Effect of Copper Ions on Chromate Conversion Coating of Pure Aluminum

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Abstract: *Chromate conversion coatings (CCC)are formed an aluminium alloys by natural immersion in a bath containing fluoride ions and chromate species. The present studies employed high purity aluminium substrates, with addition of copper to the bath as copper fluoride, in order to investigate the influence of additions of Cu^{++} ions to the chromate coating bath and to assist understanding of the mechanism of detachment of conversion coating from aluminium-copper alloys. The coatings were formed in solutions of various compositions and the electrochemical behavior of the aluminium was evaluated by open circuit potential time measurement. The structure, composition and morphology of the conversion coatings were examined by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis and Rutherford backscattering spectroscopy (RBS). Thus, the findings suggest that the influence of copper addition to the coating bath, as Cu^{++} ions, is small, and limited to a slight reduction in coating thickness.*

1. Introduction

Chemical conversion coatings are commonly applied to aluminium; zinc, magnesium and tin to improve paint adhesion and to provide added corrosion resistance. Chromate – based conversion coatings are formed on metal surfaces as a result of the chemical attack that occurs when a metal is immersed in aqueous chromium-fluoride solution. Chromate / fluoride conversion coating is a highly effective method of pre-treatment of aluminium alloys for service in corrosion environments. The coatings combine excellence as a base for paints, simplicity of application and long-term corrosion resistance, with residual chromate ions contributing to the last.

Numerous studies have been carried out of their growth, which involves formation of hydrated Cr_2O_3, typically to a few hundred nanometers or to a few microns in thickness, by immersion of the substrate in the chromate bath for several minutes. However, locally, the thickness of the coating on aluminium alloys can be greatly reduced where the second phase particles intersect the surface [1].

Conversion coatings developed on aluminium and its alloys are of key importance to subsequent application of organic coatings, where interfacial roughness, both macroscopic and macroscopic, influences mechanical keying and, together with film composition, plays a role in the initial bond strength and its durability. Conversion coatings are generally formed in solutions containing fluoride ions and other additives such as chromate and phosphate ions; these solutions are known to thin the pre-existing film on the surface of aluminium, which is eventually replaced by a film containing elemental species from the coating bath formulation. [2]

1.1 Chemical Conversion Coating of Aluminium

Conversion coatings are frequently applied to metal surfaces for the purposes of improving corrosion resistance and as a base to enhance the adhesion of organic coatings such as paints are they applied by immersion of the metal in an appropriate bath. The metal may be polarized, as in anodizing of aluminium and magnesium, or simply immersed in the bath without connection to any power supply.

The metal takes part in the reaction with the bath solution that results in conversion of a layer of the metal surface to another chemical species, for example, conversion of aluminium to aluminium oxide. Thus, a layer of the metal is consumed and the surface may develop fine scale roughness due to the non-uniformity of the reaction process on the metal surface. The adhesion between the coating and the paint film is important, being governed by the coating composition and surface morphology; further the coating should limit corrosion of the substrate if the paint film is damaged.

Suitable conversion coatings may be applied by chromate and chromate-phosphate processes, with the thickness of the initially gel-like films ranging from 5 to 60 nm. The two most common methods of conversion coatings are spraying and immersion.

The most important conversion coatings are usually classified into three types, based respectively on the thickening of the natural oxide present on aluminium surfaces (chemical oxidation process), the production of phosphate and/or chromate layers (phosphating process, chromate-phosphate process and chromate process), or on the application of special coatings (the "no-rinse" treatment) [3].

1.2 Chromate Coatings

Chromate coatings can be produced with thickness typically ranging from approximately 50 to 500 nm, with colours varying from colorless to dark brown. Chromate solutions are normally operated at room temperatures. The appearance of the coatings varies with the alloy composition and film thickness and thus with the treatment time, normally 10 seconds to 60 minutes.

A typical bath composition is [3]
CrO_3	4 g/L
$Na_2Cr_2O_7$	3.5 g/L
NaF	0.8 g/L
Temperature	25 °C
PH	1.5

During immersion of aluminium, or aluminium alloys, in the chromate bath, different regions of the alloy surface function as either anodes or cathodes. At cathodic sites, which may be at second phase or for relatively high purity aluminium, the segregated impurities of the cellular network, the cathodic reaction results in formation of amorphous hydrated Cr_2O_3 according to

$$CrO_7{}^{2-} + 8H^+ + 6e \rightarrow Cr_2O_3 + 4H_2O \qquad (1)$$
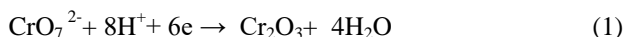
At regions of the surface between the cathodic sites, the anodic reaction results in the formation of alumina according to

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e \qquad (2)$$
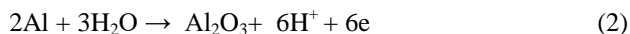
As long as the anodic reaction continues, growth of Cr_2O_3 proceeds at cathodic sites and progressively covers the aluminium surface including the anodic regions.

