

7AlCl_4^- and (ii) $7\text{AlCl}_4^- + 3\text{e}^- = \text{Al} + 4\text{Cl}^-$ [34]. At different scan rates, the insoluble-soluble exchange phenomenon of Al^{3+} was observed to be reversible in the eutectic LiBr-KBr-CsBr melt. Square wave voltammetry also suggested one step reduction and dissolution of aluminium ions in the ternary melt (Fig. 5). The cathodic peak potential was $\sim -1.6\text{V}$, which corroborated the CV findings.

3.5. Electroplating

Prior to actual coating experiments, the surface of the SS specimens was carefully prepared by using a combination of mechanical cleaning and electrochemical treatment, in order to render the coatings adherent. The specimens were first cleaned with a fine-grade emery paper, thoroughly washed with water and alcohol, kept in an ultrasonic cleaner for about 30 min, wiped with alcohol and acetone before drying them in an oven for the duration of $\sim 12\text{h}$. The electrochemical treatment consisted of two specific techniques: electrochemical etching/cleaning with reversed polarity and pulse deposition technique. In the latter technique, the specimens were subjected to a combination of galvanostatic deposition (for a short duration, usually $\sim 10\text{min.}$) followed up by an open circuit potential run until the potential got stabilized.

Initial coating experiments, carried out for durations up to 60 min. at various cathode current densities (CCDs) containing AlBr_3 in the range 10-50 wt.%. At 10 wt.% AlBr_3 , no deposits/coatings were found on the SS316 plates at various CCDs for different durations up to 1h. Although 20% AlBr_3 did show some powdery and dendritic aluminium deposits (Fig. 6), the coatings were found not to be good. Such types of powdery and dendritic deposit formation at

lower concentrations of AlCl_3 have been reported from a chloride bath at lower concentrations of AlCl_3 [27].

At higher current densities massive aluminium deposits were formed on the cathode. Also, at higher current densities and upon prolonged electrolysis, thinning of aluminium electrode was observed. At 60% AlBr_3 , electrolysis experiments showed a mixture of dendritic deposits and coatings. However, the coating did not get washed off after the water wash. At 70 wt.% AlBr_3 the coating was observed not to be uniform (in thickness) all across the covered surface. An 80 wt.% AlBr_3 plating bath produced smooth, adherent, uniform and shiny aluminium coating (Fig. 7). Such a concentration has been reported to be the optimum concentration for producing aluminium coating from NaCl-AlCl_3 and NaCl-KCl-AlCl_3 plating baths [27-28]. A 90 wt.% AlBr_3 content did not yield any significant advantage and as a result all subsequent coating experiments were carried out with 80% AlBr_3 in the melt. While variation of electrolysis temperature in the 325-400°C range was observed to have little impact on the quality of the deposited aluminium layer, cathode current density was observed to have pronounced effect on the quality of the coating. At higher and lower current densities, the coated surfaces appeared to be smooth and somewhat grainy respectively. Very low current density resulted in the formation of a thin coating layer (1-2 μm) and very high current density ($>0.5 \text{ A cm}^{-2}$) resulted in the increased porosity. Formation of good quality coatings were observed in a narrow current density range (0.1-0.5 A cm^{-2}). In most cases, duration between 1-2h could produce nice adherent coatings. Although freshly prepared plating baths always provided good coatings, some of the better coatings could also be obtained from the used bath by topping up the AlBr_3 content. The latter process suggests the advantageous feature of the bromide plating bath from the standpoint of possible industrial plating operations. Both SS 316 and 304 plates showed identical coating features under similar experimental conditions.

Experiments were also performed using mild steel (MS) rod and complex geometries as the substrate materials. Fig. 8 shows the photograph of an aluminium-coated mild steel rod. Unlike in case of planar electrodes (such as SS plates), the coating on rods, in general, was found to be much smoother and uniform. Also, the rods, when pulled out of the plating bath, were found not to have much adhered salts onto them. Fig. 9 shows the **potential** vs. time profile, obtained during the aluminium coating on the MS rod. The coating was observed to be shiny, smooth and adherent.

