# Aluminum Deposits on 42 CD4 Steel Substrates By Molten Salts Electrolysis

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Electrolytic deposition of aluminum on 42CD4 steal substrates, from a KCI-LiCI eutectic melt with AICI, additions at 600 °C, has been studied in order to improve surface properties and corrosion resistance under aggressive gaseous atmospheres. A detailed study of the aluminum reduction mechanism was carried out using the electrochemical methods of linear sweep voltammetry, cathodic chronopotentiometry and cathodic chronoamperometry. The solid state diffusion coefficient of the aluminum into the steel substrate was evaluated using cathodic chronoamperometry and was found to be  $D_{AI}$  = 1.8 x 10<sup>-11</sup> Cm<sup>2</sup>/sec. From the mechanism found by the electrochemical reaction study, the experimental parameters could be adjusted in order to obtain in a reproducible way a homogeneous, aluminum-rich surface layer of regular thickness on steel electrodes. The best results were obtained using square wave pulses with the following set of parameters: pulse amplitude  $i_{p} = -80 \text{ mA/cm}^{2}$ , pulse duration  $t_{p} = 0.5 \text{ sec}$ , and relaxation time t = 2 sec. Electron microprobe analysis showed that the electrodeposits obtained consisted of the solid compound, Fe<sub>2</sub>Al<sub>5</sub>. Microhardness measurements of the electrocoated samples showed that their superficial microhardness, as much as 950 Vickers, was improved compared to samples treated by classical methods (650 to 750 Vickers), such as nitriding, boriding or carburizing.

teels can be used in drastic service conditions provided a surface treatment is performed to improve their resistance to wear, mechanical stresses or corrosion. Conventional methods, based on thermochemical treatments under controlled atmospheres, such as nitriding, boriding or carburizing, are used for increasing steel hardness. These techniques do not give satisfactory results, however, for all applications. The necessity for development of other surface treatment techniques, therefore, leading to higher hardness values and better corrosion resistance of steels, is well established.

New techniques, such as plasma coating or vapor deposition (PVD or CVD) can sometimes provide a solution. Although plasma coating allows formation of thick layers, such coatings often show poor adhesion and high porosity.' Additional, expensive treatments are needed in order to overcome these defects. Also, in the case of complicated shapes, regular coatings cannot easily be obtained by this technique. On the other hand, PVD and CVD can yield non-porous layers with a good adhesion to the substrate. The layers obtained by PVD are very thin (-3 pm), however, and the equipment required is very expensive.<sup>2</sup>

CVD is easier to do and can lead to quite thick layers by simultaneous diffusion when performed at high temperatures (-1000 "C), but dimensional modifications of the treated items are observed as a result of treatment for very long periods at high temperatures.<sup>3</sup>By contrast, at lower temperatures, when organometallics are used, the thickness of the obtained layers is very small (-6  $\mu$ m).

The aim of the current research is to establish the experimental conditions for obtaining aluminum coatings on steel with improved hardness, corrosion resistance and strong adhesion. An electrochemical process leading to simultaneous aluminum deposition and diffusion into steel was studied. This technique has the advantage of easy control of deposit thickness, and provides a regular surface layer even on complicated shapes.

# **Experimental Conditions**

Electrochemical Study - Electrolysis Electrolyte

The solvent is a eutectic mixture of KCI and LiCI (41.5 to 58.5 percent mol) melting at 361 °C. <sup>4</sup>The working temperature is 600 "C, at which these salts are completely ionized and play the role of the supporting electrolyte. Because of the great affinity of Li<sup>\*</sup>ions for water, the electrolyte is stored in a furnace at 200 'C and transferred into the electrolytic cell just before the experiment. The same temperature is maintained for about two hr, and high-purity argon gas is allowed to flow over the electrolyte. All the experiments are performed in this same atmosphere.

The solute is anhydrous aluminum chloride, AICl<sub>3</sub>, which is further purified by sublimation according to the method proposed by Qi-Xian Qin and Skyllas-Kazacos<sup>5</sup> and stored under controlled atmosphere. During the experiment, it is introduced into the electrolytic cell through a device designed to prevent hydrolysis.

# Electrolytic Cell - Electrodes

The electrolytic cell is a cylindrical crucible made of vitreous carbon, 45 mm inner diameter and 50 mm in height. This material is chemically inert against the molten chloride salts under the given experimental conditions. The crucible is placed inside a cylindrical stainless steel cell. The upper part of this cell is closed tightly by a suitably designed cap, cooled by water circulation through it, permitting introduction of the various electrodes and a thermocouple into the cell.