Eventually, the surface is practically covered completely by hydrated Cr_2O_3 and the reaction virtually stops when the anodic sites are blocked. The conversion coating thus comprises hydrated Cr_2O_3 above a thin layer of mainly alumina. Typically, the final thickness of the coating is less than 1 micron.

1.3 Corrosion Protection of Aluminium by Chromate Coatings

Additional corrosion protection afforded to the substrate by the chromate conversion coatings has been described to be two fold. The coating material acts as a barrier to the corrosion medium, providing protection to the underlying bare metal and the hexavalent chromium entrapped in the coating acts as an effective corrosion inhibitor upon exposure to the aqueous environment [4].

The majority of theories concerned with the action of chromate usually relate in one form or another to the reduction of Cr^{6+} to Cr^{3+} species with so called "healing" of the oxide film [5]. The reduction process proceeds due to an electric field within the film material and due to flaws in the coating. In the conversion coatings, Cr^{6+} is readily leached into scratched areas where it can be cathodically reduced to form hydrated trivalent chromium oxide to repair it [5, 6].

1.4 Factors Influencing Chromate Coating Growth

1.4.1 Temperature
The coating thickness varies with the temperature of the solution (25°C-40°C). The coating is thicker at lower temperatures; thus at temperatures ranging from 40°C to 25°C, a decrease of temperature by 1°C increases the thickness of the coating by 1.5 nm [4]. One explanation is that elevating the temperature has the deleterious effect of increasing the rate of reduction of Cr (VI) so that an excessive build - up of Cr (III) occurs in the solution [4].

1.4.2 PH of Solution
The growth of the coating was studied by varying the pH of the solution from approximately 1.1 to 4.8 [4]. The coating thickness and corrosion protection are similar from pH 1 to approximately pH 2. When the pH exceeds 2.5, the coatings produced are thinner and less corrosion resistant.

1.4.3 Fluoride Concentration
The concentration of fluoride is important to coating growth. Marchand [7] found that the concentration of sodium fluoride should be 0.8 g/L; above this concentration, the coating became powdery. At reduced concentration the coating was paler in colour. Varying the fluoride concentration from 0.8 g/L by a factor of 10 in either direction [4] was also found to develop thin coatings with very poor corrosion resistance of the substrate.

2. Experimental Work

This part of research includes the details of experiments performed, preparation of specimens, material and chemicals employed, conditions of conversion coating and the information relevant to the major experimental techniques employed.

2.1 Specimens Preparation

Aluminium foil of 99.999% purity was used for all experiments. The foil was cut into pieces of dimensions 1.5 x 4 cm^2. Specimens were degreased in ethanol and etched before conversion coating treatment

2.2 Etching of Aluminium Specimens

The specimens were etched in 3 g/L NaOH solution at a temperature of 30°C for 10 minutes and rinsed thoroughly with deionised water for about 2 min. Then the specimens were immersed in 50% HNO_3 for 5 min, rinsed thoroughly with deionised water for about 5 min, and dried in a cold air stream. Finally the specimens were stored in a desiccator over silica gel prior to further treatment. All chemicals used in this research were of analytical grade. Aqueous solutions were prepared with de-ionised water.

2.3 Chromate Conversion Coating

The chromate conversion standard solution was prepared by adding 4 g of CrO_3, 3.5 g of $NaCr_2O_7$ and 0.8 g of NaF to one liter of deionized water and stirred for 1 h, to form a homogenous solution at room temperature with pH = 1.91. Chromate conversion coating was carried out by immersing

the sample for 12 min in the standard solution. Finally the sample was rinsed with deionized water, dried in air at room temperature and stored in a desiccator.

2.3.1 The Effect of Cu^{++} Concentration on the Chromate Conversion Coating

In order to study the effect of Cu^{++} on the chromate conversion coating, solutions with three different copper concentrations, in addition to the standard solution were prepared. Table 2.1, illustrates the composition and pH of each solution.