Screws, nuts and bolts are some of the complex surfaces for providing complete aluminium coverage. SS fasteners, being widely used in aerospace and shipping industries, have been successfully coated with aluminium by hot plating (aqueous) techniques. It was decided to examine if some of these complex surfaces can be coated with aluminium. Two types of such surfaces (SS screws and tool drill bit) were chosen for the present studies. Fig. 10 shows the photographs of the aluminium-coated SS screws. Like in MS rod, not much adhered salt was found on the coating surfaces. Also, coatings survived very well when subjected to polishing, on SiC papers, prior to their subsequent examination, of morphological features, under a scanning electron microscope.

Like the SS screws, the threaded zone/surface of the tool steel drill bit could be completely covered with aluminium (Fig. 11). Also, the cell **potential** stayed quite stable during the coating process (Fig. 12). The coatings on both screws and the drill bit indicated that it could be possible to provide complete coverage of aluminium under standard operating conditions. Besides, the plating bath could be used more than once after the adjustment of the AlBr_3 content to 80 wt.% every time.

Although all the coating experiments, in the present study, were carried out in an argon-controlled glove box, a furnace coupled with an inert gas (tight) flow system can be envisioned for future studies to scale up the process for coating relatively bigger and complex surfaces, such as SS fasteners.

The loss of AlBr_3 content was calculated by taking the weight of the alumina crucible, containing the electrolyte, before and after electroplating. As the weight loss of the auxiliary electrolyte (eutectic LiBr-KBr-CsBr) was very less (0.03-0.1%), it can be presumed that any significant weight loss was primarily due to the loss of AlBr_3 by way of vaporization (sublimation temp. of AlBr_3 being 268°C , Table 2). A general rising trend, in the weight loss pattern, with respect to increased AlBr_3 content was observed. The % wt. loss, after the completion of a series of plating experiments, from the plating baths containing 10, 20, 40, 50 and 80 wt.% AlBr_3 were determined to be 1.24%, 2.6%, 0.908%, 1.45% and 4% respectively. This is a significant advantage over chloride electrolytes where the reported loss of AlCl_3 has been very high (~ 50 wt.%). Higher values of (i) sublimation temperature of AlBr_3 over AlCl_3 (by a margin of 85°C) and (ii) density (higher by a factor of 0.7) (Table 1) helped minimize the loss of AlBr_3 by way of vaporization.

3.6. Coating morphology

Figs. 13 (a and b) show the formation of a dense and coherent aluminium coating on SS316 and SS304 plates respectively.

As is evident from the SEM photographs, the coatings were observed to have some porosity, which could be removed by subjecting the coatings to post-coating annealing. The coating on the mild steel rod showed the formation of dense, thick and smooth aluminium deposit (Fig. 14).

3.7. Corrosion tests of the aluminium coatings

As described above (Fig. 13), SEM photographs revealed the presence of porosity in the coatings. Presence of porosity can adversely affect the corrosion mitigation efficiency of the coatings. Both un-annealed and annealed coatings were used as the specimens for evaluating their performance characteristics first by immersing the coatings in salt solutions, for several days, and then measuring the open circuit **potential** of the coatings against a Ag/AgCl reference electrode.

Salt immersion studies were carried out at room temperature (23⁰C) by submersing the coated surfaces in 20mL of un-buffered 5 wt.% NaCl solution. Non-coated regions were masked to avoid potential corrosive influence. The salt solution was periodically replaced with the fresh solution to minimize microbial growth. The evaporative loss of the solution was minimized by sealing the tops of the corrosion vessel with para film. Optical microscopy of samples was performed on days 0, 1, 2, 6, 10 and 14. Prior to microscopy, the coatings were rinsed with deionized water and then dried. Following imaging, the specimens were immediately re-immersed in the solution. Figs 15 and 16 show the microscopic images of the coatings on SS-316 and SS-304 plates after days 1 and 14 respectively.