The working electrodes (WE) are of 42CD4 steel (composition given in Table 1). This type of steel was selected because of its current use in the mechanical engineering industry. The electrodes are either cylindrical wires (dia. 1 mm), for the electrochemical reaction mechanism study, or rectangular plates ( $15 \times 15 \text{ mm}^2$ ), for electrodeposition with the purpose of microscopic characterization or mechanical tests.

The counter electrode (CE) is either a pure aluminum rod (dia. 5 mm) or a tungsten wire (dia. 1 mm). The reference electrode (RE) is a silver wire (dia. 1 mm) dipped into a silver chloride solution in KCI-LiCI eutectic (0.05 mol fraction AgCl), placed in a sillimanite tube closed at one end. This electrode is one of the most commonly used with molten chloride salts

<sup>&#</sup>x27;Merck Chemical Products, Darmstadt, Germany

# Table 1 Composition of 42CD4 Steel

Element	Percentage
Carbon	0.38-0.45
Manganese	0.50-0.80
Silicon	0.40 max.
Chromium	0.90-1.20
Molybdenum	0.15-0.30
Phosphorus	0.035 max.
Sulfur	0.030 max.

electrolytes, because of its good stability, reproducibility and reversibility. <sup>4, 6</sup>A nickel wire (dia. 2 mm) is also used as a comparison electrode.

## Electrical Circuit

For application of the various electrochemical methods, a potentiostat, <sup>b</sup>monitored by a signal generator,' is used. The response of the system to each imposed electrical signal is registered using an oscilloscope with numerical memory<sup>d</sup> and transferred to an X-Y recorder.<sup>e</sup>

# Characterization of the Electrodeposits and Microhardness Measurements

Well-polished cross sections of electrocoated steel samples (15 x 15 mm') were analyzed by scanning electron microscopy and microprobe analysis. Microhardness measurements were made with a microhardness tester and, for comparison, similar measurements were made on 42CD4 steel samples subjected

<sup>b</sup>Model 173, EG&G Princeton Applied Research, Trenton, NJ <sup>c</sup>Model 175, EG&G Princeton Applied Research, Trenton, NJ <sup>c</sup>Tektronix, Beaverton, OR <sup>b</sup>EG&G Princeton Applied Research, Trenton, NJ

<sup>1</sup>Durimet 060,366002, Ernst Leitz GmbH, Wetzlar, Germany

Potential sweep rates, V/sec

Potential sweep range: -0.55 to -1.2 to -0.55 V Temp. 600 °C

1: 0.2 2: 0.3 3: 0.4 4: 0.5 5: 0.6 to the conventional surface treatments of nitriding and carburizing; also on aluminized samples subjected to post-nitriding or post-carbutizing treatments. Loads were in the 0.025 to 0.050 kg range. Microhardness profiles were also obtained by measurements on cross sections of treated 42CD4 samples.

### Experimental Results and Discussion Linear Sweep Voltammetry

The electroactivity range of the pure solvent was studied by linear sweep voltammetry, using a 42CD4 steel working electrode. The cathodic limit of the electroinactivity range occurs at -1.6 V/RE, which probably corresponds to the alkali ions reduction or possibly to the remaining water traces.

The voltammetric curves obtained after addition of 8.69 x 10<sup>-5</sup> mol/cm<sup>3</sup>AlCl<sub>s</sub>are shown in Fig. 1. Two successive voltammetric peaks are observed in the cathodic area at Ep<sub>c1</sub> = -0.890 V/RE and Ep<sub>c2</sub> = -1.080 ± 0.010 V/RE. The first peak is attributed to an aluminum-iron intermetallic compound formation on the electrode surface. The second is attributed to the reduction of aluminum ions to pure aluminum metal. This peak potential corresponds to those given in the literature for the aluminum deposition under similar experimental conditions.