Table 2.1 Composition and pH of chromate conversion solutions

Solution g /L	Composition				pH
	CrO$_3$	NaCr$_2$O$_7$	NaF	CuF$_2$	
Standard	4	3.5	0.8	-	1.91
Solution I	4	3.5	0.712	0.1	1.8
Solution II	4	3.5	0.758	0.05	1.75
Solution III	4	3.5	-	0.966	1.8
Solution IV	4	3.5	1.26	-	2.92
Solution V	4	3.5	-	1.52	2.78

Each sample was immersed in one solution for 12 min followed by rinsing in deionised water, drying in air at room temperature and storage in a desiccator.

2.4 Open Circuit Potential / Time Measurement

The potential/ time behavior of various specimens wererecorded at room temperature. The potentials of the working electrodes were measured using a saturated calomel reference electrode (SCE) (+241 mV vs NHE).

2.5 Specimen Examination

Visual examination of the specimens was carried out after coating, with specimens examined by Scanning Electron Microscopy (SEM) using Amray 1810 and DS130 and the presence of coating material by Energy Dispersive X-ray (EDX) instruments respectfully. The efficiency of conversion coating was determined by measurements of the chromium contents of coating by Rutherford Backscattering Spectroscopy (RBS) using 1.5 MeV He$^+$ ions.

3. Results and Discussion

3.1 Open Circuit Potential / Time Measurement

The potential / time behavior of various specimens were recorded at roomtemperature. (Figures.3.1 A, B, C, D, E and F for each solution). During the first 2 min, the potential developed increasing oscillations, before settling to a more regular pattern. The minimum and maximum potentials are given in Table.3.1

3.2 Visual Appearance

The presence of the standard conversion coating was evident from the golden appearance of the surface, as indicated in Figure.3.2. The coating was used as a reference for comparison with specimens coated with other solutions. Most coated specimens disclosed appearances close to that of the reference specimen.