The images showed the evolution of aluminium corrosion processes with the primary mechanism being associated with the coupled pitting of aluminium and subsequent growth of aluminium oxyhydroxides which are evident from the appearance of lighter colored regions (Fig. 16). In both SS316 and SS304 specimens, the coating remained intact with no evidence of the formation of any SS corrosion products (such as oxides/hydroxides of iron). As expected uncoated SS surfaces (in both SS304 and 316 plates respectively) showed significant corrosion within two

days of immersion in the salt solution. In both the specimens, majority of the surface evolution features occurred in the first 10 days with little change between days 10 and 14. The formation of oxides/hydroxides and the appearance of shiny regions, where pitting has occurred, was an indication of the exposure of aluminium to a chloride ion containing environment.

Analysis of the open circuit **potential** (OCP) in unpurged solution, for various samples, indicated varying degrees of passivation of the underlying steel surfaces. Fig. 17 showed the OCP obtained for both the coated and uncoated surfaces of the drill bit (showed in Fig. 11). Al-coated surface initially showed a positive trend and slowly drifted towards the negative region. The negative incursion progressed to a value of $\sim -0.55\text{V}$. As a comparison, the uncoated zone although started positive rapidly progressed towards negative region ($\sim -0.6\text{V}$) (Fig. 17). The progression of the **potential** towards negative region can be ascribed to the initiation of the electrochemical reduction of dissolved oxygen on the surface of iron at $\sim -0.5\text{V}$ [35]. The final OCP of the uncoated surface indicated a competition between the reduction of oxygen (which is facilitated by the chloride ion induced pitting) and oxidation of iron [36]. The behavior of coated surface can thus be rationalized in a similar and yet more complicated manner. The rapid decrease perhaps indicated the initiation of pitting of the aluminium surface. Following pitting there was a simultaneous competition between oxygen reduction and aluminium oxidation (Al^{3+}) at $\sim -0.5\text{V}$. It should be noted that the oxidation of aluminium (forming oxides and hydroxides of aluminium) is faster as compared to that of the iron. The initiation of aluminium dissolution process exposes the SS (iron) surface to the corrosive media which in turn facilitates further oxidation (of iron) and reduction (of oxygen) processes. A somewhat discoloration, only at one point in the aluminium coated region, indicated the oxidation of iron. The exposure of iron might have happened because of the inadequate aluminium coverage, due to the non-planarity of the

edged surface or the presence of porosity on the coated surface (which allowed the transportation of the chloride ions to attack iron). The smooth (non-edge) surface of the coated region did not show any trace of corrosion. As opposed, the uncoated section showed significant corrosion, which was evident by the formation of a thick brown-black film that surrounded the uncoated region, upon exposure to the salt solution for 48h. As with the optical microscopic image, OCP measurements using coated tool steel drill bit indicated that a somewhat nobler surface can be obtained with aluminium plating that will have better corrosion resistance properties. The slow progression of the OCP of the coated specimen towards negative region indicated the exposure of steel surface followed by the onset of subsequent corrosion phenomenon.

The gradual decline of the open circuit **potential** in coated drill bit (Fig. 17) indicated that perhaps the absence of porosity can enhance the corrosion protection efficiency. To verify such a hypothesis, an aluminum-coated SS316 plate was annealed up to a temperature of 500°C, in argon atmosphere, for the duration of 12h in order to render the coating pore-free and homogeneous. The coating looked somewhat dull in appearance after annealing. The OCP, even after an exposure to ~ 100h (Fig. 18), remained in the **potential** regime that can be ascribed to the competition between chloride induced pitting and the formation of oxides/hydroxides of aluminium. No trace of corrosion could be observed. The observed stability highlighted the need for the introduction of a post-annealing treatment to improve the corrosion protection ability of the aluminium-coated specimens.

3.8.SEM images of the post-corrosion specimens

The SEM images of the slightly corroded (showed up as a brownish colored spot after the OCP measurement) section of the drill bit revealed the presence of iron-rich phase in the aluminium

coating which indicated that the chloride ions could easily move through the porous coating and oxidize the iron which then diffused away from the surface (Figure 19). Also, the interface between the coating and the substrate was observed to be corroded. Although the aluminium coating section lost its compactness, to some extent perhaps due to the formation of oxides/hydroxides of aluminium and/or presence of corrosion products, it however did not undergo substantial thinning or degradation as can be seen in the Fig. 19.