Despite the interference of the first reduction peak, which hinders precise determination of the experimental cathodic curves, the investigation of the mechanism of aluminum ion reduction to aluminum metal is conducted via the following functions:

$$Ep_{c2} = f(v), Ip_{c2}/v^{1/2} = f(v), IEp_{c2}/2 - Ep_{c2}| = f(v^{1/2})$$

where Ep<sub>2</sub>, Ip<sub>2</sub> are the cathodic voltammetric peak Potential and the corresponding peak current intensity, and Ep<sub>2</sub>/2 is the potential corresponding to the half cathodic peak current intensity and v is the potential sweep rate. Convolution analysis, proposed bv Oldham<sup>7</sup> and Imbeaux,<sup>8</sup> is also used. This method consists of Studying the current function:

$$m(t) = \frac{1}{\sqrt{\pi}} \int_{O}^{t} \frac{i(u)du}{(t-u)^{1/2}}$$



Fig. 1—Voltammetric curves for aluminum ion reduction on a 42CD4 steel working electrode (S=  $0.223 \text{ cm}^3$ ) in a KCI-LiCI eutectic mixture containing AICI<sub>3</sub>, (C°AICI<sub>3</sub>=  $8.69 \times 10^{\circ} \text{ mol/cm}^3$ .

Epc,

Epc-

0.55 V/RE

10 mA

0.1 V

Fig. 2—Ip<sub>a</sub> variation with  $V^{\alpha}$ . Values of Ip<sub>a</sub> measured on the voltammetric curves of Fig. 1.

# Table 2 Aluminum Ion Reduction on a 42CD4 Steel Electrode\*

v (v/sec)	v <sup>1/2</sup> (v <sup>1/2</sup> /sec <sup>1/2</sup> )	Ep <sub>c2</sub> (V)	Ep <sub>c2</sub> /2 (V)	Ep <sub>c2</sub> - Ep <sub>c2</sub> /2   (V)	lp <sub>c2</sub> (A)	n*
0.2	0.447	-1.070	-1.005	0.065	-1.35 x 10 <sup>-2</sup>	-
0.3	0.548	-1.077	-1.008	0.069	-1.61 x 10 <sup>-2</sup>	-
0.4	0.632	-1.080	-1.011	0.069	-1.96 x 10 <sup>-2</sup>	2.6
0.5	0.707	-1.085	-1.015	0.070	-2.27 x 10 <sup>-2</sup>	2.7
0.6	0.775	-1.088	-1.016	0.072	-2.42 x 10 <sup>-2</sup>	2.7

\*Results obtained from the voltamperometric curves given in Fig. 1. The number of exchanged electrons was calculated by the convolution method.

where i and t are the current density and time, respectively. This function varies according to the electroreduction mechanism. In the case of a simple and reversible electrochemical reaction, this function takes on a constant value equal to  $m^*=nF(D_{ox})^{12}C^\circ_{ox}$  and the Nernst equation can be written as

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{m^* - m(E)}{m(E)}$$

where  $E_{\nu z}$  is the polarographic half-wave potential. The logarithmic function,  $E = f[ln(m^* - m)/m]$ , is linear. Its slope is equal to RT/nF, from which the number of exchanged electrons can be calculated.

The results obtained are given in Table 2. The variation of  $Ip_{e2}$  with v<sup>12</sup> is also presented in Fig. 2. It can be seen that this function is linear, while  $Ep_{e2}$  and  $Ep_{e2}/2$  remain almost constant when the potential sweep rate increases. It is concluded, therefore, that the whole phenomenon is controlled by the diffusion of the electroactive aluminum ions in the electrolyte and that the electrode cathodic reaction is rapid.

The calculated number of electrons exchanged, taking into account the variation of  $IEp_{e2}/2 - Ep_{e2}I$  with  $V'^{z}$ , as well as the results of convolution analysis (Fig. 3),<sup>e</sup> is close to 3. The convolution technique permits, in the case of diffusion-controlled processes, suppression of the influence of a reaction



Fig. 3—Convolution method characteristic curves calculatedly voltammetric curve 4 of Fig. 1: Curve 1, voltammetric, I = f(E); Curve 2, current function, m = f(E); Curve 3, logarithmic analysis function,  $ln[(m^*-m)/m] = f(E)$ .

preceding and interfering with the studied process. In these calculations, it is assumed that the oxidized and reduced species are soluble in either the electrolyte or the steel electrode.

#### Cathodic Chronopotentiometry

The potential variation with time, E(t), for different values of the applied current density is shown in Fig. 4. Two transition times  $\tau_1$  and  $\tau_2$  can be observed, corresponding respectively to the two cathodic voltammetric peaks obtained, using linear sweep voltammetry. The first, related to the first voltammetric cathodic peak, corresponds to an aluminum-iron intermetallic compound formation. The second appeared at a potential of -1.085 V/RE and corresponds to the aluminum ion reduction to aluminum metal.