Table 3.1: Corrosion potential measurements

| Solution g /L	Composition					Corrosion potential V$_{SCE}$		
	CrO$_3$	NaCr$_2$O$_7$	NaF	CuF$_2$	F$^-$	Maximum	Minimum	Max-Min
Standard	4.00	3.500	0.800	-	0.362	-0.547	-0.731	0.184
Solution I	4.00	3.500	0.712	0.100	0.362	-0.541	-0.743	0.202
Solution II	4.00	3.500	0.758	0.050	0.362	-0.545	-0.738	0.193
Solution III	4.00	3.500	-	0.966	0.362	-0.535	-0.736	0.201
Solution IV	4.00	3.500	1.260	-	0.570	-0.590	-0.833	0.243
Solution V	4.00	3.500	-	1.520	0.570	-0.585	-0.824	0.239
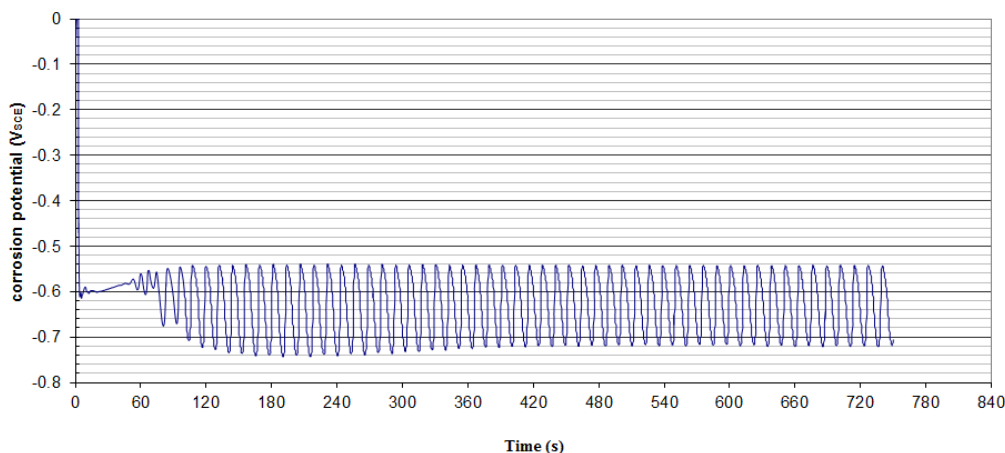
Figure 3.1 A: Potential/Time behavior of aluminum (99.999%Al) in standard CCC solution of PH=1.91
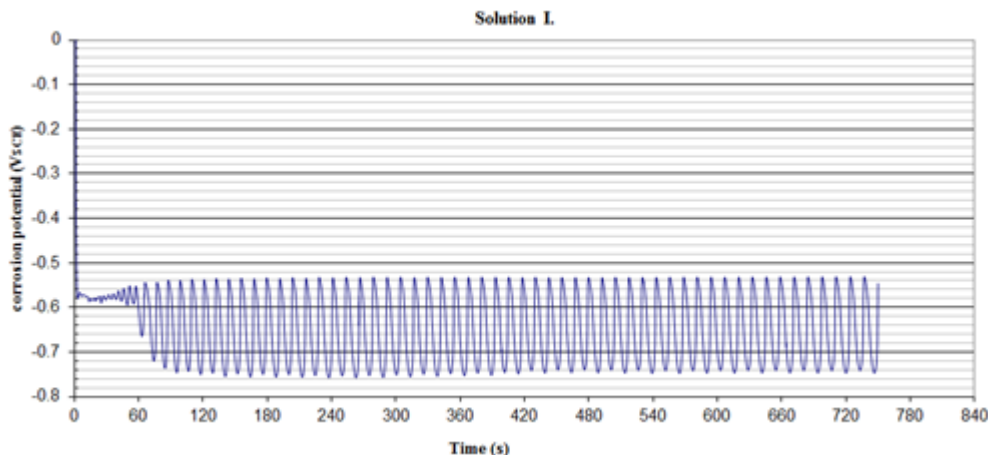
Figure 3.1 B: Potential/Time behavior of aluminum (99.999%Al) in CCC solution containing 0.1 g/L of CuF_2 of PH=1.80
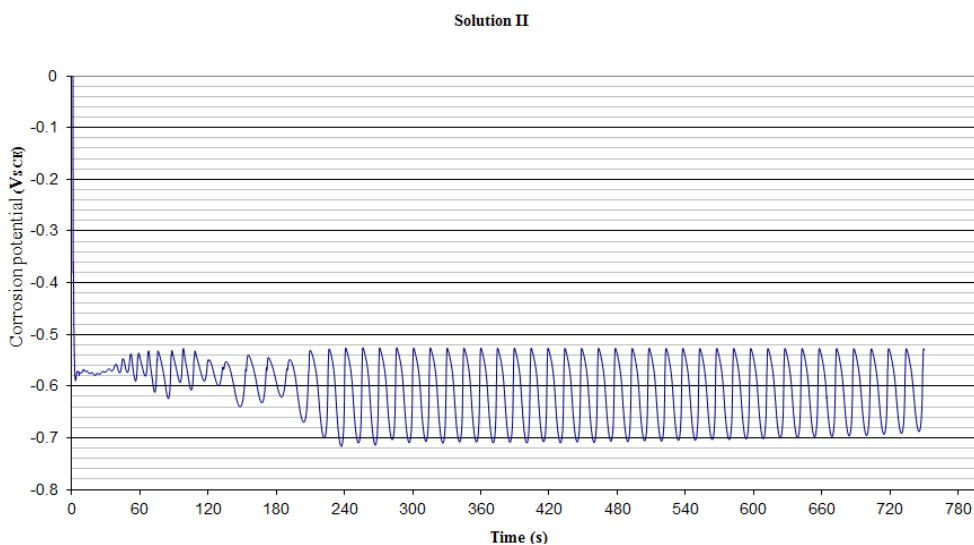

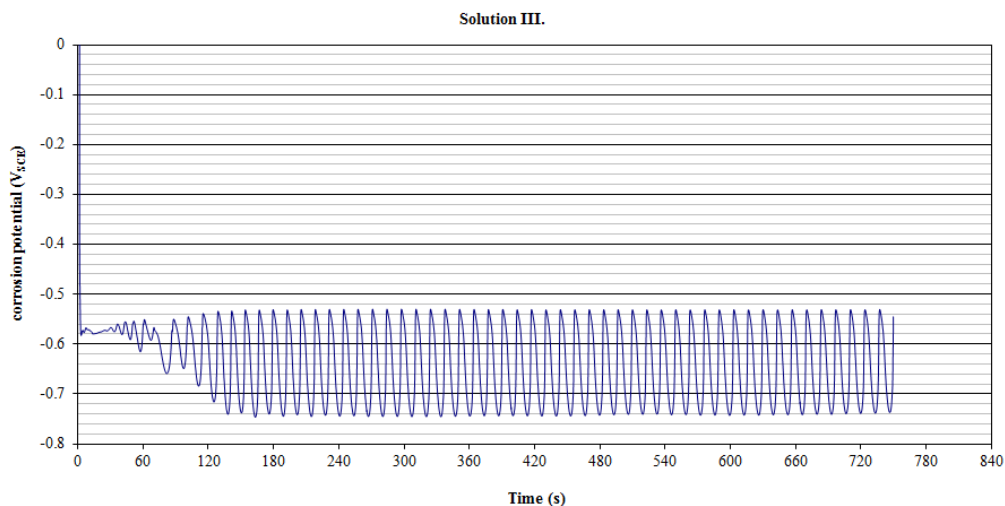**Figure 3.1 C:** Potential/Time behavior of aluminum (99.999%Al) in CCC solution containing 0.05 g/L of CuF2 of PH=1.75