The aluminium coating on the un-corroded section (smooth surfaces of the drill bit after the OCP) was found to be in tact without any sign of degradation and/or thinning (Figure 20). Also, the extent of corrosion of the substrate was found to be minimum. Such an observation perhaps indicated that the sharp edge of the drill bit was inadequately covered with aluminium.

Unlike in the un-annealed aluminium coatings, the annealed coating on the SS 316 substrate (after the OCP) was found to have a two-tier structure, made from the inter-diffusion of aluminium and iron (Figure 21). Aluminum, during annealing, from the coating surface seemed to have migrated towards the substrate surface and formed a rigid, as well as smooth Al-Fe (iron aluminide) alloy layer with traces of chromium and nickel. It seemed that the formation of the alloy layer very effectively prevented the SS316 from getting corroded. According to Fellner et al, AlCl_3 -NaCl electrolyte offers the advantage of depositing Al at a temperature 175°C in order to avoid the formation of brittle Al-Fe intermetallic phase for imparting higher corrosion-resistance efficiency [28]. On the other hand, Paucirov et al suggested that formation of an intermetallic Al-Fe under layer or diffusion layer helped achieving very good adhesion that also resulted in better corrosion resistance properties [27]. They also mentioned that the formation of an Al-Fe solid solution and not the brittle intermetallic compound(s) contribute to the good

adhesion and better corrosion resistance characteristics of aluminium coating. Although the Al-Fe phased diagram does suggest the formation of intermetallic compounds (Al_2Fe , Al_5Fe_2 and Al_3Fe_4), the SEM image of the Al-Fe alloy layer suggested the formation of a smooth and continuous Al-Fe solid solution under layer, without any secondary phases, between aluminum and the SS316 plate. The aluminum layer was found to consist of mostly aluminium and oxygen. Although this layer was found to have cracks (the cracks might have resulted from polishing operation), presence of the alloy layer seemed to have prevented the migration of the chloride ions to effect the corrosion of the SS 316 substrate.

4. Conclusions

The ternary eutectic LiBr-KBr-CsBr melt, containing 80 wt.% AlBr_3 , was found to offer significant advantages over the binary/ternary chloride electrolytes and hence can potentially offer an alternative molten salt electrolytic process to prepare pure aluminium coatings for SS substrates. Some of the advantages of this electrolyte include (i) comparatively lower loss of AlBr_3 (ii) possibility of obtaining thicker, dense, smooth, pore-free, adherent and shiny aluminium coatings on both ferrous and non-ferrous substrates including complex/intricate surfaces. Studies indicated that perhaps thicker (several microns) aluminium coatings can provide adequate protection, from corrosion, to steel surfaces. Alternatively, incorporation of an annealing step, as a post-coating treatment, can significantly improve the corrosion mitigation ability of the aluminum coating. Another effective corrosion protection mechanism could be to form a mixed layer, consisting of aluminium and its oxide.

5. Acknowledgement

The authors gratefully acknowledge the Idaho National Laboratory Directed Research and Development Program under DOE Idaho Operations Office for supporting the present research and development program. The manuscript was authorized by Battelle Energy Alliances under the contract No. DE-AC07-05ID14517, with the US Department of Energy, for publication. The US government retains and the publisher, by accepting the manuscript for publication, acknowledges that the US government retains a non-exclusive, paid up irrevocable worldwide license to publish or reproduce the published form of this manuscript or allow others to do so for United States Government purposes.