The expression  $i(\tau_2)^{1/2}$  is practically constant and independent of the applied current density (Table 3). Sand's law is accordingly verified. On the other hand, the study of the



Fig. 4—Chronopotentiometric curves for aluminum ion reduction on a 42CL steel working electrode (S= 0.408 cm<sup>3</sup>) in a KCI-LiCI eutectic mixture containing  $AICI_3$  (C° $AICI_3$ = 8.69 x 10° mol/cm<sup>3</sup>).

		Т	able	e 3			
Aluminum	lon	Reduction	on	а	42CD4	Steel	Electrode*

l (mA/cm²)	τ <sub>2</sub> (sec)	τ <sub>2</sub> <sup>1/2</sup> (sec <sup>1/2</sup> )	iॄ⊄ৢ <sup>1/2</sup> (mAsec¹²/cm²)	n
-146.91	0.550	0.742	-108.951	_
-159.16	0.495	0.704	-111.979	2.4
-171.40	0.430	0.656	-112.387	2.4
-183.64	0.385	0.621	-113.948	2.5
-195.89	0.343	0.585	-114.642	2.5

\*Results obtained from the chronopotentiometric curves given in Fig. 3. The number of exchanged electrons was calculated from the slope of the linear function  $E = f[\ln(\tau_2^{1/2} - t^{1/2})/t^{1/2}].$ 

variation of the following functions:  $E = f[ln(\tau_2^{1/2} - t^{1/2})/t^{1/2}]$  and  $E = f[ln(\tau_2^{1/2} - t^{1/2})/\tau_2^{1/2}]$  confirms that the species involved in the aluminum ion redox reactions are soluble either in the electrolyte or in the steel electrode, inasmuch as only the first function is linear (Fig. 5). The calculated number of exchanged electrons derived from the slope of this function for different values of the applied current density is close to 2.5.

This value of n is subject to error because of the interference of the first wave preceding the main aluminum reduction wave. The most reliable values are, therefore, those obtained by the convolution technique that yielded n = 3.

#### Cathodic Chronoamperometry

The current density variation with time, i(t), when successive potential values, ranging between -0.95 V/RE and -1.1 V/RE, are applied to the working electrode, are shown in Fig. 6. The variation of I with  $t^{1/2}$  is found to be linear; Cottrell's law corresponding to the case of a simple diffusion-controlled electrochemical reaction is then followed.

### Diffusion Coefficient

An approximate value of the diffusion coefficient  $D_{AI}$  of the reduced AI in the bulk of the 42CD4 steel electrode is calculated by use of the chronoamperometric curves, according to a method proposed in a previous work using the following Cottrell expression: <sup>9</sup>

$$\frac{i_{1}(t)}{i_{2}(t)} = \frac{D^{1/2} + \theta_{2}}{D^{1/2} + \theta_{1}}$$

where  $\theta = \exp [nF/RT(E - E^{\circ})]$ ,  $D = D_{red}/D_{ox}$ , and  $i_1$  and  $i_2$  are current densities for two different values of the applied potential, measured at the same time t.  $D_{red}$ , was calculated at 600 °C

# Table 4 Vickers Hardness Measured on 42CD4 Steel Samples Subjected to Various Surface Treatments

42C04 Steel Sample	Vickers Microhardness
untreated	400 HV <sub>25-500g</sub>
nitrided	665-675 HV 500g
carburized	720-725 HV <sub>1000g</sub>
aluminized	920-946 HV <sub>25g</sub>
aluminided & post-nitrided	895-925 H $V_{_{25g}}$
aluminided & post-carburized	200-214 HV <sub>25g</sub>



g. 5—Graphic representation of the functions a:  $E = f[ln(\tau_2^{1/2} - t^{1/2})/t^{1/2}]$  and b:  $E = f[ln(\tau_2^{1/2} - t^{1/2})/\tau_2^{1/2}]$ , calculated by curve b of Fig. 4. a:  $X = ln(\tau_2^{1/2} - t^{1/2})/t^{1/2}$ t; b:  $X = ln(\tau_2^{1/2} - t^{1/2})/\tau_2^{1/2}$ .

and found to be equal to 2.5 x 10<sup>s</sup> cm<sup>2</sup>/sec.<sup>10</sup> The standard potential E° is determined graphically by measuring the equilibrium potential of a pure aluminum working electrode for different AICl<sub>3</sub>concentrations, C°(AICl<sub>3</sub>), in the KCI-LiCl electrolyte (Fig. 7). The intersection point of the linear part of the function  $E_{sq}$ =f[ln C°(AI<sup>-3</sup>)] with the potential axis corresponds to the E" value, which is found to be -0.85 V/RE.