Figure 3.1 D: Potential/Time behavior of aluminum (99.999%Al) in CCC solution containing 0.966 g/L of CuF_2 of PH=1.80
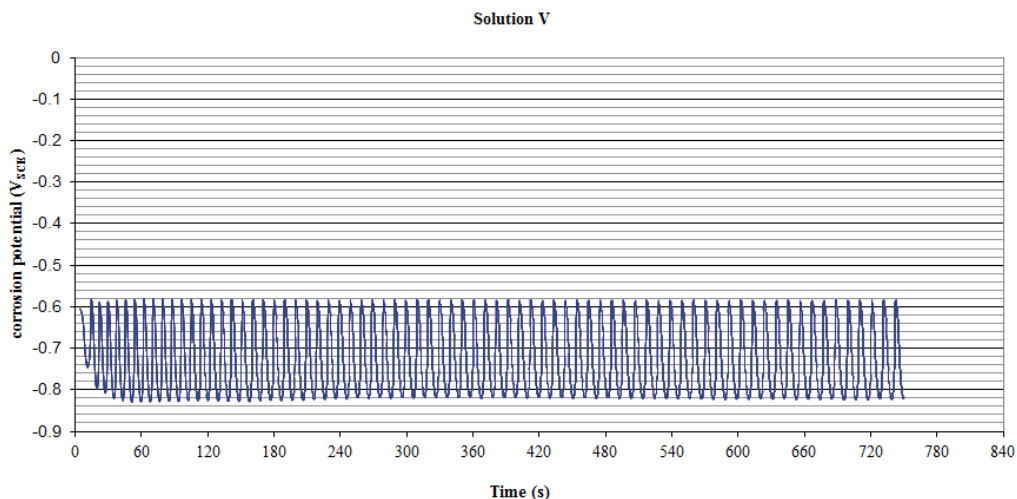
Figure 3.1 E: Potential/Time behavior of aluminum (99.999%Al) in CCC solution containing 1.52 g/L of CuF_2 of PH=2.78
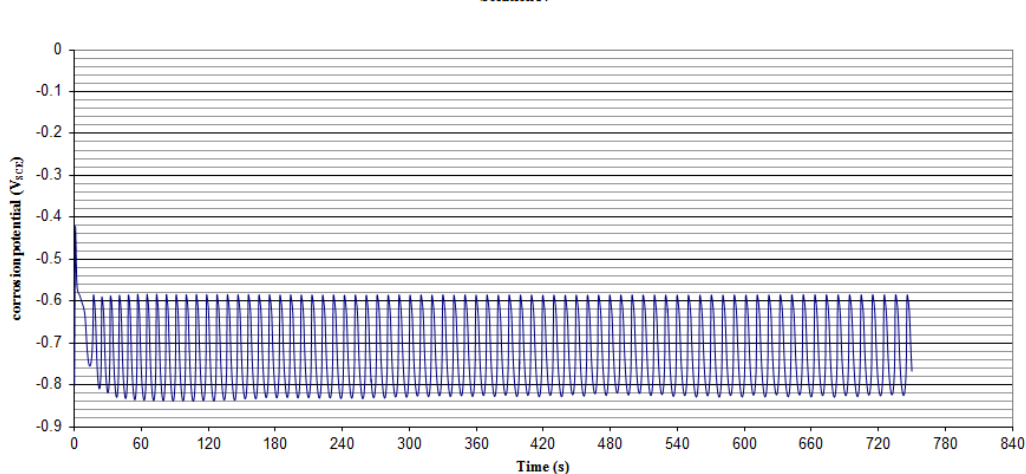

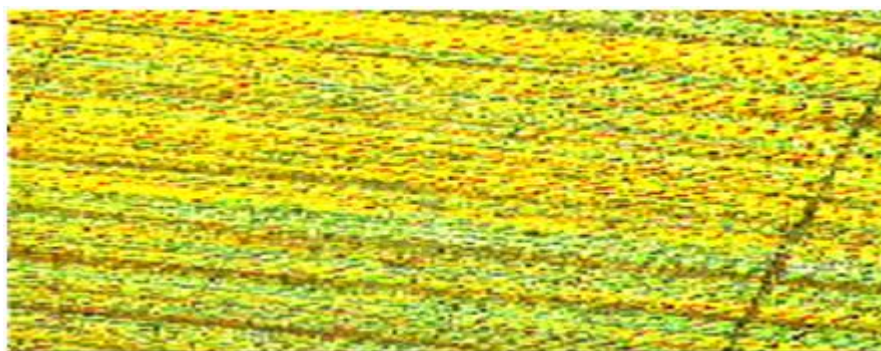**Figure 3.1 F:** Potential/Time behavior of aluminum (99.999%Al) in CCC solution containing 1.26 g/L of NaF of PH=2.92