References

1. R.W. Revie and H.H. Uhlig, *Corrosion and Corrosion Control - An Introduction to corrosion science*, John Wiley & Sons., 4th Edition, 2008, pp. 1-7
2. E. Jeannine, *Chromate-free Nanoparticle Corrosion Inhibitors for Steel, Small Business Innovation Research-Phase I Report*, United States Environmental Protection Agency Contract No. EPD05042, 2005
3. D.Q.Wang, Z.Y.Shi, L.J.Zou, "A Liquid Aluminium Corrosion Resistance Surface on Steel Substrate", Appl. Surf. Science, 214 (2003) 304-311
4. D.Q.Wang and Z.Y.Shi, "Aluminizing and Oxidation Treatment of 1Cr18Ni9SS", Appl. Surface Science, 227 (2004) 255-260
5. R.S.C Paredes, S.C.Amico, A.S.C.M d'Oliveira, "The Effect of Roughness and Pre-heating of the Substrate on the Morphology of Aluminium Coatings Deposited by Thermal Spraying", Surf. Coat. Technology, 200 (2006) 3049-3055
6. A. Boogard, J.J.van den Broek, "Crystallization and Electrical Resistivity of Super-deposited Aluminium-Germanium Alloy Films", Thin Solid Films, 401 (2001) 1-6
7. H. Kersten, G.M.W. Kroesen, R. Hippler, "On the Energy Influx to the Substrate during Sputtering Deposition of Thin Aluminium Films", Thin Solid Films, 332 (1998) 282-289
8. C. Charrier, P. Jacquot, E. Denisse, J.P. Millet and H. Mazille, "Aluminium and Ti/Al Multilayer PVD Coatings for Enhanced Corrosion Resistance", Surf. Coating Technology, 90 (1997) 29-34
9. D. Yang, R. Jonnalagadda, B.R. Rogers, J.T. Hillman, R.F.Foster and T.S. Cale, "Texture and Surface Roughness of PRCVD Aluminium Films", Thin Solid Films, 332 (1998) 312-8
10. M. Galova, "Electrodeposition of Aluminium from Organic Aprotic Solvents", Surf. Technology, 11 (1980) 357-69

11. Y.G. Zhao, T.J. VanderNoot, “*Electrodeposition of Aluminium from Non-aqueous Organic Electrolytic Systems and Room Temperature Molten Salts*”, *Electrochim Acta*, 42 (1997) 3-13
12. G.A. Capuano and W.G. Davenport, “*Plating Aluminium onto Steel or Copper from Alkyl Benzene Electrolytes*”, *Plating*, 60 (1973) 251-5
13. E. Peled and E. Gileadi, “*Electroplating of Al from Aromatic Hydrocarbons*”, *Plat. Surf. Finish*, 62 (1975) 342-7
14. T. Hirato, J. Fransaer, and J.P. Celis, “*Electrolytic Co-deposition of Silica Particles with Aluminium from $AlCl_3$ -dimethylsulfone Electrolytes*”, *J. Electrochem. Soc.*, 148 (2001) C280-3
15. T. Jiang, M.J.B. Chollier, G. Dube, A. Lasia and G.M. Brisard, “*Studies on the $AlCl_3$ -dimethylsulfone ($DMSO_2$) Electrolytes for the Aluminium Deposition Processes*”, *Surf. Coat. Technol.*, 201 (2007) 6309-17
16. N. Ishibashi and M. Yoshio, “*Electrodeposition of Aluminium from the NBS type Bath Using Tetrahydrofuran-benzene Mixed Solvents*”, *Electrochim Acta*, 17 (1972) 1343-52
17. M. Yoshio and N. Ishibashi, “*High-rate Plating of Aluminium from the Bath containing $AlCl_3$ and $LiAlH_4$ in Tetrahydrofuran*”, *J. Appl. Electrochem.*, 3 (1973) 321-5
18. B. Siegfried and S. Klaus, “*US Patent 4,417,954*”, 1983
19. M. Yoshio, “*Electrodeposition of Aluminium from Non-aqueous Solutions*”, *Met. Finish*, 85 (1987) 33-8
20. G. Yue, S. Zhang, Y. Zhu, X. Lu, S. Li and Z. Li, “*A Promising Method for Electrodeposition of Aluminium on Stainless Steel in Ionic Liquid*”, *American Institute of Chemical Engineers (AIChE)*, 55, 3 (2009) 783-796
21. N. Godshall, “*Molten Salt Metallizing of Nickel Alloys*”, *J. Electrochem. Soc.*, 123 (1976) 137C-140C