The calculated mean value of the diffusion coefficient of the reduced Al in the bulk of the 42CD4 steel electrode is  $1.8 \times 10^{-11}$  cm<sup>2</sup>/sec. This value is of the same order of magnitude as those given in the literature for an iron working electrode.<sup>11,12</sup> Fellner *et al.*<sup>11</sup> give *a* value of  $5.4 \times 10^{-12}$  cm<sup>2</sup>/sec, while Lantelme *et al.*<sup>12</sup> give *a* value of  $1.5 \times 10^{12}$  cm<sup>2</sup>/sec for the Al/Fe system at 474 °C.

#### Electrocoating of 42CD4 Steel

The above analysis established the experimental conditions and parameters determining the formation of a homogeneous aluminum-rich surface layer on the 42CD4 steel.



Fig. 6—Chronoamperometric curves for aluminum ion reduction on a 42CD4 steel working electrode ( $S = 0.223 \text{ cm}^2$ ) in a KCI-LiCl eutectic mixture containing AICl<sub>3</sub> (C°AICl<sub>3</sub> = 8.69 x 10<sup>5</sup> mol/cm<sup>3</sup>.



Fig. 7—Variation of the equilibrium potential, Eeq, of a pure aluminum electrode, as a function of the AICI<sub>3</sub>concentration in the KCI-LiCI electrolyte.

Cathodic square wave pulsed currents leading to uniform and less porous electrolytic deposits were used.<sup>13-16</sup> The selected pulsed current parameters were:

pulse amplitude,  $i_p = -80 \text{ mA/cm}^2$ pulse duration,  $t_p = 0.5 \text{ sec}$ 

relaxation period,  $t_r = 2 \text{ sec}$ 

During deposition, the electrode potential was recorded in order to verify that it remained in the vicinity of that of the aluminum ion reduction to aluminum metal (i.e., = -1.08 V/RE).

A scanning electron micrograph of a well-polished cross section of a sample obtained by this procedure is presented in Fig. 8. Dispersion energy spectra were also recorded in order to analyze the species present at the 42CD4 steel surface.

Figure 9 shows the concentration profiles of AI, Fe and the more important minor elements of this type of steel: Mn, Cr and Si, obtained by shifting the electron beam by 0.5-µm steps. A continuous layer can be observed where the AI and Fe concentrations remain constant, corresponding to the Fe<sub>2</sub>AI<sub>s</sub> interme-



Fig. 9-Concentration profiles of Fe, Al, Mn, Cr, Si, measured on a cross section an electrochemically aluminized 42CD4 steel electrode.



Fig. 8—SEM micrograph of a cross section of an electrochemically aluminided 42CD4 steel electrode (15 x 15 x 2 mm<sup>2</sup>). Electrodeposition by cathodic square wave pulsed current with the following parameters:  $i_{e}$  = -80 mA/cm<sup>2</sup>,  $t_{e}$  = 0.2 see,  $t_{e}$  2 sec; electrolysis duration, 2 hr; thickness of the electrodeposited layer, 26 µm.

tallic compound. This layer is followed by an interracial zone of about 3  $\mu$ m thickness, where the Fe and Al concentrations change regularly. Moreover, it can be seen that the minor elements, Mn, Cr and Si, are virtually missing in the Fe<sub>2</sub>Al<sub>s</sub>layer.

#### Microhardness Measurements

Table 4 lists the results of superficial microhardness measurements made on 42CD4 steel samples subjected to various surface treatments. The microhardness profiles obtained for the same samples are also shown in Fig. 10. It is apparent that the aluminized coating increases the surface hardness of the 42CD4 steel. The superficial hardness in this case is much



gure 10: Microhardness profiles for 42CD4 steel samples subjected to various surface treatments: (1) nitrided (HV<sub>2500</sub>); (2) carburized (HV<sub>10000</sub>); (3) aluminided (HV<sub>250</sub>); (4) aluminided and post-nitrided (HV<sub>250</sub>); (5) aluminided and post-carburized (HV<sub>250</sub>).