Figure 3.2: Optical image (2.5x) of Standard Conversion Coating

3.3   Copper-free solution

3.3.1 Standard Conversion Coating

3.1.1.1 SEM/EDX
Figure 3.3.A low magnification, and Figure 3.3.B high magnification, scanning electron micrograph reveal uniform, but micro cracked, coatings. The typical EDX spectrum in Figure 3.3 C shows the presence of aluminium, oxygen and chromium. Table 3.2 gives the results of analyses at 13kV, 15Kv and 20Kv

Table 3.2: Results of EDX analysesat accelerating voltages of 13kV, 15Kv and 20Kv

Elements	13kV	15kV	20kV
Oxygen (O)%	23.1	22.2	20.8
Aluminium(Al)%	62.4	68.0	73.6
Chromium(Cr)%	14.5	9.8	5.6

Figure 3.3 A: Scanning Electron Micrograph at 20 kV of standard conversion coating
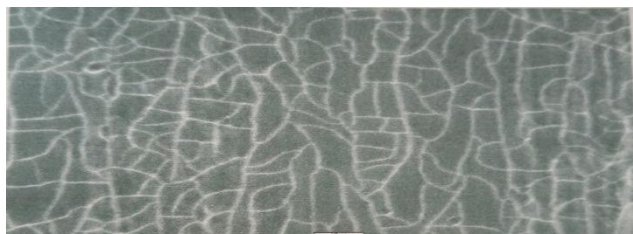

Figure 3.3 B: Scanning Electron Micrograph of standard conversion coating, revealing coating in greater detail.
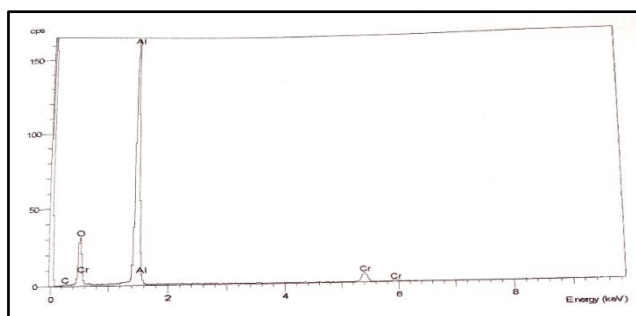

Figure 3.3 C: Typical EDX spectrum, at 13 Kv obtained from surface probes of the standard conversion coating.

Conversion coating proceeded on all the pre-treated surfaces employed. A long-time immersion in the standard chromate /fluoride bath resulted in a relatively thick coating of mud-cracked appearance,but assists retention of organic coatings. Additionally, incorporation of soluble Cr^{6+} species in the coating also assists in corrosion inhibition at damaged regions [1].

Concerning the mechanism of the conversion coating formation, previous work [8] has shown that in relatively pure aluminum, reduction of Cr^{6+} species to Cr^{3+}, with resultant hydrated Cr_2O_3 development, proceeds at cathodic sites.

The associated anodic process, i.e. dissolution of Al^{3+} ions, proceeds on the general flawed surface. F$^-$ Species in the acid bath result in thinning of the air formed alumina film; the film thickness is reduced to a level at which the field strength is sufficient for ionic transport and the anodic process of film reformation proceeds.

This gives rise to a dynamic equilibrium of growth at metal/film interface and dissolution at the film/ electrolyte interface. Loss of Al^{3+} ions to solution proceeds since the anodic process involves ionic migration of Al^{3+} species outwards and O^{2-} ions inwards over the residual alumina film. Under acidic interfacial conditions, the outwardly

mobile Al^{3+} ions are ejected directly to solution without forming alumina film material at the film / electrolyte interface.