22. R. C. Howie and D. W. Macmillan, "*The Electrodeposition of Aluminium from Molten Aluminium Chloride/Sodium Chloride*", J. Applied Electrochemistry, 2 (1972) 217-22
23. B. Nayak and M.M. Mishra, "*The Electrodeposition of Al on Mild Steel from a Molten $AlCl_3$ -NaCl Bath*", J. Applied Electrochem., 9 (1979) 699-706
24. M. Jafarian, M.G. Mahjani, F. Gobal and I. Danaee, "*Electrodeposition of Al from Molten $AlCl_3$ -NaCl-KCl Mixture*", J. Appl. Electrochem., 36(2006) 1169-73
25. M. Ueda, H. Kigawa and T. Ohtsuka, "*Co-deposition of Al-Cr-Ni Alloys using Constant Potential and Potential Pulse Techniques in $AlCl_3$ -NaCl-KCl Molten Salt*", Electrochim Acta, 52 (2007) 2515-9
26. M. Jafarian, M.G. Mahjani, F. Gobal and I. Danaee, "*Effect of Potential on the Early Stage of Nucleation and Growth during Al Electrocrystallization from Molten Salt ($AlCl_3$ -NaCl-KCl)*" J. Electroanal. Chem., 588 (2006) 190-6
27. M. Paucirov and K. Matiasovsky, "*Electrolytic Al Plating in Fused Salts based on Chlorides*", *Electrodeposition and Surface Treatment*, 3 (1975) 121-8
28. P. Fellner, M. Chrenkova-Paucirova and K. Matiasovsky, "*Electrolytic Al Plating in Molten Salt Mixtures based on $AlCl_3$ I: Influence of the Addition of Tetramethyl Ammonium Chloride*", Surface Technology, 14 (1981) 101-8
29. P.K. Tripathy, Steven D. Herrmann, S. X. Li, Guy L. Fredrickson and Tedd E. Lister, *Unpublished Results*
30. S.H. White and U.M. Twardoch, "*The Chemistry and Electrochemistry associated with the Electroplating of Group VIA Transition Metals*", J. Applied Electrochemistry, 17, 2 (1987) 225-242
31. S. Inazawa, K. Nitta, K. Okda and T. Nohira, "*Molten Salt Bath, Deposit, and Method of Producing Metal Deposit*", US Patent No. 0093222A1, dated April 24, 2008

32. T.Kasajima, T.Nishikiori, T.Nohira, and Y.Ito, “*Electrochemical Window and the Characteristics of ($\alpha+\beta$) Al-Li Alloy Reference Electrode for a LiBr-KBr-CsBr Eutectic Melt*”, J. Electrochem. Soc., 151, 11 (2004) E335-9
33. R.W. Berg, “*The CsBr-AlBr₃ Phase Diagram and the Crystal Structure of CsAlBr₄*”, Acta Chimica Scandinavica, 51 (1997) 455-61
34. Z. Wang, H. Kan, Z. Shi, B. Gao, Y. Ban and X. Hu, “*Electrochemical Deposition and Nucleation of Aluminum on Tungsten in AlCl₃-NaCl Melts*”, J. Mater. Sci. Technol., 24, 6 (2008) 915-2
35. E. J. Dufek, J. C. Seegmiller, R. C. Bazito and D. A. Buttry, “*Dioxygen Reduction affects Surface Oxide Growth and Dissolution on AA2024-T3*”, J. Electrochemical Society, 154, (2007) C458-64
36. G. S. Frankel, “*Pitting Corrosion of Metals: A Review of the Critical Factors*”, J. Electrochemical Society, 145 (1998) 2186-98

Table 1

Galvanic Series of metals and alloys

+ Corroded End (anodic/less noble)
Mg Mg Alloys Zn
Al (1100) Cd Al (2004-T4) Steel/Fe Cast Fe CrFe (active) Ni-Resistant cast Fe
304 SS (active) 316 SS (active)
PbSn solder Pb Sn
Ni (active) Inconel NiCr alloy (active) Hastelloy C (active)
Brass Cu Bronze CuNi alloy
Ag solder Ni (passive) Inconel NiCr alloy (passive)
CrFe (passive) 304 SS (passive) 316 SS (passive)
Ag Ti Graphite Au Pt
-Protected End (cathodic/more noble)