The overall reaction for coating formation, including the parallel processes of oxidation of aluminium to form alumina and reduction of chromate ions is given by [1];
$$2Al + Cr_2O_7^{2-} + 2\,H^+ + (n-1)\,H_2O \rightarrow Cr_2O_3 \cdot n\,H_2O + Al2O3 \quad (3)$$

3.4 Solution with Increase Fluoride Content (Solution IV) "Solution IV contains 0.570 g/l of fluoride ions (F$^-$) compared with 0.362 g/l in the standard conversion coating"

3.4.1SEM/EDX
Figure 3.4A, high magnification, scanning electron micrograph reveal uniform, but micro cracked, coatings. The typical EDX spectrum in Figure 3.4B shows the presence of aluminum, oxygen and chromium. Table 3.3 gives the results of analyses at 13kV, 15Kv and 20Kv.

Table 3.3: Results of EDX analyses at accelerating voltages of 13Kv, 5Kv and 20Kv

Elements	13Kv	15Kv	20Kv
Oxygen (O) %	26.2	24.3	22.5
Aluminum(Al) %	57.5	63.5	71.5
Chromium(Cr) %	14.8	10.9	6.0
Fluoride (F$^-$) %	1.5	1.3	-

Accordingly, one Cr^{6+} ion is reduced with oxidation of one aluminium atom fluoride ions dissolve the alumina at the base of the coating, forming soluble aluminium fluoride, by the reaction
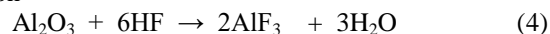$$Al_2O_3 + 6HF \rightarrow 2AlF_3 + 3H_2O \quad (4)$$

Figure 3.4 A: Scanning Electron Micrograph at 20 kV of the coating produced in solution IV
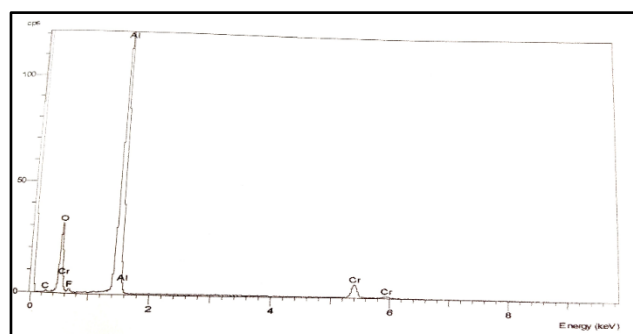

Figure 3.4 B: Typical EDX spectrum, at 13 Kv obtained from surface probes of the coating produced in solution IV.

3.5 Low and High copper Containing Solution

3.5.1 Low Copper Containing Solution (Solution III)
Solution contained 0.966g/l of CuF2 and 0.362g/l of fluoride(F-) the latter being the same as the standard conversion coating bath.

3.5.1.1 SEM/EDX
Figure 3.5.1A, high magnification, scanning electron micrograph reveal uniform, but micro cracked, coatings. The typical EDX spectrum in Figure 3.5.1B shows the presence of aluminium, oxygen and chromium. Table3.4 gives the results of analyses at 13kV, 15Kv and 20Kv.

Table 3.4: Results of EDX analyses at accelerating voltages of 13kV, 15Kv and 20Kv

Elements	13kV	15kV	20kV
Oxygen (O)%	20.9	19.2	18.4
Aluminium(Al)%	68.6	72.7	77.4
Chromium(Cr)%	10.5	8.1	4.2

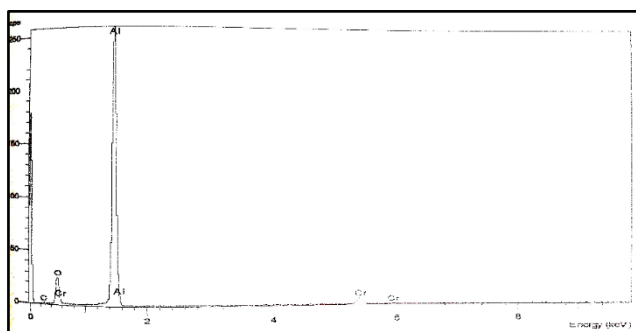**Figure 3.5.1A**: Scanning Electron Micrograph at 20 kV of the coating produced in solution III

Figure 3.5.1 B: Typical EDX spectrum, at 13 Kv obtained from surface probes of the coating produced in solution III.

3.5.2 High Copper Containing Solution (V)
Solution contained 1.520 g/l of CuF2 and 0.572g/l of fluoride(F-) the latter being the same as in solution (IV).

3.5.2.1 SEM/EDX
Figure 3.5.2.A, high magnification, scanning electron micrograph reveal uniform, but microcracked, coatings. The typical EDX spectrum in Figure 3.5.2.B shows the presence of aluminium, oxygen and chromium. Table3.5 gives the results of analyses at 13kV, 15Kv and 20Kv.

Table 3.5: Results of EDX analyses at accelerating voltages of 13Kv, 15Kv and 20Kv

Elements	13Kv	15Kv	20Kv
Oxygen (O) %	20.9	19.2	18.4
Aluminium(Al) %	68.6	72.7	77.4
Chromium(Cr) %	10.5	8.1	4.2
Fluoride (F-) %	1.1	0.9	0.8

Recent study [1] has shown that the rate of coating growth is reduced on Al-Cu alloys, due to thermodynamic and kinetic factors. The enrichment of the copper in the alloy leads to a positive shift in the corrosion potential [9], which may indicate a shift in the equilibrium potential of the anodic reaction.

The results suggest that copper in either the solution or the substrate has detrimental consequences to the conversion coating. The addition of copper to the coating bath, as CuF_2, resulted in insignificant changes in the open-circuit potential behavior. However, increase of the concentration of F- ions, added as either NaF or CuF_2, led to a reduction in the open-circuit potential, consistent with enhanced thinning of alumina layer beneath the main region of $Cr_2O_3.nH_2O$ with incorporated $Cr_2O_7^{2-}$ ions.

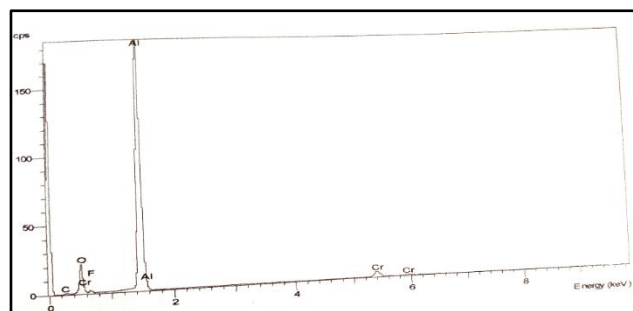**Figure 3.5.2A:** Scanning Electron Micrograph at 20 kV of the coating produced in solution V

Figure 3.5.2 B: Typical EDX spectrum, at 13 Kv obtained from surface probes of the coating produced in solution V.

3.6 Rutherford Backscattering Spectroscopy (RBS)

Typical RBS spectra for the conversion coating reveal for chromium as shown in Figure (3.6.A, and 3.6B for each solution), with peak width dependent upon coating thickness.
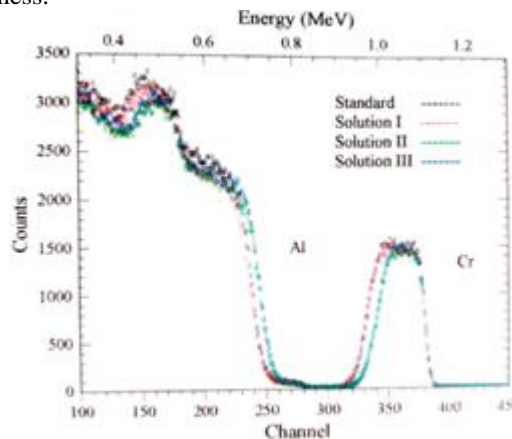

Figure 3.6A: RBS spectra of standard coating for comparison and solution I,II and III
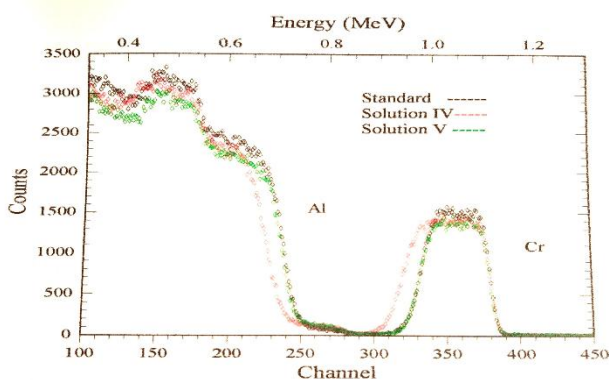
Figure 3.6B: RBS spectra of standard coating for comparison and solution IV and V

Table 3.6: Results of RBS measurements

Solution	Cr content (atms/cm^2)
Standard	3.5075E+17
Solution I	3.5339E+17
Solution II	3.9721E+17
Solution III	3.8943E+17
Solution IV	3.1137E+17
Solution V	3.3158E+17

Table 3.6 shows RBS measurements analysis suggested that coatings formed in the copper-containing solution were slightly thinner than these formed in the copper-free solution, by about 10-20%. A thicker coating was also indicated for the coating formed in solutions of higher fluoride concentration, presumably due to the higher growth rate with increased alumina thinning.

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