Table 2

Physicochemical Properties of AlBr_3 vis-à-vis AlCl_3

Property	AlBr_3	AlCl_3
Melting Point ($^{\circ}\text{C}$)	94-98	194
Boiling Point ($^{\circ}\text{C}$)	268 (sublimes)	182.7 (sublimes)
Density (gcm^{-3} , 25°C)	3.205	2.48
Vapor Pressure (mmHg)	1.0 (81.3°C)	1.0 (100°C)
Flash Point ($^{\circ}\text{C}$)	268	-

Table 3
Salt compositions and their melting temperatures (DTA vs DSC measurements)

Salt Composition (mol%)	Literature Data ³² , MP (⁰ C)		Present Data (⁰ C)		
	Eut. MP	Liq. Temp.	Eut. MP	Liquidus Temp.	≠%wt. loss
1. 59.5LiBr-33.5KBr-7CsBr	222	320	234.4	325	0.07
2. 50.5LiBr-28.5KBr-21CsBr	224	279	239.6	283	0.1
3. 56.1LiBr-18.9KBr-25CsBr	225	-	238.6	-	0.11
4. 61.1LiBr-13.5KBr-25.4CsBr	225	323	239.9	327	0.09

≠ % wt. loss indicates the weight loss before and after melting of the salts. These figures suggest that even after a holding time of ~30min. at 750⁰C, the loss of the electrolyte by way of volatilization was negligibly small

Table 4*
Eutectic and Liquidus temperatures of various compositions (DSC measurement)

Composition (wt.%)	Eutectic MP ($^{\circ}\text{C}$)	Liquidus Temp. ($^{\circ}\text{C}$)
1. $^{\#}\text{EC}+10\text{AlBr}_3$	240.2	331.7
2. $\text{EC}+20\text{AlBr}_3$	239.8	330.0
3. $\text{EC}+30\text{AlBr}_3$	238.7	325.3
4. $\text{EC}+40\text{AlBr}_3$	238.9	323.7
5. $\text{EC}+50\text{AlBr}_3$	239.4	317.0
6. $\text{EC}+60\text{AlBr}_3$	239.4	313.4
7. $\text{EC}+70\text{AlBr}_3$	236.7	311.9
8. $\text{EC}+80\text{AlBr}_3$	Absent	310.7
9. $\text{EC}+90\text{AlBr}_3$	Absent	302.6

**Only heating cycles were considered for measuring the eutectic and liquidus temperatures; $^{\#}\text{EC}$ -Eutectic Composition*

List of Figure Captions

Figure 1: Schematic representation of the experimental assembly (re-modified).

Figure 2: DSC thermograms of the eutectic LiBr-KBr-CsBr salts containing (a) 10 wt.% and (b) 80 wt.% AlBr_3 (re-modified).

Figure 3: X-ray diffraction pattern of LiBr-KBr-CsBr-20% AlBr_3 (bottom) and LiBr-KBr-CsBr 80% AlBr_3 (top). Three phases are identified in the diffractogram: LiBr, KBr (indicated) and CsAlBr_4 . The remainder of the unlabeled peaks correspond to CsAlBr_4 , with the exception of the large, broad peak approximately at $2\theta = 26$ degrees, which is produced from the Mylar® film, used to cover the solidified salt samples to prevent their reaction with atmospheric moisture (re-modified).

Figure 4: CV of Al^{3+} in the LiBr-KBr-CsBr (eutectic) melt, operating temperature – 275°C , $[\text{AlBr}_3] = 0.5$ wt.%, Scan rate - 0.025Vs^{-1} , $[\text{S}] = 0.3\text{ cm}^2$, cathodic peak (indicating aluminium deposition) occurred at $\sim -1.67\text{V}$, WE – 0.1cm dia. tungsten wire ; CE – Mo coil, made of 0.1 cm dia. wire ; RE – Glassy carbon rod (0.3 cm dia. and 10 cm long) (re-modified).

Figure 5: Square Wave voltammetry of Al^{3+} in the LiBr-KBr-CsBr melt, operating temp. – 275°C , $[\text{AlBr}_3] = 0.5$ wt.%, pulse height-25 mV, potential step-10 mV, frequency-8Hz, Apparent $\text{S} = 0.3\text{ cm}^2$, WE – 0.1cm dia. tungsten wire ; CE – Mo coil, made of 0.1 cm dia. wire ; RE – Glassy carbon rod (0.3 cm dia. and 10 cm long) (re-modified).

Figure 6: Aluminium deposit on SS 316 plate after 70 mins. of electrolysis, $[\text{AlBr}_3] = 20$ wt.%, melt temperature – 350°C , $\text{CCD} = 0.03\text{Acm}^{-2}$, rod – glassy carbon

Figure 7: Photograph showing aluminium coated SS316 plate (a) before and (b) after cleaning, operating temperature – 325°C , $[\text{AlBr}_3] = 80$ wt.%, Cathode Current Density – 0.5Acm^{-2} , duration – 2h, electrolyte – freshly prepared

Figure 8: Aluminium-coated MS rod

Figure 9: Potential vs. time profile (at a constant current, 3A) during electroplating of aluminium on a MS rod, $\text{CCD} = 0.8\text{Acm}^{-2}$, duration – 90 min., coating temperature – 325°C

Figure 10: Photographs showing the complete coverage of the threaded zones of the SS screws. Coatings were performed under a constant current mode (1-3A) for a total duration of 1h ; plating temperature – 325°C ; $[\text{AlBr}_3] = 80$ wt.%, electrolyte – freshly prepared (re-modified).

Figure 11: Photograph showing uncoated and coated zones of the tool steel drill bit

Figure 12: Potential vs. time profile at a constant current of 3A, plating temperature – 325°C , coating time – 100min., $[\text{AlBr}_3] = 80$ wt.% ; electrolyte – used with topped up AlBr_3 (re-modified).

Figure 13: SEM photograph of the aluminium coating on (a) SS 316 plate (shown in Figure 6b), magnification – 5K, coating thickness – $5.12\mu\text{m}$ and (b) SS304 plate, coating thickness - $26.8\mu\text{m}$ (re-modified).

Figure 14: SEM photograph showing aluminium coating on the mild steel rod, coating thickness – 7.0 μ m (re-modified).

Figure 15: Optical microscope images of the coated surface on SS316: (a) and (b) after day 1 and (c) and (d) after day 14 (re-modified).

Figure 16: Optical microscope images of the coated surface on SS304: (a) and (b) after day 1 and (c) and (d) after day 14 (re-modified).

Figure 17: Comparison of open circuit potential (V) vs. Ag/AgCl of coated and uncoated sections of aluminium coated drill bit, clearly the coated section showed better corrosion resistance

Figure 18: Open circuit potential (V) vs. Ag/AgCl of the coated and annealed SS316 plate. The stable OCP (for the duration of 100h) suggested the robustness of the annealed aluminium film in resisting the corrosion of the underlying steel surface

Figure 19: SEM image of the corroded spot on the coated drill bit, bright shapes consisted of iron, molybdenum and tungsten and no aluminium. Aluminium rich zones contained higher amounts of oxygen, which indicated the formation of oxides and/or hydroxides (re-modified).

Figure 20: SEM image of the smooth surface of the drill bit where the coating remained intact without any trace of corrosion after the OCP, bright shapes consisted of iron, cobalt, molybdenum and tungsten (re-modified).

Figure 21: SEM image of the annealed aluminium coating on the SS316 plate (after ~100h) of OCP, [1]- SS substrate ; [2] : AlFe alloy layer and [3] : Al-O layer ; [4] : Epoxy (re-modified).

Figureg

Figure 1

(a)

(b)

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

(a)

(b)

Figure 7

Figure 8

Figure 9

(a)

(b)

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

(a)

(b)

(c)

(d)

Figure 15

(a)

(b)

(c)

(d)

Figure 16

Figure 17

Figure 18

Figure 19

Figure 20

Figure 21